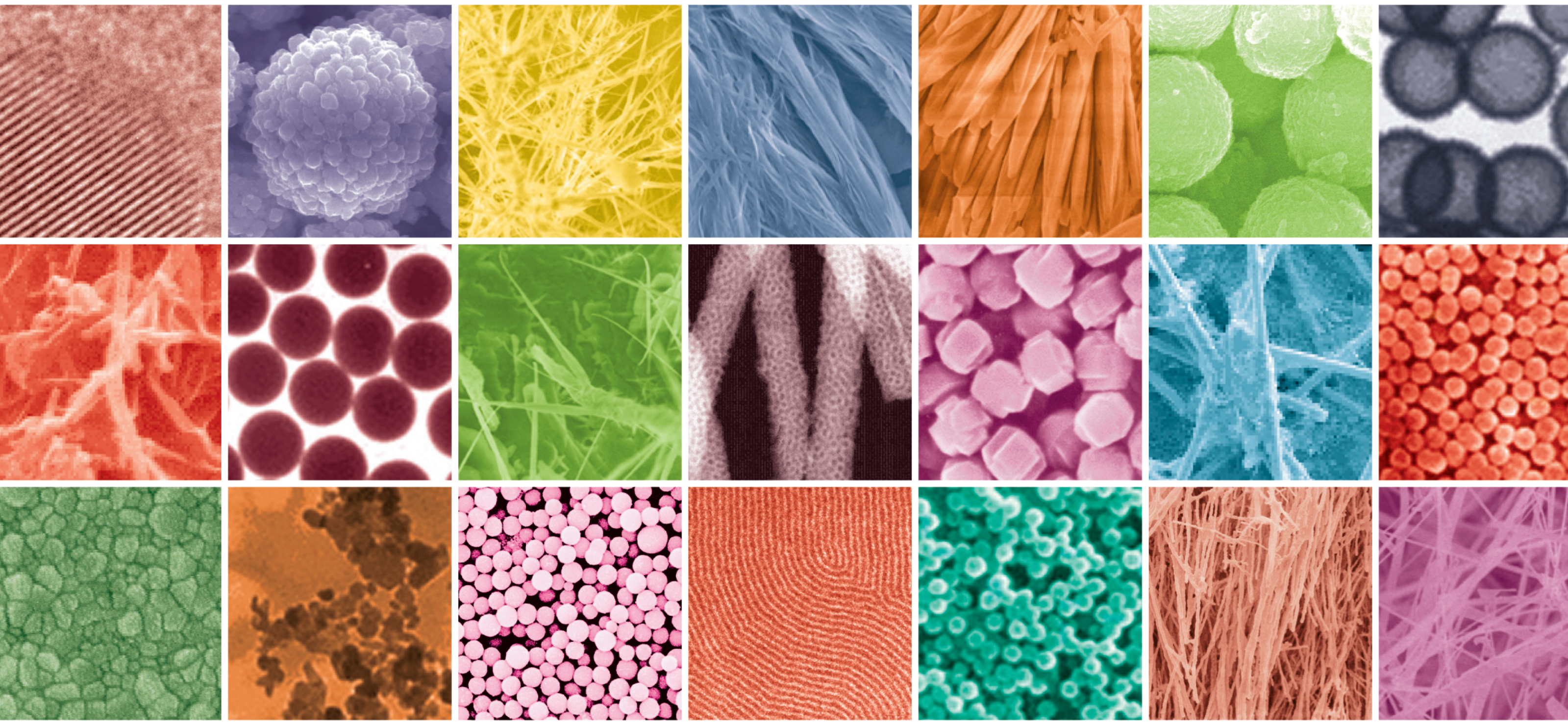
Journal of Nanomaterials

Nanotechnology for Environment and Biomedical Applications

Lead Guest Editor: Arivalagan Pugazhendhi
Guest Editors: S MANIGANDAN and Kathirvel Brindhadevi



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Research Article

Design of a New Coating Agent Based on Graphene Oxide and Antimicrobial/Spermicidal Peptide (Sarcotoxin Pd) for Condom Coating: New Strategy for Prevention of Unplanned Pregnancy and Sexually Transmitted Infections

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In this study, sarcotoxin Pd-functionalized graphene oxide (GO-Pd) was synthesized as a new condom-coating agent. Antimicrobial activity was evaluated by radial diffusion assay (RDA) and absorbance-based methods. Sperm motility and morphology were assessed in different concentrations of designed nanostructures. Peptide stability on the GO structures was assessed by the CD technique. GO-Pd showed the highest contact angle. The results approved that GO-Pd had broad-spectrum antimicrobial activities against examined pathogens, especially vaginal infections such as *Candida vulvovaginitis*. This antimicrobial activity was more than pristine peptides, vancomycin, and fluconazole. GO-Pd also had a higher inhibitory activity on the sperm motility and viability than pristine peptides. GO-Pd had high stability and activity in all examined conditions. But, naked peptides had low stability and activity after incubation in acidic pH and high temperatures (>38°C). In all tests, GO-Pd showed a significant difference compared to naked peptide. Based on the results, GO-Pd can be used as a condom coating to prevent unplanned pregnancy and sexually transmitted infections.

1. Introduction

Sarcotoxin Pd is an antimicrobial peptide purified and identified from *Paederus dermatitis* [1]. In our previous studies, these peptides have potent antimicrobial and spermicidal activity [1, 2]. Sarcotoxin Pd has been introduced as a powerful contraceptive agent in preventing unplanned pregnancy and sexually transmitted infections (STIs) [2]. The limitation of applying these peptides is low stability in various environments (with different pH and temperatures) [3–5]. Different strategies have been developed to increase the metabolic stability of peptides, such as cyclization, substituting amides with sulfonamides, etc. [6–8]. In between, nanotechnology can be used to design new biocompatible and biodegradable systems to enhance peptide stability, slow-release, targeted delivery, maintenance of peptide's structure and function, and so on [9–12]. Among all nanostructures, carbon nanostructures have potent properties as drug delivery systems, especially graphene oxide (GO) [13–15]. GO, as a derivation of graphene, can enhance the beneficial properties of natural and synthetic materials due to its unique characteristics, e.g., tensile strength, elasticity, conductivity, and more [16]. Functionalizing GO with natural compounds can increase these agents' local concentration and efficacy [16, 17]. Covalent interaction (peptide bond) between GO and peptides may establish the peptide structure [18, 19]. Due to the antimicrobial activity of GO, functionalized GO with antimicrobial peptides can lead to enhancement of this activity. On the other hand, spermicide-coating condoms are used for effective pregnancy and STIs prevention [20]. Studies showed that spermicide condoms are ~99% effective in preventing pregnancy [21, 22]. Nonoxynol-9 (N-9) is known as the main spermicide. However, regular and spermicide condoms can reduce the risk of STIs, but there is no evidence to show that these condoms increase that protection [23–25]. Using a compound with dual function (a compound with both spermicide and antimicrobial effect) in the design of condoms can double the effectiveness of condoms in preventing pregnancy and transmission of infection [26]. Sarcotoxin Pd has this dual function [1, 2]. Therefore, if the stability of this peptide is somehow increased, its use in condom design can be more effective than the existing condoms. So, this study aims to increase peptide stability by using GO and designing a dual-function coating (spermicidal and antimicrobial) for condoms. The design of a new cover with a double function for condom coating is the innovation of this study.

2. Materials and Methods

Based on previous studies, GO was synthesized using a modified Hummers method [16, 17]. Briefly, graphite powder was mixed with $NaNO_3$ and H_2SO_4 at 0°C. Then $KMnO_4$ was slowly added. Mixture temperature was increased to 40°C in this stage. The acquired solution was diluted with deionized water and stirred for 10 min. The reaction was stopped by adding H_2O_2 (30 wt%). The final mixture was centrifuged, and precipitation was washed with HCl solution and deionized water several times. This solution was dried at room temperature and in vacuum condition. The microwave method was used for GO functionalization to form a covalent bond between GO and peptide. GO powder was dissolved in deionized water and sonicated by probe sonication. Synthesized sarcotoxin Pd was dissolved in phosphate buffered saline (PBS). These two solutions were mixed on a shaker. After 10 min, this solution was irritated in an industrial microwave (with an output power of 700 W) at 150°C for 20 min. Centrifugation was used to remove unbound peptides. Acquired precipitations in this stage were dispersed in deionized water on the shaker. Characterization was done by TEM and FTIR methods. Contact angle measurement was also done by a contact angle analyzer.

2.1. Antimicrobial Assay. The antimicrobial assay was done by two methods: radial diffusion assay (RDA) and absorbance-based methods. One Gram-positive bacterium (*Staphylococcus aureus*), one Gram-negative bacterium (*Escherichia coli*), and one fungal strain (*Candida vulvovaginitis*) were used for antimicrobial evaluation.

In the RDA method, bacteria were cultured for 18 hr at 37°C in 50 ml of tryptic soy agar (TSA) medium (w/v 3%). After culture medium solidification, some holes were created on a medium for sample loading (5 μg of the nanostructure is poured into the well). After 18 hr incubation at 37°C, the antimicrobial effects appear as bright halos around the wells (the diameter of the halo observed around the wells indicates the amount of antimicrobial activity of the samples). The diameter of the created growth inhibition halo was measured and reported as millimeters. A similar procedure was done for the fungal strain on potato dextrose agar (PDA) medium.

In the adsorption method, the bacterial and fungal suspensions were injected into the microplate wells. The first well is considered blank. Each well will be equivalent to 200 μl of solution. In the second well, regarded as a control, 180 μl of culture medium containing bacteria and 20 μl of PBS buffer was injected. In subsequent wells, 180 μl of culture medium was mixed with 20 μl of prepared nanostructure solution. The microplate was incubated for 18 hr at 37°C. After this time, the absorbance of the samples was read at 630 nm by an ELISA reader. The minimum concentration of nanostructures that have stopped bacterial growth is considered minimal inhibitory concentration (MIC). Vancomycin and fluconazole were used as positive control.

2.2. Spermicidal Activity. To evaluate spermicidal activity, acquired washed sperms from 10 healthy volunteers (people with normal sperm count and parameters) were treated with different concentrations of designed nanostructures (1,000, 800, 500, 250, 100, 50, and 25 μg/ml) and sperm motility and morphology were assessed at 0, 0.3, 5, 10, and 15 min. B2 medium and nonoxynol-9 (N-9) were used as a negative and positive control, respectively. The lowest concentration exhibited 100% sperm immobilization during 0.3 min was considered a maximal effective concentration (EC100).

2.3. Peptide Stability Evaluation. The stability of the peptide on the GO structures was evaluated by CD technique after treatment in different environments with different physical conditions. This determination was done by measurement of the CD signal at 220 nm.

3. Results

We prepared flexible nanocoating agents for condom design with antimicrobial and spermicidal activities by functionalized GO with sarcotoxin Pd.

3.1. Characteristics of Design Nanostructure. The results of FTIR are shown in Figure 1. Based on these data, the presence of –COOH groups was confirmed by absorption peak at 1,077 cm^{-1}. The absorption peaks at 3,331, 2,153, 1,958, 1,644, 1,566, 1,073, and 679 cm^{-1} indicated the peptide bond formation between the amine group of sarcotoxin Pd and the –COOH group of GO.

GO and GO-Pd were characterized by TEM, FTIR, and contact angle analyzer. In the TEM image (Figure 2), GO has a multilayered structure with a highly wrinkled shape. These

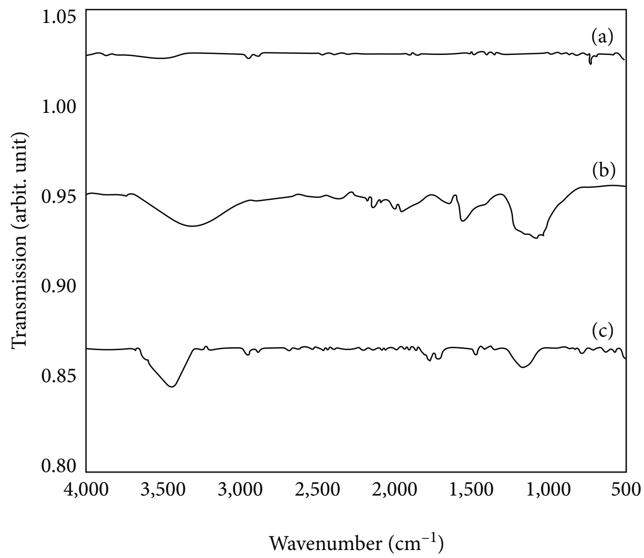
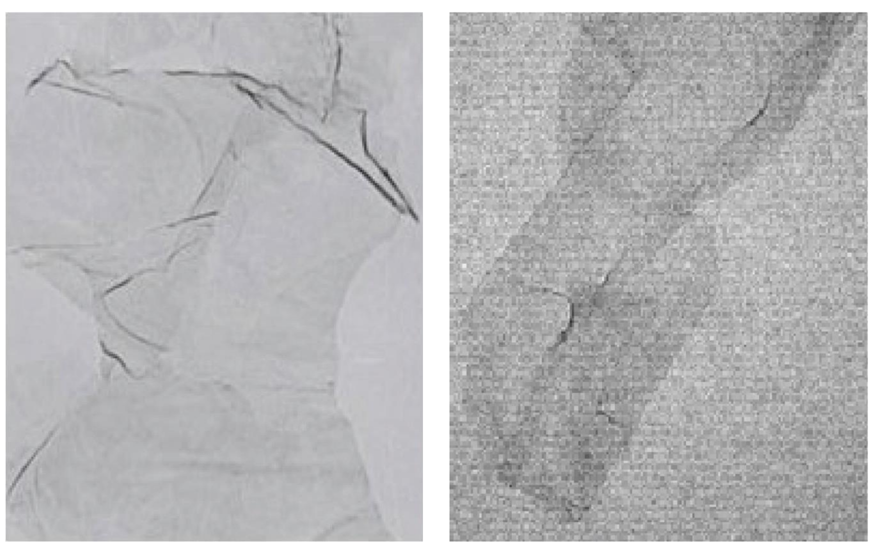


FIGURE 1: FTIR spectra for synthesized nanostructures, graphene (a); sarcotoxin Pd-functionalized GO (GO-Pd) (b); graphene oxide (GO) (c).



(a) (b)

FIGURE 2: TEM image of sarcotoxin Pd-functionalized GO (GO-Pd) (a) and graphene oxide (GO) (b).

pd properties were also observed in GO-Pd. In the structure of GO-Pd, the amount of shrinkage is more than GO, so graphene is almost crumpled.

The lowest (20°) and highest angles (150°) were observed for GO-Pd and graphite, respectively (Figure 3).

3.2. Peptide Stability. Peptide stability was evaluated by structure analysis with CD spectra (Figure 4). The change in peptide structure was slightly observed after functionalization on GO. It is indicated that covalent interaction between sarcotoxin Pd and GO leads to partially unfolding induction and change of α-helix structure. However, this helix reduction was insignificant compared to the naked peptide.

3.3. Antimicrobial Activity. RDA test showed that naked peptide, GO, and GO-Pd had antibacterial and antifungal activities. Among these three compounds, GO-Pd had higher microbicidal activity. GO-Pd showed higher inhibitory activity on Gram-positive bacteria, Gram-negative bacteria, and fungus. The sequence for antimicrobial activity was GO-Pd > sarcotoxin Pd > GO for all examined strains. The results for MIC determination by absorbance method conformed to the RDA data. MIC values for GO-Pd were lower than naked peptides and GO. In between microbial strains, the lowest MIC of GO-Pd was observed for *Escherichia coli*, *Staphylococcus aureus*, and *Candida vulvovaginitis*. These data were similar to RDA results (Figure 5).

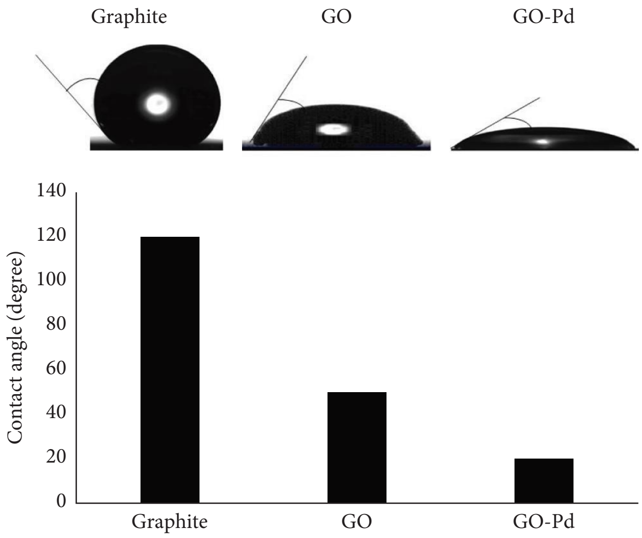


FIGURE 3: Water contact angle (WCA) between water droplets with graphite, graphene oxide (GO), and sarcotoxin Pd-functionalized GO (GO-Pd).

3.4. Spermicidal Activity. Acquired data indicated that all concentrations of naked peptide and GO-Pd have inhibitory effects on sperm motility. After 0.3 min, the 100% inhibitory concentration (EC100) was 100 and 250 μg/mL for sarcotoxin Pd and GO-Pd, respectively. GO showed no significant effects on sperm motility (Figure 5). Inhibitory effects of sarcotoxin Pd and GO-Pd on sperm motility were dose-dependent. The highest concentration of naked peptides and GO-Pd had the best inhibition. At EC100 of sarcotoxin Pd (100 μg/mL) and GO-Pd (250 μg/mL), peptide immobilization occurred after 30 s (Figure 6).

4. Discussion

Condoms are the most important contraceptive vehicles [27]. The development of new condoms with more effective preventive effects can be beneficial for reproductive health. Using spermicidal compounds in the design and manufacture of condoms can double its effectiveness in preventing unwanted pregnancy [28, 29]. In addition to preventing pregnancy, preventing the transmission of infection between couples during sex is also of double importance [30]. Compounds with dual spermicidal and antimicrobial activity can effectively achieve the two mentioned goals. This study used an antimicrobial peptide, sarcotoxin Pd, for this goal. Based on previous studies, this peptide has antimicrobial effects on various microorganisms, mainly STIs. This peptide also has spermicidal activity in low concentrations [1, 2]. We loaded this peptide on the GO surface. This interaction led to the enhancement of peptide stability in various temperatures and acidic conditions. With this strategy, the limitation of low peptide stability was overcome [3, 4]. N-9 has spermicidal and antimicrobial activity. However, N-9 harms the vaginal epithelium with low effective antimicrobial activity [31, 32]. The physiology of sperm function has not been considered in the design of spermicidal compounds such as N-9 [33]. Paying attention to this issue in the design of contraceptive compounds is vital. In this context, the mode of spermicidal and antimicrobial activity of sarcotoxin Pd has been determined. In addition, our study also considered another positive approach. We used GO for peptide loading and coating fabrication. Graphene condoms are thinner than regular condoms. Due to the high strength of the graphene layer, it is possible to design a thinner condom [34, 35]. This point causes the heat to be better directed, and couples experience more sexual pleasure in addition to ensuring pregnancy prevention. The high flexibility of the graphene layer also makes it easier to use in condoms [36]. Designed GO-Pd includes the mentioned positive points: the presence of a strong, flexible, and thin graphene layer that is functionalized with a spermicidal and antimicrobial compound. Based on reported studies, graphene in rubber latex enhances tensile strength and thermal conductivity. These two changes are useful for the materials for skin-contacting applications, such as male and female condoms [37, 38]. Maintaining the secondary structure of peptides and proteins after loading on nanostructures and other substrates is one of the most important challenges. It is reported that all nanostructures had no similar effects or patterns on structural change of peptides and proteins [39, 40]. For carbon nanostructures, interaction sites, peptide/protein stability, and the shape of nanostructures are primary factors for structural changes after functionalization [41]. Similar articles showed that the interaction of SWCNTs, MWCNTs, graphene, and their derivatives with various peptides/proteins leads to unfolded structures by destroying secondary structures [42–44]. Based on a previous study, structure prediction showed that the secondary structure of sarcotoxin Pd is α-helix with the amphipathic and amphiphilic amino acid arrangement. CD spectra in the current study proved this structure. Our result also showed that GO leads to partially unfolded induction and changes of α-helix structure. However, this helix reduction was not significant compared to the naked peptide. The results of this section are similar to related studies [45–48]. The less spermicidal activity of GO-Pd than sarcotoxin Pd may also be due to this slight change in the peptide's secondary structure after loading GO. The sequence for spermicidal activity was sarcotoxin Pd > GO-Pd > GO. This result can be justified according to the CD results. Sarcotoxin Pd with an α-helical structure has an amphipathic structure with two hydrophilic and hydrophobic faces and a net charge +6. These properties have a crucial role in peptide interaction with sperm membranes and the destruction of sperm cells [1, 2]. Preservation of these two facial α-helical structures after binding to GO led to the spermicidal effect of functionalized GO. A comparison of antimicrobial activity showed a different order than spermicide activity. The sequence for spermicidal activity was GO-Pd > sarcotoxin Pd > GO. According to these data, the higher antimicrobial effect of GO-Pd than sarcotoxin Pd may be due to the synergistic effect of these compounds. The antimicrobial effect of GO and sarcotoxin Pd has been demonstrated in previous studies [1, 2, 49, 50]. The synergistic effect led to a multiplication of antimicrobial effects. Although partial degradation of the peptide structure can reduce its antimicrobial activity, the presence of the antimicrobial effect

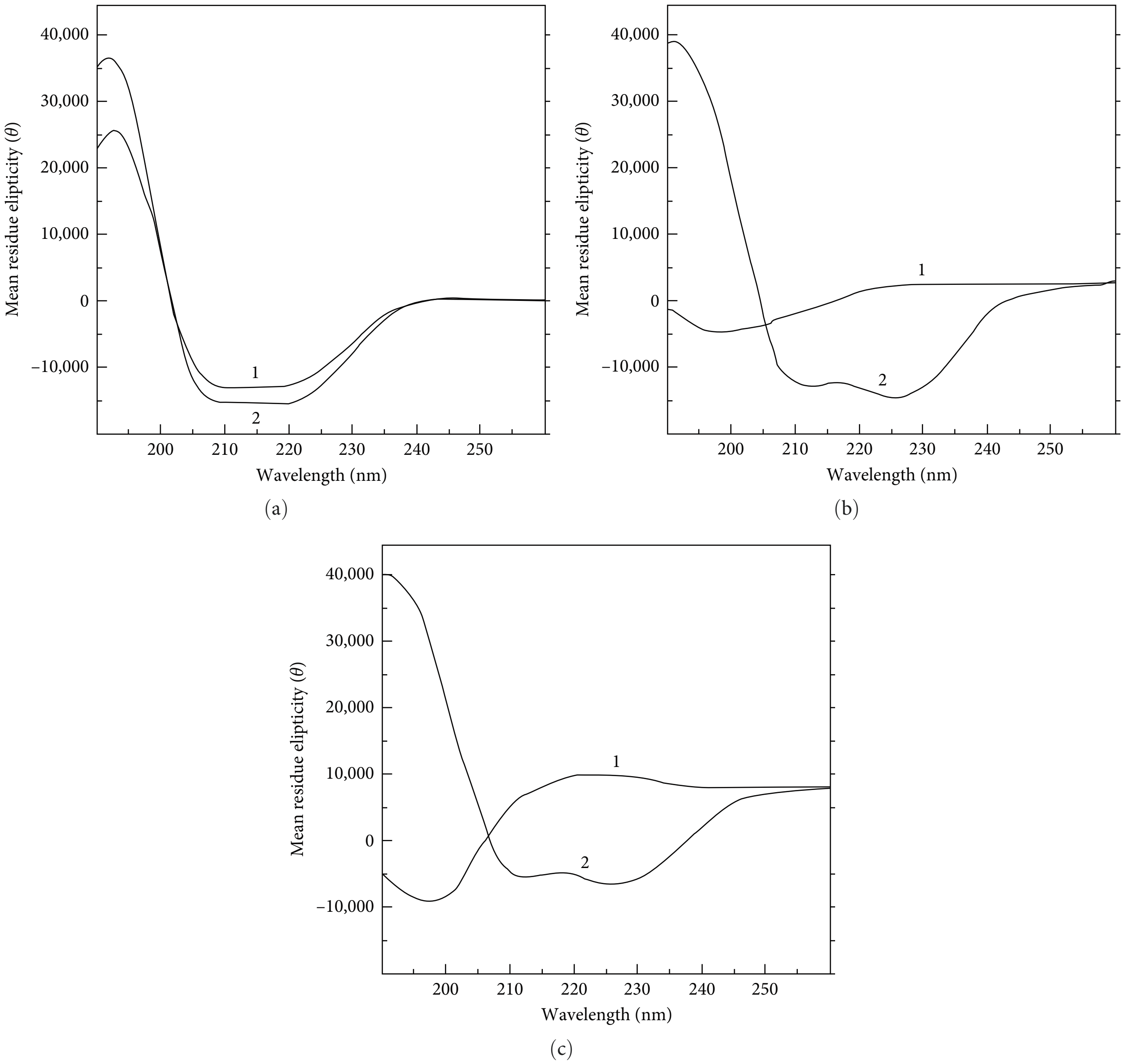


Figure 4: The CD spectra for peptide stability in physiologic conditions (a); high temperature (40°C) (b); and acidic pH (4.6) (c). 1: naked peptide, 2: sarcotoxin Pd-functionalized GO (GO-Pd).

of GO compensates for this reduction. Two facial α-helical structures sarcotoxin Pd also justifies its antimicrobial effect. Like other antimicrobial peptides, sarcotoxin Pd inhibits microbial growth by barrel-stave mechanism [51, 52]. This peptide interacts with negative phospholipids of the membrane by a cationic face and disrupts the membrane with the help of a hydrophobic face. By covalent interaction between sarcotoxin Pd and GO, two faces of the peptide are free for disruption of microbial membrane. So, a similar antimicrobial mechanism is used in naked peptides and sarcotoxin Pd-functionalized GO. However, for sarcotoxin Pd-functionalized GO, the antimicrobial effect of GO is also added and doubles its effect. Graphene and its derivation (i.e., graphene oxide (GO)) have attracted significant research interest in biomedicine due to their excellent physical and chemical properties. There are two critical strategies for a load of peptides on GO: covalent and noncovalent interaction [53]. In our study, covalent interaction was used. Sukumar et al. [34] showed that the functionalization of graphene with the right ingredients (e.g., surfactant/compatibilizer) could increase its dispersion and aid in good interfacial interaction to achieve the desired properties. This point is not excluded from using graphene in the design of condoms. A decrease in contact angle indicates an increase in the moisture content of the compound [54]. In our study, reduction of WCA was proven for GO and functionalized GO. The lowest and the highest angles were observed for graphite and GO-Pd, respectively. Functionalization of GO with sarcotoxin Pd led to a significant increase in wettability. So, the hydrophilicity of GO and GO-Pd is higher than graphite. This hydrophilicity

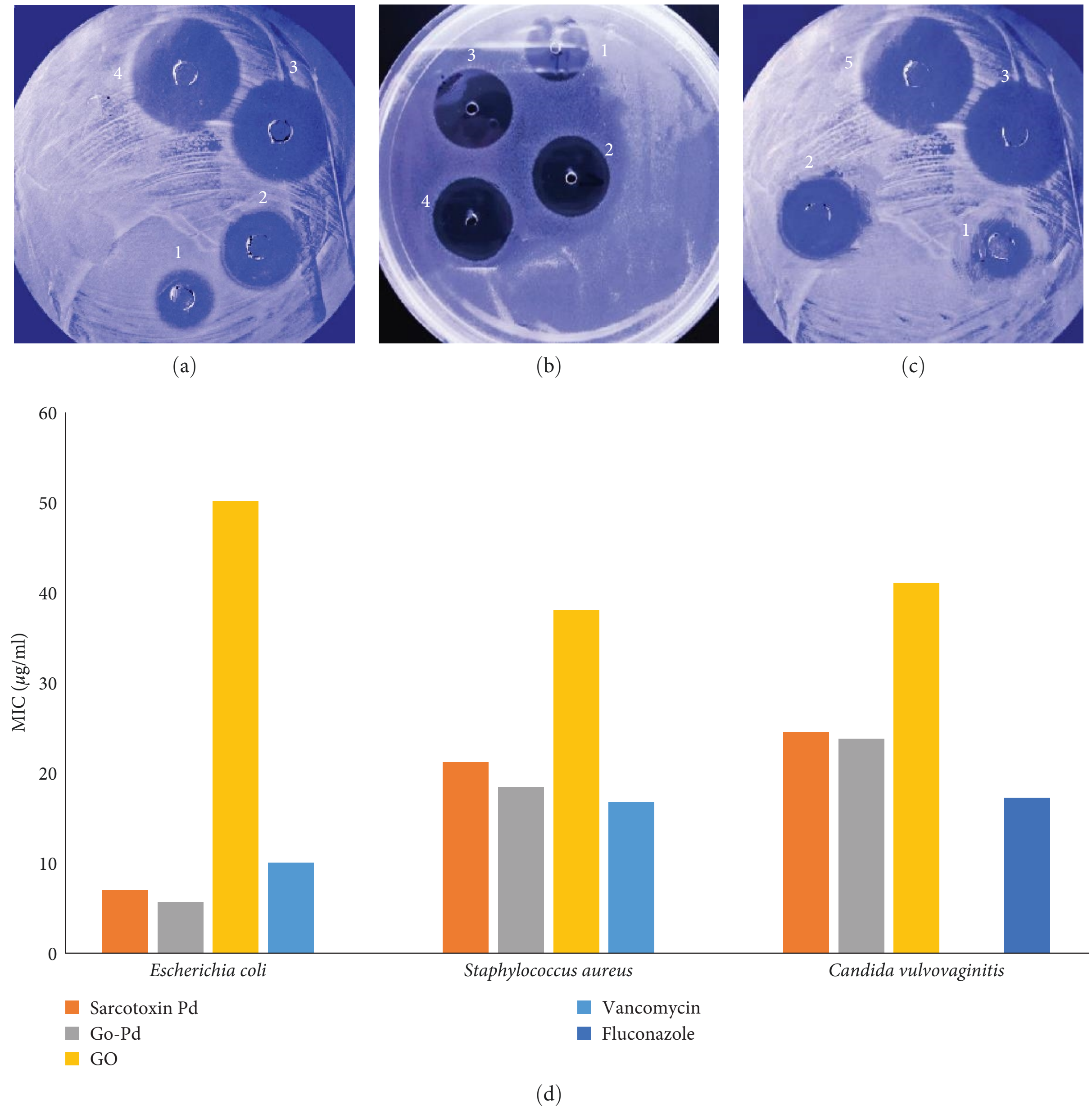


Figure 5: Antimicrobial activity of the naked peptide, graphene oxide (GO), and sarcotoxin Pd-functionalized GO (GO-Pd) on examined pathogens by RDA (a–c) and MIC test (d). 1: GO, 2: sarcotoxin Pd, 3: GO-Pd, 4: vancomycin, and 5: fluconazole. (a) *Escherichia coli*, (b) *Staphylococcus aureus*, and (c) *Candida vulvovaginitis*.

improves biological and biomedical applications [3, 14, 55]. Structural stability and changes are the most critical challenge in the functionalization of nanostructures with peptides and proteins [52, 56]. This high wettability of the designed GO-Pd also increases the better lubricating properties of the condom.

5. Conclusion

The main aim of the study was to enhance the stability of the antimicrobial peptide, sarcotoxin Pd. This aim was achieved. GO-Pd has higher stability than a naked peptide. Other related purposes were also completed. Our results showed that GO-Pd has strong antimicrobial and spermicidal activities. These designed nanostructures also have suitable flexibility and malleability. So, our study showed that GO-Pd could be used as a condom coating for creating a new spermicidal and antimicrobial condom. This new condom can effectively prevent unplanned pregnancies and STIs. Although GO has better solubility in a polar solvent such as water than graphene, the low solubility was one of the main challenges in using GO. Functionalization with peptide led to the higher solubility of GO. The high price of peptide purification is also one of the significant problems. To solve this challenge, in this study, we used synthesized peptides. The use of polar functional groups can lead to an increase in GO solubility. Therefore, it is suggested to use polar groups-functionalized GO to load peptides and investigate their antimicrobial and spermicidal effects in future

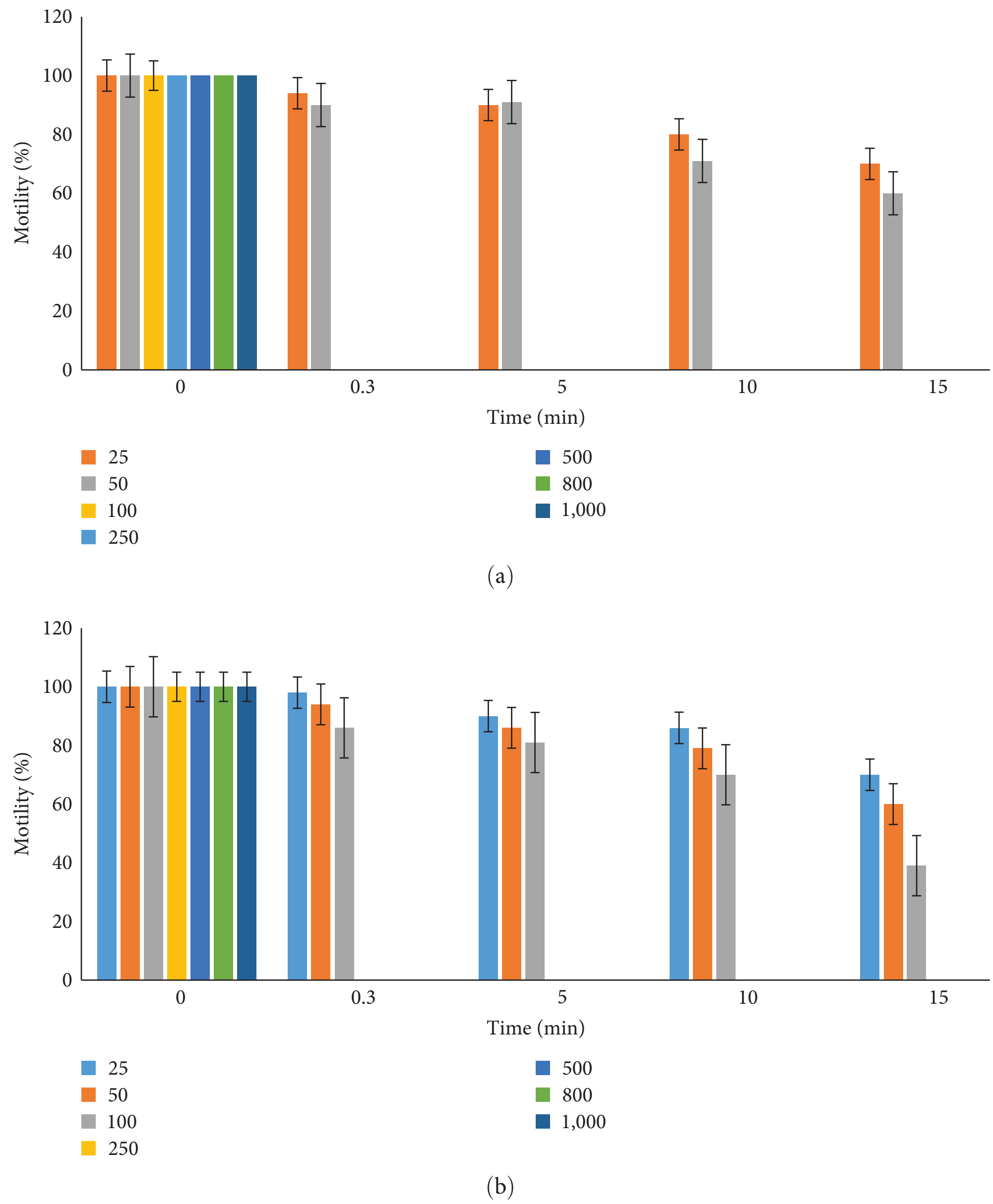


Figure 6: Sperm motility after treatment of sarcotoxin Pd (a) and sarcotoxin Pd-functionalized GO (GO-Pd) (b). At EC100 of sarcotoxin Pd (100 μg/mL) and GO-Pd (250 μg/mL), sperm immobilization occurred after 30 s.

research. It is also recommended to examine the impact of changing the amino acid sequence of the peptide on its antimicrobial and spermicidal activities and its stability through bioinformatics and computer modeling and use the designed peptide to make the condom coating.

Data Availability

The data used to support the findings of this study are included within the article.

Ethical Approval

The study was approved by the Ethics Committee of Abadan University of Medical Sciences, Abadan, Iran (AIR.ABADA-NUMS.REC.1399.215).

Disclosure

The abstract of this study has been presented as conference in "Proceedings of the Fourth National Conference on Protein and Peptide Sciences" according to the following link: https://conf.ui.ac.ir/fa/article.php?lrId=40&cnfId=12.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

In this study, all authors contributed to the manuscript's design, writing, and review. HZZ contributed to experimental sections, including material synthesis and animal treatment. AA led the execution of laboratory and fieldwork for the entire project and managed and supervised the experiments and results. MZ contributed to the biological assessment of nanostructures and article editing. HS did the synthesis of nanomaterial and biological tests. HG contributed to material synthesis. MF did the statistical analysis of the data. SAH contributed to biological tests as well as article editing. ND contributed to data collection and analysis.

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Research Article

Mechanical and Wear Behaviour of Nano-Fly Ash Particle-Reinforced Mg Metal Matrix Composites Fabricated by Stir Casting Technique

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In recent years, magnesium-based alloys and composites have great attention in automobile, structural, and biomedical industries due to their desirable characteristics such as lower density, low elastic modulus, high specific strength, better damping properties, and excellent castability. The pure magnesium was used as a matrix material and reinforced with fly ash fillers of different compositions with a weight percentage of 2.5%, 5%, and 7.5% to compare with the pure magnesium. The three different weights (wt%) of fly ash/Mg samples were prepared using the bottom pouring stir casting method. Fabricated samples sliding wear characteristics and mechanical behaviour (ASTM standard) were studied. Wear, tensile, and hardness results portray that 7.5 wt% fly ash composites possess better elongation and hardness and good wear resistance. The tensile strength values were improved by 42% in sample 4 compared with pure Mg. Hardness values were also improved by 21% in sample 4 compared with pure Mg. The wear rate and coefficient of friction are also reduced by the increased weight percentage of fly ash reinforcement. SEM images display casted pure magnesium's morphology and wear-tested samples' worn surface characteristics.

1. Introduction

Nowadays, tremendous demand for lightweight metal matrix composites for structural applications in biomedical, structural, and automobile industries [1]. In the new lightweight materials, more energy-efficient and recyclable magnesium is one of the best dominant materials which replaces all existing materials. Pure magnesium is 75% lighter than steel and 33% lighter weight than aluminium. The report states that overall fuel savings can be 20 to 30% by replacing aluminium with magnesium-based materials in the automotive industry [2]. The magnesium alloy system has combinations of Al, Mn, Zn, Zr, and rare earth material constituents. However, the available magnesium alloy system has limitations, such as low strength and poor flexibility. Magnesium has less flexibility due to its hexagonal closed pack structure and possesses only three independent slip systems [3]. In order to overcome those limitations and enhance their mechanical and wear properties, the addition of micron-scale fly ash is preferred among industrialists.

Recent studies have shown that adding reinforcements such as SiC, Al_2O_3, MgO, ZrO_2, and CNTS improves mechanical properties and ductility. Fly ash is the most easily available and inexpensive material, and land pollution can be limited with proper utilisation. It greatly impacts the environmental effect of thermal power plants and other combustion processes of industries that use coal as fuel [4]. Fly ash can be categorized into solid precipitator and cenosphere types. The fly ash constitutes the major composition of SiO_2, Al_2O_3, Fe_2O_3, and CaO. The yearly production estimation of fly ash worldwide is 900-1000 million tonnes (fly ash and slag) [5, 6]. Dinaharan et al. produced AZ31/10 vol% FA MMC using conventional stir casting and compared the same composites with friction stir processing. They reported that the wear and hardness of the two fabrication methods show that the huge differences are due to undesirable microstructures [7]. Kondaiah et al. fabricated AZ31/fly ash composites using a friction stir process and stated increased hardness and better wear characteristics [8]. Viswanath et al. developed AZ91/SiC composites (5, 10, 20, and 25 wt%) using stir casting. They observed improved creep resistance in 15, 20, and 25 wt% of SiC composites [9]. Matina et al. fabricated pure magnesium/SiC and AZ80/SiC composites by stir casting. They proved that hardness values were increasing according to the increment percentage of SiC reinforcement [10]. Rohatgi et al. demonstrated that the addition of fly ash in AZ91 magnesium alloys enhanced electrical resistivity and electromagnetic interference shield [11].

Lim et al. developed AZ91/D-fly ash composites by die casting method. They reported that composite density decreased when the fly ash percentage increased, and the maximum tensile strength was achieved in 5 wt% reinforced fly ash composites [12]. Hassan et al. investigated the wear behaviour of Mg-/SiCp-reinforced composites. They achieved that the composites improved wear resistance up to 15-30% due to their excellent load-bearing capacity. They stated that Young's modulus decreased with increased fly ash reinforcement percentage [13, 14]. Al-Mg-Cu alloys were manufactured using various weight percentages of Cu using powder metallurgy. The mechanically mixed layer (MML) formations result in counter face disk wear rather than material wear which contradicts the overall results [2]. Composting detected an almost 5-7% reduction in porosity and enhanced mechanical properties to stir casting. However, it showed specific impairments in the development at rising temperatures [15].

The liquid state synthesis route is a simple and inexpensive method to produce complex geometry shapes in metal matrix composites. After reviewing the above literature, it was noticed that so much research is needed to be conducted on fly ash-reinforced magnesium metal matrix composites to explore their advantages over other traditional filler materials. The present work is aimed at improving the mechanical properties and wear behaviour, conducting microstructural studies of Mg-fly ash-reinforced composites, and comparing configuration with pure magnesium.

Table 1: Chemical composition as-received magnesium (in wt%).

Element	Mg	Al	Si	Fe	Cu	Mn	Cl
wt%	99.9277	0.017	0.022	0.0012	0.0001	0.024	0.004

Table 2: Chemical composition of as-received fly ash (in wt%).

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MnO_2	K_2O	TiO_2	LOI
wt%	50.5	22.54	7.3	5.1	1.0	0.5	0.35	Balance

Table 3: Test samples and their reinforcement percentages.

Test samples	The weight percentage of magnesium and fly ash
Sample 1 (PMg)	Pure magnesium
Sample 2	Mg 97.5% + fly ash 2.5%
Sample 3	Mg 95% + fly ash 5%
Sample 4	Mg 92.5% + fly ash 7.5%

2. Materials and Methods

2.1. Materials. Pure magnesium is supplied by Shree Bajrang sales private limited, Raipur. Magnesium composition includes 99.9277% pure magnesium and the remaining small amount of Al, Si, Fe, Cu, Mn, etc. The detailed percentage of compositions is shown in Table 1. Fly ash was collected from the Mettur Thermal Power Station, a coal-fired electric power station located in Mettur, Tamil Nadu [16]. The detailed chemical composition of as-received fly ash percentages is shown in Table 2. The average particle size of fly ash is 10 nm [17].

2.2. Experimental Procedure

2.2.1. Stir Casting. The composites were prepared by the liquid state stir casting method. Stir casting is a cost-effective and relatively simplest method for producing metal matrix composites. First, a graphite crucible was melted, and the commercially available premeasured quantity of pure magnesium metal was cast by an electrical resistance furnace [18]. Then, magnesium samples as received from the supplier (unreinforced) and magnesium composites were prepared with three fly ash reinforcements (2.5, 5, and 7.5 wt%) shown in Table 3. The high-purity magnesium (99.93%) melted in a graphite crucible using an electrical resistance heating at 750°C. The fly ash particles were preheated to 300°C to remove the moisture content for two hours [19]. The fly ash particles were added during vortex formation due to the stirring process in the melt [20]. The weight percentage of 2.5, 5, and 7.5% fly ash was added into the magnesium matrix under the protected inert atmosphere

Figure 1: Experimental setup of stir casting furnace.

Figure 2: Fabricated tensile and wear samples.

of argon gas. Experimental setup of stir casting furnace is shown in Figure 1.

The steel impeller was used to properly distribute the preheated reinforcement fly ash with the matrix material. The stirring rod rotates at the speed of 750 rpm and stirs continuously for 10 minutes. Then immediately, the molten metal was poured into a 300°C preheated graphite mould to obtain the castings [21]. Figure 2 shows the fabricated tensile and wear samples.

2.3. Mechanical Characterization

2.3.1. Tensile Test. The tensile strength of fabricated samples was measured at room temperature using Instron -4208 Universal Testing Machine (UTM). ASTM standard E8M-09 was followed to prepare cylindrical cross-section tensile test specimens. Every three specimens were prepared for pure monolithic magnesium and Mg/fly ash-reinforced composite. The tensile strength results were based on the three samples' average results. Crosshead speed has been considered as 0.5 mm/min [22].

Figure 3: Pin on disc apparatus.

2.3.2. Microhardness Test. Microhardness tests were conducted by using the Vickers microhardness instrument. Hardness values are measured at five different places in every sample, and average values are tabulated. ASTM E384 standard was followed for the hardness test [23].

2.3.3. Low-Velocity Impact Test. Measuring the energy absorption nature of any metal used as an industrial counterpart is important. The proposed fabricated samples were tested for their low-velocity energy absorption. The pure magnesium and composite samples' energy absorption was used to measure the toughness property of the samples. It is also necessary to evaluate the ductile or brittle characteristics of the pure magnesium and fabricated composite samples. ASTM D7136 standard was followed for the low-velocity impact test [24].

2.3.4. Wear Test. The pin on the disc wear apparatus was used to conduct a wear test, as shown in Figure 3. The wear test was conducted at room temperature under dry sliding conditions according to the ASTM G99-04A standard. Initially, the specimen was polished, and the burrs were removed by emery sheet [25]. The pin size of 8 mm diameter and length of 30 mm were used for the wear apparatus. The wear test was carried out by constant values of sliding at a distance of 1200 m with a force of 20 N and a sliding speed of 500 rpm. The wear rate and coefficient of friction values were observed. The morphology of worn surfaces was captured and analyzed using a scanning electron microscope [26].

3. Results and Discussion

3.1. Tensile Strength. The tensile test was conducted for three samples of every configuration, and the average values were collected and presented. The variation of tensile strength values by the influence of fly ash reinforcement content is shown in Figure 4. The improvement of elasticity and yield strength was based on the synthesis technique and the percentage of reinforcements. In ceramic reinforcements, the flexibility was improved by grain refinements, texture modification, and nonbasal slip systems [27].

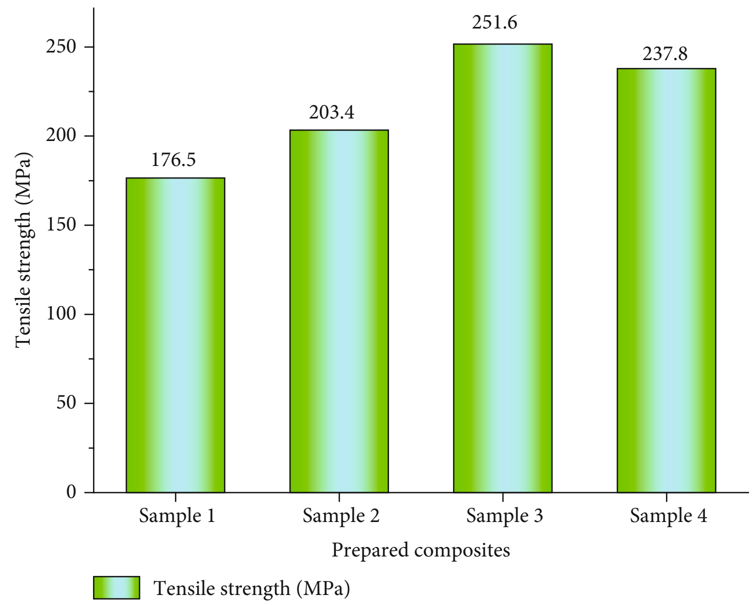


Figure 4: Tensile strength comparison of fabricated metal matrix composites.

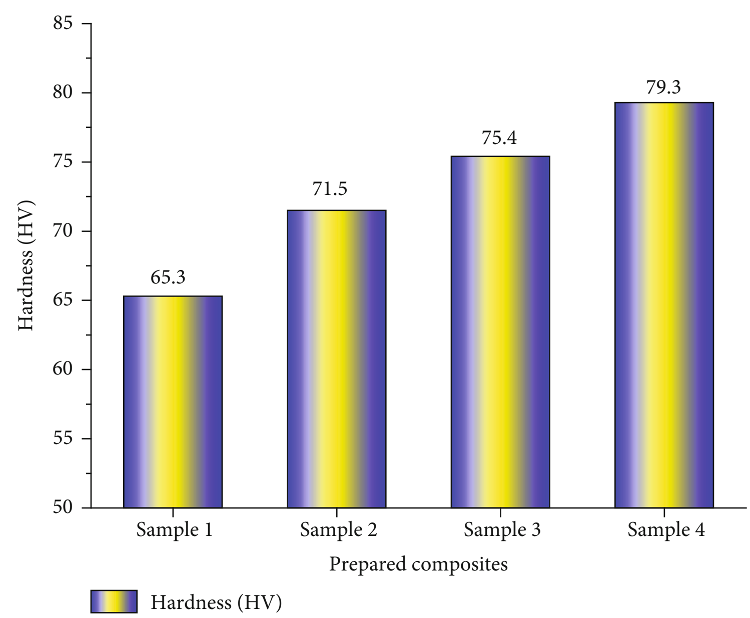


Figure 5: Microhardness results of the fabricated metal matrix composites.

The yield strength is mainly enhanced by the homogeneous distribution of reinforcements, grain refinement, and limited pores in the fly ash-reinforced composites. The fabricated metal matrix composites in sample 3 have higher tensile strength (42% increment) value when compared with pure magnesium, samples 2 and 4. Figure 4 shows the gradual increase in tensile strength up to sample 3; afterwards, its tensile strength value was significantly reduced. Mean tensile strength ± four standard deviations were observed. The fly ash particles in the matrix alloy protect the softer matrix, thus limiting the deformation and also resisting the penetration and cutting of slides on the surface of the composites.

3.2. Microhardness. The addition of fly ash reinforcements showed greater improvement in microhardness values of fabricated metal matrix composite samples, as shown in Figure 5.

Sample 4 has an improved hardness value of 21% compared with pure magnesium in sample 1. Hardness values improve due to the equal dispersion of fly ash reinforcement. Hardness results were three times average result of indentation in the Vickers hardness test [28]. The same effects observed in AZ91 Mg/fly ash composites improved hardness value with an increasing percentage of reinforcements [29]. Mean hardness ± 2 standard deviations were observed.

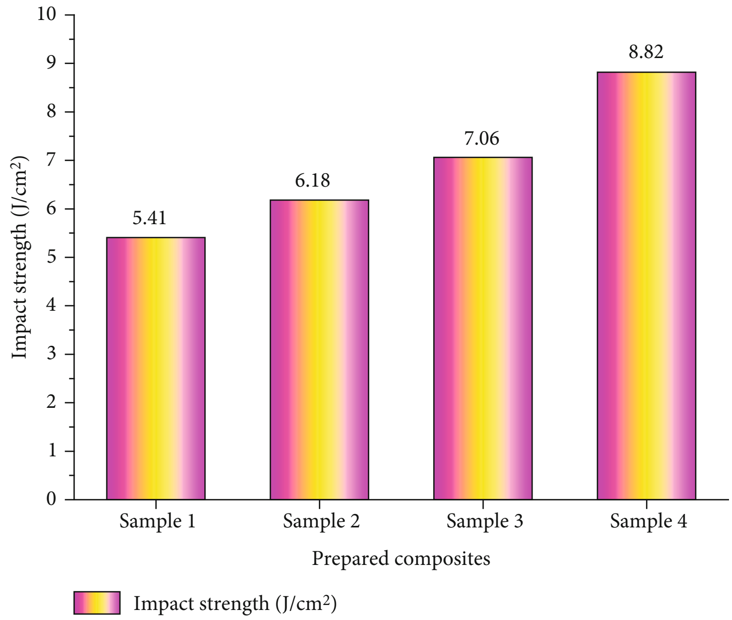


Figure 6: Energy absorption impact strength.

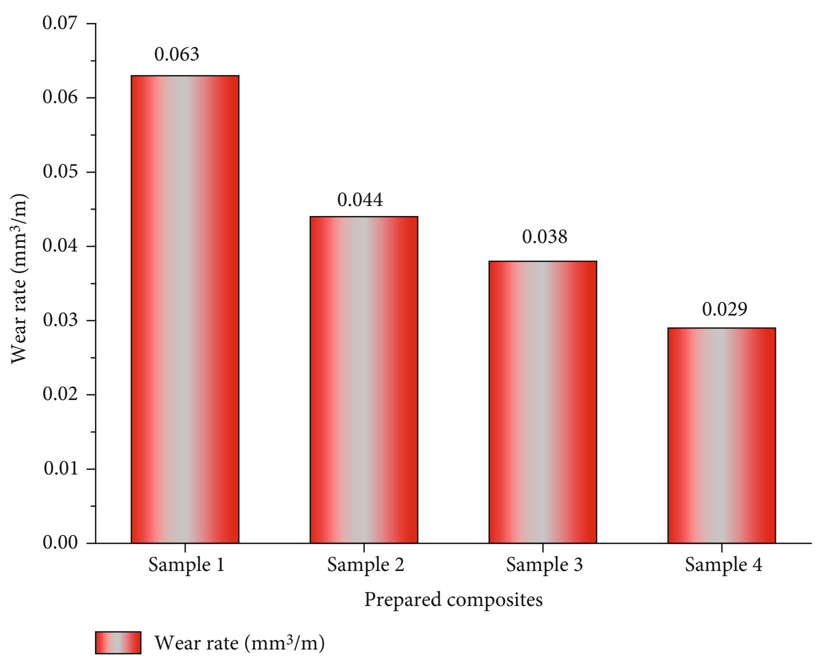


Figure 7: Wear rate of comparison of fabricated metal matrix composite samples.

3.3. Impact Strength. The energy absorption results of the samples are presented in Figure 6. It was observed from the result that the inclusion of fillers into the metal matrix gradually improves the energy management of the fabricated metal matrix composites samples. Higher energy absorption can be obtained by enhancing filler percentage. Sample 4 shows a higher energy absorption capacity of 8.82 J/cm^2, a remarkable value compared with a pure Mg sample [30]. Mean impact strength ± 0.5 standard deviations were observed.

3.4. Sliding Wear Behaviour. The wear test of the proposed samples was conducted at the temperature of 25°C, and the relative humidity was about 50%. The results indicate that wear rates and friction coefficient values decreased with the weight percentage of fly ash, as shown in Figures 7 and 8. There was a remarkable reduction in the wear rate of 53% compared to pure magnesium and sample 4. Similarly, the reduction percentage of wear rate was 13 and 30% vice versa for samples 2 and 3 compared with pure magnesium. The reduced wear rate correlates

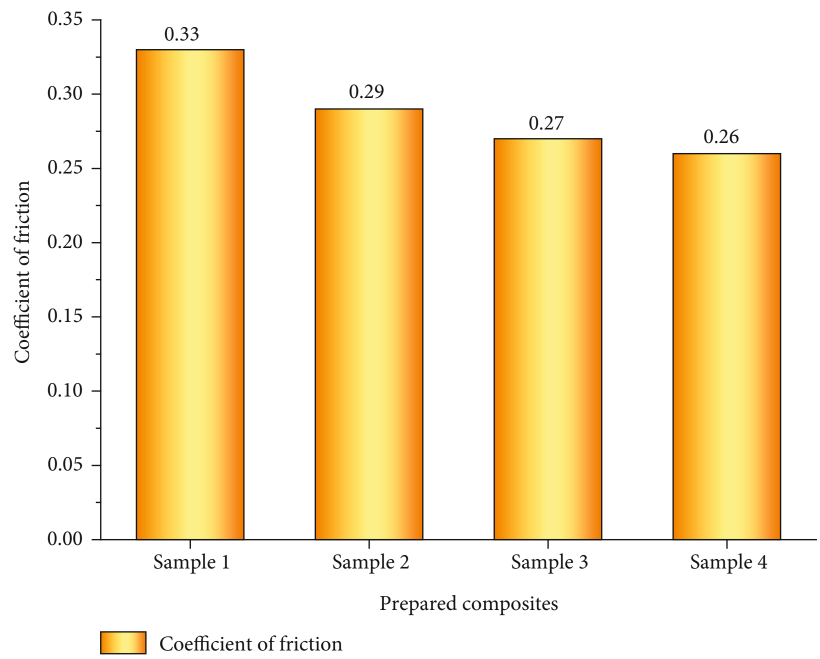


Figure 8: Coefficient of friction of fabricated metal matrix composite samples.

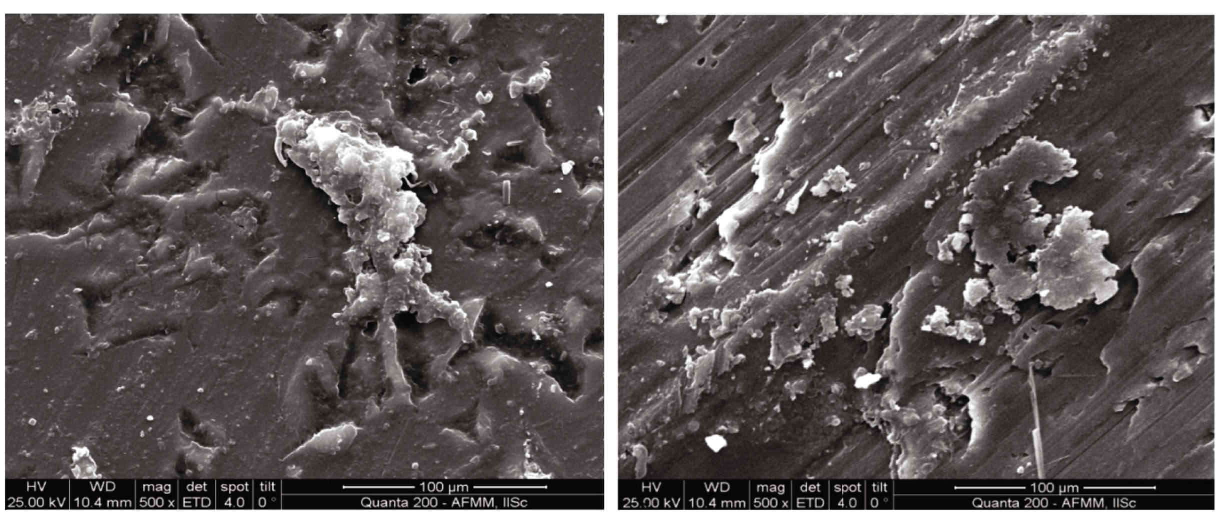
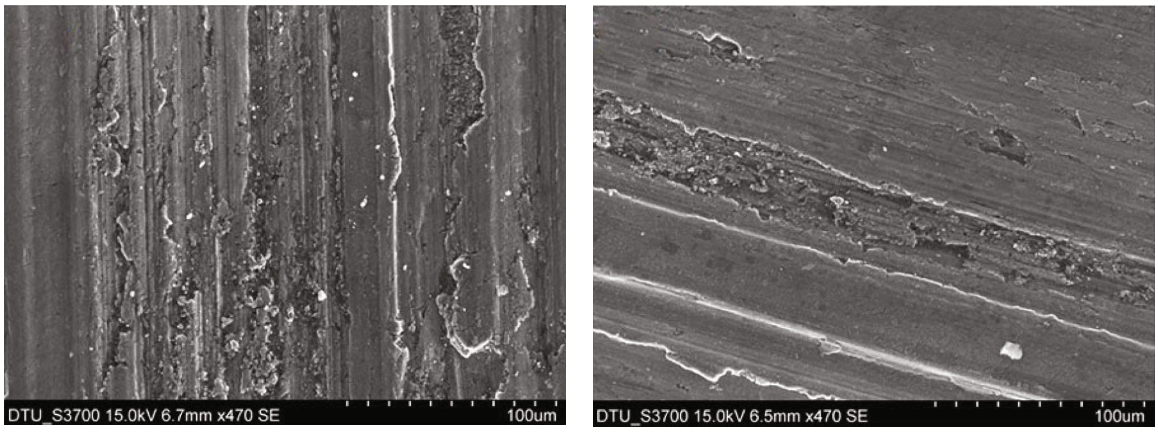


Figure 9: SEM images of pure magnesium samples.

with increased hardness values according to the Archard's wear law of the inverse relationship between wear rate and hardness [31].

3.5. Scanning Electron Microscope. The microstructure of pure Mg fabricated using stir casting is shown in Figure 9. The interfacial reaction and oxidation occurred during pure magnesium casting, as displayed in Figure 9. The worn surfaces of pure magnesium and highly reinforced fly ash sample 4 images are shown in Figures 10(a) and 10(b). The worn surfaces represented that the adhesive wear occurred on the unreinforced magnesium. The most important characteristics, such as groove pattern and abrasive wear, were found in the worn surface of SEM images. The craters were created due to applied load and ploughing action on the surfaces in the unreinforced magnesium samples [32]. The wear rates were reduced by adding reinforcements to the samples [33]. The increased load carrying capacity and reduced wear rate on sample 4 were observed, as shown in Figure 10(b). From Figure 10(b), worn surface images observed that smaller craters and grooves evidenced that fly ash fillers influenced improved load carrying capacity and reduced wear rate [34]. The SEM images have shown that the fly ash was homogeneously distributed in magnesium matrix composite [34].



(a)

(b)

Figure 10: SEM images of worn surfaces of (a) pure magnesium and (b) sample 3.

4. Conclusion

This proposed research successfully fabricated pure Mg and fly ash (2.5, 5, and 7.5 wt%) composites. The mechanical properties and wear behaviour on its microstructure were compared between pure Mg and fabricated metal matrix composite samples.

(i) The tensile strength values were improved by 42% in sample 3 compared with pure Mg. Similarly, the hardness values were also improved by 21% in sample 4 compared with pure Mg

(ii) The wear rate and coefficient of friction are also reduced by the increased weight percentage of fly ash reinforcement. The presence of fly ash was beneficial in reducing the wear rates and coefficient of friction

(iii) SEM images show interfacial reactions in fly ash particles during the casting process, concluding that reduced wear rates and improved mechanical properties have favourable responses to wear-resistant applications

Data Availability

The data used to support the findings of this study are included within the article. Should further data or information be required, these are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Research Article

Ensuring Information Disclosure and Environmental Impact on Nanoradioactive Operation of Civil Nuclear Facilities in China

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Japan was struck by a massive earthquake that triggered a tsunami in March 2011, which led to a severe nuclear accident at the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company. Now, more than 10 years later, it is widely acknowledged that the civil nuclear industry is of great importance in reducing greenhouse gas emissions, improving natural environmental quality, and safeguarding national energy security. Nanomaterials and nanotechnologies, which have gained wide consideration in recent years, have shown a wide variety of application potentials in the future nuclear energy system. Thus, China has been developing its civil nuclear industry throughout the years, despite the nuclear accident in Fukushima, Japan. As a result, China is currently one of the countries with the most nuclear power plants. However, due to the potential radioactive risk, the public has an instinctive fear of civil nuclear development. To alleviate the public's antinuclear sentiment, the *Nuclear Safety Law* was formally implemented in 2018, and *Measures for Disclosure of Nuclear Safety Information* were issued by the Ministry of Ecology and Environment of China in 2020, both stipulating that the public has the right to obtain information about nuclear safety and be involved in related activities. The purpose of such legislation is to eliminate the public's doubts and phobia about the development of the civil nuclear industry. However, challenges still exist. Although such suggestions have been proposed, such as information disclosure and social involvement should begin as early as the siting of such nuclear facilities, mechanisms to provide sufficient compensation to the public living near nuclear facilities should be established, and these suggestions still have not been applied in the law of China and either not been practiced exactly so far. So, even though all the suggestions have strong feasibility themselves under today's circumstances in China, it is not easy to judge the effectiveness of these suggestions until they are fully practiced. It is the biggest problem of existing works in this paper. To highlight the serious problems in information disclosure and public involvement in the siting and construction of civil nuclear facilities, several case studies were investigated as the major methodology in this research. Moreover, a legislation study was used to analyze the current content of related legislation and regulations. A qualitative methodology was also adopted to summarize the legal problems surrounding information disclosure and social involvement during the siting and construction of civil nuclear facilities. Information disclosure and public participation still face several obstacles in China, even though laws and regulations guarantee people the right to access available information and take part in pertinent decision-making. This is particularly true when it comes to the siting and construction of civil nuclear facilities. Thus, in the last several years, several antinuclear incidents have been initiated by the public due to a lack of information and mechanisms to participate. According to the examined cases, information disclosure and public involvement are still not sufficient during the siting of nuclear facilities. A relevant compensation mechanism for people living around nuclear facilities has not been established, and public education on basic nuclear safety is lacking. Therefore, public involvement cannot be completely realized. To ensure information disclosure and public involvement in civil nuclear facilities, this article proposes that information disclosure and social involvement begin as early as the siting of such facilities. Furthermore, operators of nuclear facilities and local governments should establish mechanisms to provide sufficient preventive compensation to the public living near nuclear facilities and attempt to popularize the science of nuclear safety to avoid public misunderstanding.

1. Introduction

A large portion of the early development of nuclear energy came from military initiatives that started during the Second World War. Governments at the time and for a long time afterward treated information on nuclear technology and material as confidential because they believed it to be very sensitive [1]. Because nuclear activities may have an impact on the environment and produce environmental data, it has become crucial to provide the public with as much information as possible about the development and use of all nuclear facilities to foster public understanding of and confidence in the civil nuclear industry. But at the beginning of the civil nuclear industry, most decisions about the siting, construction, and operation of nuclear facilities have been made by senior officials and specialists in the nuclear field. Therefore, the public could not understand nuclear science and technology. They generally estimated the nuclear risks from "Intuition" by a process called "Perception of Risk" [2]. There has been a big gap between the evaluation of nuclear risks of the specialists in the nuclear field and the cognition of this risk of the public [3]. According to Beck's theory of "Risk Society," the public's concern for civil nuclear facilities is because nuclear risks have outstanding particularities compared with other risks of today's world [4]. For instance, even when the maximum level of safety has been attained, nuclear and radiological mishaps still have a chance of happening. And the concern of the public has become one of the most significant reasons that hinder the development of the civil nuclear industry in many countries [5].

At all stages of advanced nuclear plants, nanomaterials and nanotechnologies are projected to be able to play significant roles and have enormous application potential. The necessary individuals must be aware of what is going on in their environment, comprehend what is happening, and participate in the decision-making process to assure the development of the civil nuclear business. The Rio Declaration, commonly known as the Earth Charter, which was published in 1992, declares in Principle 10 that it is better to address environmental challenges with the involvement of all interested persons. The 1998 Convention on Access to Information, Public Participation in Decision-making, and Access to Justice in Environmental Matters (Aarhus Convention) mandates the establishment of both a system that allows the public to ask for and receive environmental information from public authorities as well as a system that allows public authorities to actively gather and disseminate environmental information to the public without being asked. All nuclear facility construction and operation information unquestionably qualifies as critical environmental information. The Aarhus Convention's Article 6 also guarantees the public's right-to-participate. Therefore, during the entire process of civil nuclear facility siting, building, operation, and even decommissioning, governments that are developing such facilities must ensure information transparency and public involvement.

As the most important legislation in the nuclear field of China, the *Nuclear Safety Law* was established as a mechanism of overall-process safety supervision. The aims of the *Nuclear Safety Law* include protecting the public interest and involvement, strengthening information disclosure, eliminating people's distrust, and increasing people's confidence in the development of the civil nuclear industry. Article 11 of the *Nuclear Safety Law* states, "A citizen, a legal person or any other organization shall be entitled to access to nuclear safety information by the law." Additionally, Chapter Five of the *Nuclear Safety Law*, named "Information Disclosure and Public Participation," stipulates the measures and methods of guaranteeing information disclosure and social involvement. *Measures for Disclosure of Nuclear Safety Information*, issued by the Ministry of Ecology and Environment in 2020, also include the information disclosure obligation of operators of nuclear facilities and governmental supervisors of nuclear safety.

This essay covers China's civil nuclear facility siting, building, and operating laws as they relate to information disclosure and public participation. Although laws and regulations guarantee individuals the right to obtain information and participate in pertinent decision-making, public participation and information disclosure nevertheless confront several obstacles, particularly when civil nuclear plants are being built and siting takes place.

Since very few scholars would like to do specific academic research in human and social sciences on civil nuclear facilities and nuclear-related matters, few books on this topic have been published, such as the following:

"Social Construction of Nuclear Risks in China: the Public's Participation in Civil Nuclear Issues from the Start of the 21st Century" written by Dr. Xiang Fang

"Public Communication: the Ideal mode to solve the difficulty of NIMBY" by Yue Zuo

"Government Communication Effectiveness on Local Acceptance of Nuclear Power: Evidence from China" by Dr. Yue Guo

"Public Acceptance of Nuclear Power: Research, Reflection, and Ways to Go" by Professor Chao Fang and Yuhong Chen

However, all of these above academic achievements are from the aspects of sociology, public administration, and public policy science, and they study the topic through statistics, questionnaires, and modeling methodologies; none of them explore this issue from the legal perspective or apply methodologies from the field of law.

Thus, it is the characteristic of this paper to summarize the related challenges by analyzing real cases and propose suggestions on how to improve information disclosure and public involvement in the field of civil nuclear from the perspective of the law.

2. Literature Survey

Castiglione et al. [6] in a study titled "Rule of law and the environmental Kuznets curve: evidence for carbon emissions" show that there exists a negative relation between the status of laws and pollution. They argue that when there is a strong governing law, therefore, we observe improvement in environmental preservation.

Kueny [7] in a study titled "Environmental radiological protection and nuclear law: from the protection of humans to the protection of the environment per se?" addresses the problem of international laws and regulations regarding the effects of ionizing radiation on the environment and nature; and that nuclear laws not only cover human societies, but nonhuman species are also protected from hazardous effects of ionizing radiations.

Sousa Ferro [8] in research titled "The future of the regulation of nuclear safety in the EU" considers the prevention of harm to workers, people, and the environment among the fundamental issues discussed in nuclear safety laws and regulations, although he stresses that regulations must not limit themselves to nuclear power plants but should cover all effective factors within the nuclear fuel cycle including radioactive waste management.

Qiang [9] in a study titled "Nuclear energy and the environment" attempts to compare the environmental effects of generating electricity through nuclear technology and coal. This comparison shows that the nuclear electricity generation process, effect on the environment, human health, and emission of greenhouse gases are far less than generating electricity using coal. In this course, accelerating the development of nuclear energy is considered one of the main solutions for solving environmental pollution problems.

Riley [10] in his research titled "Justification of the continued development of the peaceful use of nuclear energy" to justify the development of peaceful nuclear energy applications explains the scientific application of nuclear energy in different fields, the economic advantage of this technology compared to many other current options, and its positive effects on health, safety, security, and finally environmental protection.

Gharib [11] in his evaluation titled "Nuclear energy and nonproliferation," while explaining the legal issues around peaceful applications of nuclear energy, accounts for it as a new, effective, and efficient source of energy and realizes that the prerequisite of a world transition of movement toward peaceful nuclear energy usage, apart from utilizing related technical and scientific equipment, requires governments and international organizations' adherence to international laws.

Bhattacharjee [12] in his study showed that by expanding diverse applications of nuclear technology in various fields including industrial, medical, and agricultural fields, governments have realized the fact that to respond to technical and managerial requirements of environmental protection, safety, and human health, creating a well-organized legal framework, especially in the fields of government liability instead of nuclear harm, is essential.

3. The Current Legislation of Public Involvement throughout the Whole Process of the Siting, Construction, and Operation of Civil Nuclear Facilities in China

The public has the right to be protected from radioactive harm by nuclear facilities. Thus, for the public, the right to nuclear safety is always a type of passive protection [13]. However, the public's fear of nuclear activity caused by the lack of relevant information hinders the construction and operation of civil nuclear facilities. Therefore, relevant information disclosure and public involvement are of great significance. From the aspect of the law, people's right-to-know and right-to-participate must be realized and protected [14]. In 2013, the China Nuclear Energy Association suggested increasing the transparency of information and promoting the involvement of the public, and both of these recommendations were written into the *Nuclear Safety Law* in 2018. In addition to the *Nuclear Safety Law*, other laws and regulations about information disclosure and public involvement in the civil nuclear industry have been established, as listed in Table 1.

Figure 1 clearly depicts the simplified summary of suggestions of this work. Article 11 of the *Nuclear Safety Law* defines the public (including citizens, legal persons, and other organizations) as subjects who have the right to obtain information related to nuclear safety (right-to-know). This means that the *Nuclear Safety Law* guarantees the disclosure of information about nuclear safety and public involvement in related activities. Information disclosure is the basis of public involvement because, without the relevant information, the public is not able to participate during the siting, construction, and operation of nuclear facilities.

Chapter Five of the Nuclear Safety Law lays out the procedures that serve to ensure information disclosure and society involvement in nuclear safety in addition to Article 11, which lays out fundamental principles. By the law, the public may apply to the nuclear safety supervision and administration department of the State Council and the department information for access to information relating to nuclear safety. For instance, Article 65 mandates that nuclear safety information be made publicly available by the law and that it be done so promptly through government announcements, websites, or any other means facilitating public knowledge. The second example is Article 68, which grants the public the right to report any act that poses a hidden risk to nuclear safety or violates applicable legal and administrative requirements to the State Council's department responsible for nuclear safety supervision and administration or any other relevant department. Additionally, the public assumes the obligation to not fabricate or spread false nuclear safety information. Moreover, based on the *Nuclear Safety Law*, *Measures for Disclosure of Nuclear Safety Information* stipulates the kind of nuclear safety information that should be disclosed and the methods of the disclosure. All of these provisions are the foundation of the public's right-to-know and the right-to-participate.

Before the *Nuclear Safety Law* went into effect, Articles 53 and 56 of the *Environmental Protection Law*, Articles 21 and 23 of the *Environmental Influence Assessment Law*, and Articles 11 and 15 of *Construction Project Environmental Protection Regulation* were issued by the State Council, and *Environmental Protection Public Participation Regulation* issued by the Ministry of Ecology and Environment also required the disclosure of nuclear safety information and guaranteed public involvement in the civil nuclear field. By the above legislation and regulations, the operators of

Table 1: China's related laws currently.

Legislation	(i) *Nuclear Safety law* (ii) *Environmental Protection Law* (iii) *Environmental Influence Assessment Law* (iv) *Law on Prevention and Control of Radioactive Pollution*
Regulations	(i) *Construction Project Environmental Protection Regulation (issued by the State Council in 1998, and revised in 2017)* (ii) *Environmental Protection Public Participation Regulation (issued by the Ministry of Environmental Protection in 2015)* (iii) *Measures for Disclosure of Nuclear Safety Information (issued by Ministry of Ecology and Environmental in 2020)*

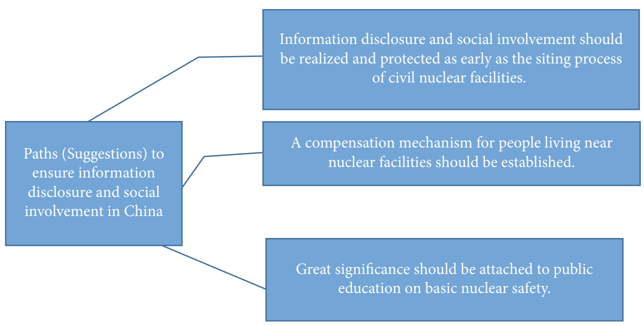

Figure 1: The simplified summary of suggestions for this paper.

nuclear facilities are required to submit environmental influence reports for certification. Before submitting, the operators are obligated to hold public hearings about nuclear safety situations. Furthermore, all environmental protection departments are required to disclose environmental information and establish a public participation mechanism. Otherwise, the *Law on Prevention and Control of Radioactive Pollution* grants the public the right to accuse nuclear operators of radiation pollution when supervising the nuclear safety of nuclear facilities. It is believed that "accuse" is one of the most important functions in allowing the public to realize "public involvement".

4. Typical Cases of Antinuclear Activity during the Process of Siting and Construction of Civil Nuclear Facilities

Despite the above legislation and regulations, relevant information disclosure and public involvement still face several challenges. Therefore, in the past several years, several antinuclear incidents have been initiated by the public due to a lack of information and methods to participate.

(For several reasons, the real names of the relevant places and operators of nuclear facilities are anonymized, and abbreviations are used instead.)

4.1. The Siting of the First-Stage Project of the PZ Nuclear Power Plant Was Boycotted by the WJ Public. In 2009, the safety analysis report and environmental influence report about the siting of the first-stage project of the PZ Nuclear Power Plant were ratified by the National Nuclear Safety Administration. However, residents of WJ County, located in another province on the other side of the river, were fiercely against the siting. Four retired cadres in WJ County wrote a Petition to Suspending PZ Nuclear Power Plant. Their petition claimed that the nuclear plant's safety analysis report contained false information, that the seismic standard was inadequate, and that the reactor was located close to an industrial area; moreover, there were serious problems with the process and results of the public opinion survey. Due to the petition, the public in WJ County, whose right-to-know and right-to-participate were not realized, began to boycott this project.

The manner in which the Nuclear Engineering Institute disclosed information and surveyed the public was inadequate. At first, the target audiences of information disclosure and involvement were only the people who lived in PZ County, but the people who lived in WJ County, merely 10 kilometers away from the siting of the nuclear power plant, were completely ignored. At that time, the relevant information about the siting of the PZ Nuclear Power Plant was only disclosed on the local government website and in the local newspaper, but the public from WJ County seldom checked this website, and the newspaper was not sold in WJ County. As a result, the people of WJ County were not able to obtain relevant information. It had infringed on the WJ County public's right-to-know about nuclear safety.

Moreover, when the public opinion survey was performed in WJ County, some people from PZ County who were very familiar with several villagers in WJ County collected opinions only from acquaintances and bribed them with small gifts. Thus, only 10 percent of the participants of the opinion survey lived in WJ County, and most of them responded to the survey to receive gifts. These approaches infringed on the WJ County public's right-to-participate. Thus, the results of the public opinion survey were not accurate.

Furthermore, one Nuclear Engineering Institute conducted two subsequent surveys. However, the government and public of WJ County did not receive any information before the siting of the PZ Nuclear Power Plant. The institute did not analyze the results of the public opinion survey and release the relevant results to the public nor did it receive suggestions from the public after the opinion survey. Both of the surveys violated the principles of scientific design and information transparency, so the WJ County public's right-to-know and right-to-participate about nuclear safety could not be realized. Meanwhile, the hearings held by this Nuclear Engineering Institute were also questioned by the WJ public. This Nuclear Engineering Institute held two hearings, and only one participant involved in the hearings was from WJ County; the remaining 52 participants were from other places. Thus, without sufficient involvement of the WJ County public, there were serious problems with the hearings.

Since the public from WJ County fiercely boycotted the nuclear project, and some people even stopped construction, the construction of the PZ Nuclear Power Project was suspended, and more than 3 billion CNY of investment was wasted.

4.2. The Project of a Nuclear Fuel Factory Was Strongly Opposed by the Public of HS. One large Nuclear Corporation planned to construct a nuclear fuel factory in HS of JM City. In July 2013, the government of JM published a "Social Stability Assessment" for the project and asked the public to provide opinions within 10 days. In other words, the JM public only had 10 days to obtain the information, express their opinions, and participate in the decision-making process. Thus, the public thought that 10 days was too short and that the government did not really care about their opinion and just wanted to start the project. The public of JM City was strongly opposed to the plan. In order to boycott the project, the JM public held a demonstration along the main street of the city and even held a rally in front of the municipal government. To ease the anger of the JM public and sustain social stability, the nuclear fuel factory plan was abolished, and a large amount of money was wasted.

4.3. The Siting of a Commercial Spent Fuel Recycling Factory Was Boycotted by the Public of LYG. With more nuclear power plants being constructed over the last several years, spent fuel is increasing in China. In China, the ability to process spent fuel does not satisfy the demand for processing it. In order to solve this problem, one of the largest Nuclear Corporations in China, in cooperation with a nuclear operator in France, planned to establish a large commercial spent fuel recycling factory. In the plan, the French corporation was in charge of technology research, and the Nuclear Corporation in China was responsible for the siting of the future spent fuel recycling factory. In July 2016, the members of the Nuclear Corporation in China visited the city of LYG, which was announced on the website of the Nuclear Corporation. The announcement said, "the establishment of the large commercial spent fuel recycling factory can realize the sustainable development of nuclear power projects and promote the technical level of the civil nuclear industry." Actually, at that time, this project was still in the first stage, and the city of LYG was just one possible site. However, the reports on the website were processed by We Media, and the spent fuel recycling factory was misunderstood to be a nuclear waste processing factory. After that, reports spread rapidly and became a hot topic on WeChat, Weibo, and other social platforms. Finally, the spread of this misinformation caused a public demonstration to protest the siting plan. In order to calm the angry LYG public, the local government published an announcement on their official Weibo account that "the people's government of LYG decided to prevent the Nuclear Corporation from taking LYG as the siting of the commercial spent fuel recycling factory."

Although the LYG government and the Nuclear Corporation compromised, giving up the siting not only wasted a large amount of money but also did nothing to alleviate antinuclear sentiments among the public. Table 2 shows the summary of above cases.

5. Legal Challenges of Public Involvement Have Been Exposed by the Cases above

Although there are relatively sound legislation and regulations, the three typical antinuclear cases above clearly demonstrate that there are still legal challenges about information disclosure and social involvement, especially during the siting and construction of civil nuclear facilities.

5.1. The Lack of Information Disclosure and Public Involvement during the Siting of Nuclear Facilities. Insufficient information and the preclusion of public participation can exacerbate the public's nuclear phobia and antinuclear activities. Information disclosure and public involvement are important ways to alleviate nuclear phobia of the public. The *Environmental Protection Law*, *Environmental Influence Assessment Law*, *Construction Project Environmental Protection Management Regulation*, and other legislation and regulations all stipulate that after determining the site of facilities such as nuclear power plants, all information must be published, and public opinions need to be collected. Moreover, the *Law on Prevention and Control of Radioactive Pollution* stipulates that during the operation of nuclear facilities, the public can ask for information to be disclosed and even initiate a lawsuit if some of their rights cannot be realized. By Chapter Five of the Nuclear Safety Law, operators of nuclear facilities and relevant local governments are required to publicly disclose information regarding nuclear safety as part of their respective roles and responsibilities. "The nuclear site operators shall collect the opinions of relevant parties on key nuclear safety concerns involving social interests through questionnaire survey, hearing, discussion meeting, and symposium or by any other methods and submit feedback in a suitable form," states Article 66. Thus, it is clear that information related to the construction, operation, and other activities of nuclear facilities must be disclosed to the public, and the public should be involved in these processes, including during decision-making. However, it is unclear whether the process of siting, which occurs just before determining the size of a nuclear facility, falls under Article 66, "major nuclear safety matters involving public interests." In other words, do people have the right-to-know and right-to-participate before the site is determined? Should potential alternative sites be presented to the public? Should the public be involved during the siting period?

By current legislation and regulations in China, the siting process before determining the actual site does not seem to fall under "major nuclear safety matters involving public interests." Therefore, during the siting process, relevant information need not be disclosed, and public involvement in decision-making is not required. However, in the case of "the siting of commercial spent fuel recycling factory was boycotted by LYG public," the project was just in the preliminary siting phase of the recycling factory, so relevant departments only described the issue briefly in the news on the website of the Nuclear Corporation, and the LYG public had no way to obtain such information or become involved in the decision-making. Thus, their right-to-know and right-to-participate were restricted. In fact, at that time, the

Table 2: The summary of above cases.

What happened	*When*	*How*	*Result*	*Why*
The siting of first-stage project of the PZ Nuclear Power Plant was boycotted by public	*2009*	*People were fiercely boycotted the nuclear project*	*Project was suspended, and investment was wasted*	*Disclosed information and surveyed the public was inadequate*
The project of a nuclear fuel factory was strongly opposed by public	*2013*	*Public held a demonstration along the main street of the city a rally in front of the municipal government*	*Plan was abolished, and investment was wasted*	*Time for participate in the decision-making process was too short*
The siting of a commercial spent fuel recycling factory was boycotted by public	*2016*	*Public demonstration to protest the siting plan, the local government prevent the Nuclear Corporation from taking LYG as the siting*	*Siting was cancel and cannot alleviate public's antinuclear sentiments*	*Information disclosure channels and means were wrong, and the public were lack of knowledge of nuclear*

recycling factory was just at the siting stage, and it had not been determined whether LYG would be the site of the spent fuel recycling factory; therefore, based on the existing legislation, the local government and environmental protection departments were not obligated to publish information about the influence of the factory, which directly caused the event of "LYG public boycotted the siting plan of recycling factory" and postponed the whole project of the recycling factory in China. It is believed that if the people of LYG had received information about the siting of the future recycling factory through public official media and had been able to participate and express their views about it, they would not have protested the factory so violently, and the spent fuel recycling factory could have been constructed in LYG or other sites of China by now.

Taking the case of "The project of nuclear fuel factory was strongly opposed by the HS public" as another example, the local government and the operator of the nuclear facility did not publish any information for the public until they confirmed the siting in HS. Then, they only gave the public 10 days to become involved by expressing their opinions. "Ten days" was too short for the public to read all of the information about the nuclear fuel factory and participate in decision-making. As a result, the public was easily misled by incorrect information and became terrified about the nuclear fuel factory plan, which resulted in its cancellation of the nuclear fuel factory plan.

Therefore, the length of time for information disclosure and public involvement of Civil Nuclear Facilities in China is not long enough, and information disclosure and social involvement are difficult to realize during the siting process of nuclear facilities. This not only infringes on the public's right-to-know and right-to-participate and potentially exacerbates nuclear phobia, but it also hinders the development of the civil nuclear industry in the whole country since, in the above cases, large nuclear-related plans have been canceled just because the public could not obtain sufficient information and be involved in decision-making during the siting process.

5.2. The Lack of a Relevant Compensation Mechanism for People Living Near Nuclear Facilities. During siting and construction, people living near nuclear facilities can participate in two ways. On the one hand, the public can realize its right-to-know and right-to-participate by focusing on scientificity and rationality during the siting and construction processes of nuclear facilities. On the other hand, the public can advocate for compensation during the siting and construction processes, as people are likely to worry about their health and financial interests. In other words, the public pays close attention to whether compensation from the siting and construction of nuclear facilities is sufficient and can satisfy their personal expectations. It was said that "an important failing of current practice in siting locally noxious facilities is the strategic problem which results from failure to pay compensation to neighbors who suffer costs (loss in property values or less measurable amenity costs) not covered by the law" [15]. Likewise, paying compensation is an effective method of realizing public involvement, because nuclear facilities constructed and operated nearby may influence the quality of life and the surrounding environment and cause real estate value to decline.

Article 31 of the *Environmental Protection Law* states that "the State establishes and improves eco-compensation system." Based on this part of the legislation, if people living near nuclear facilities had been provided with enough economic compensation for the decreasing value of their real estate and other potential losses associated with the risks of nuclear facilities, the public's hostility towards nuclear facilities could have decreased, and people would have been more likely to accept the nearby construction of nuclear facilities. Once again, taking the case of "the siting of commercial spent fuel recycling factory was boycotted by LYG public" as an example, the regulations of *Temporary Measures for the Use and Management of the Spent Fuel Treatment and Disposal Fund for Nuclear Power Plants* and *Management Measures for the Spent Fuel Treatment and Disposal Fund for Nuclear Power Plants* in China state that the spent fuel processing fund can be used for the transportation, storage, further processing, and even retirement of spent fuel, as well as other outcomes of spent fuel reprocessing. However, *Measures* does not specify a portion of the fund that can be provided as financial compensation to people living in the area. Currently, there is no such public compensation mechanism for people living near civil nuclear facilities in China. Local governments and operators of nuclear facilities do not compensate individuals who may be influenced by the siting and construction of nuclear facilities.

Bestowing economic compensation according to the public's opinion would not only make the public accept the siting and construction of nuclear facilities but also benefit the nuclear industry itself. Paying compensation to the affected public is the result of realizing public involvement. However, at present, the public's opinion about requiring compensation is ignored, decreasing the value of public involvement to some extent. Therefore, the lack of a relevant compensation mechanism for people living near nuclear facilities is a key problem in China.

5.3. The Lack of Public Education on Basic Nuclear Safety. Even if all information is disclosed and transparent, the public's right-to-know cannot be effectively realized because of the lack of knowledge about the civil nuclear industry and nuclear safety, which limits public involvement during the siting, construction, and operation of civil nuclear facilities in China. The largest contributor to the public's nuclear phobia is the lack of knowledge of nuclear safety. One of two trends appears when the public only knows a little about nuclear safety. One is that the public ignores the danger of nuclear activities and overly trusts in the safety of nuclear facilities, so the construction of nuclear facilities is always encouraged, regardless of the actual influence. The other one is that the danger of nuclear facilities is exaggerated, and all types of nuclear facilities are boycotted by the public. Due to the lack of relevant knowledge or a misunderstanding of nuclear safety, the danger of nuclear facilities will be exaggerated, which causes tension between the public and nuclear projects and results in public opposition to the siting, construction, and operation of civil nuclear facilities.

Taking "the project of nuclear fuel factory was strongly opposed by the HS public" and "the siting of commercial spent fuel recycling factory was boycotted by the LYG public" as examples, the local governments and operators of nuclear facilities overlooked the importance of public education on nuclear safety, which caused people to lack relevant knowledge and to be easily misled by false information available on the Internet. In the era of the Internet, misinformation can spread rapidly on different We Media, which increases the fear that people have of nuclear facilities (nuclear fuel factory and spent fuel recycling factory). If the public in LYG had been effectively educated about spent fuel, they would not have been misled by misinformation and believed that spent fuel was a radioactive waste, which caused people to fear that spent fuel pollutes the surrounding environment and poses risks to their safety. The existing challenge in China is that regardless of education level, including master's and Ph.D. levels, people lack basic knowledge of nuclear safety and blindly boycott nuclear facilities.

Although the current legislation and regulations in China grant the public the right-to-know and provide ways to be involved in decision-making during the construction and operation of nuclear facilities, due to the lack of knowledge on nuclear safety, public involvement cannot be completely realized.

6. Paths Forward to Ensure Information Disclosure and Social Involvement

To meet the above challenges and ensure public involvement during the siting, construction, and operation of civil nuclear facilities in China, several recommendations are proposed below:

6.1. Information Disclosure and Social Involvement Should be Realized and Protected as Early as the Siting Process of Civil Nuclear Facilities. The Rio Declaration of 1992's Principle 10 states that it is best to address environmental concerns with the involvement of all concerned persons. The Convention on Access to Information, Public Participation in Decision-making, and Access to Justice in Environmental Matters (Aarhus Convention) of 1998 calls for a system that allows the public to request and receive environmental information from public authorities as well as a system that allows the public to participate in environmental decision-making in an informed manner. Environmental information also includes nuclear-related information, such as the location of nuclear facilities, and should be made available to the general public.

The International Atomic Energy Agency (IAEA) recommended that bodies involved in the development, use, and regulation of nuclear energy make available all pertinent information regarding how nuclear energy is being used, particularly concerning incidents and abnormal occurrences that could have an impact on public health, safety, and the environment. France is a good example of the effectiveness of such an approach. The French government communicates with the public during the siting process, which helps the public obtain information about planned nuclear facilities and participate as early as the siting of facilities. Thus, more than 70% of energy in France is nuclear power, and the people who live around nuclear facilities seldom complain about the siting, construction, and operation of the facilities, because all relevant information is open and transparent, and the public's opinions and questions are respected [16]. In Finland, numerous surveys and interviews are held during siting, and the public can receive the latest information about nuclear facilities and related environmental effects. In addition, the public in Finland can express their opinions freely, and great importance is attached to these opinions.

The *Nuclear Safety Culture Policy Announcement*, which was published in 2015, proposed that "By information disclosure, public involvement and public education, the public's right-to-know, right-to-participate, and right-to-supervise should be realized and protected; the decision makers should hear different opinions on different channels from the public on civil nuclear safety and development." This mechanism gives the public right-to-know and right-to-participate during different processes, including the siting, construction, operation, and even decommission of civil nuclear facilities. The earlier that people understand civil nuclear-related information and are involved in such activities as decision-making, the more easily they can accept nuclear facilities constructed in the area.

Therefore, the siting process, which occurs before determining the actual site, needs to be viewed as one of the "major nuclear safety matters involving public interests" in Article 66 of the *Nuclear Safety Law*. The public should have the right-to-know and right-to-participate as early as the sitting process. Local governments, related governmental departments, and operators of nuclear facilities should communicate with the public, establish a communication mechanism, disclose relevant information, collect opinions from the public, and increase the democracy of decision-making as early as the siting process. In this way, the public should be rendered sufficient time to get all the information, become involved, and fully demonstrate their views.

6.2. A Compensation Mechanism for People Living Near Nuclear Facilities Should Be Established. Acceptance by the public is one of the great difficulties in the development of the civil nuclear industry and nuclear safety supervision. There are several reasons to compensate people living near nuclear facilities. For instance, nuclear facilities may harm the health of people nearby, and the value of the surrounding real estate may decrease because of the siting, construction, and operation of nuclear facilities. As a response, the law should protect people who live in the area, because they might be exposed to more risks. A preventive compensation mechanism means that the public can demand preventive compensation because they might be physically and financially influenced by nuclear facilities. Giving a certain amount of compensation to the public can alleviate their phobia of and resistance to civil nuclear facilities.

Thus, a preventive compensation mechanism should be established by designing compensation standards, processes, amounts, and channels for people living near nuclear facilities. More importantly, standards and assessments of the compensation should be released to the public during the siting process, which would promote the acceptance of civil nuclear facilities by the public living in the area. As a result, the public's phobia and resistance to nuclear facilities' siting, construction, and operation in nearby areas can be alleviated, and their physical and financial interests and right-to-know and right-to-participate can be protected by this kind of financial motivation.

6.3. Great Significance Should Be Attached to Public Education on Basic Nuclear Safety. Nuclear power is a form of clean energy, which has certainly been accepted in the professional field. However, the public lacks relevant knowledge, so high-quality public education on basic nuclear science is a good tool against nuclear resistance and phobia among the public. Public education on basic nuclear science, the popularization of nuclear safety culture, and the cultivation of the public's informed view of nuclear safety are of great significance. Most developed countries focus on educating the public about basic nuclear science. For example, most nuclear facilities in Finland have a science museum that is open all day, so the public can visit these museums without any application. In America, professionals assist people who live around nuclear facilities to understand different professional standards and data on nuclear safety in order to improve the rational judgment of the public and alleviate their nuclear phobia [17]. Local governments in France teach people living near nuclear facilities the basic science of nuclear safety and radiation protection. The operators of nuclear facilities in France offer such public education on basic nuclear science through the Internet and other modern technologies to promote information transparency and public involvement. Overall, public education on basic nuclear science is as important as disclosing information and public involvement.

In China, according to Article 67 of the *Nuclear Safety Law*, "the operators of civil nuclear facilities should take the following measures to conduct nuclear safety science education: (1) Opening the nuclear facility to the public in an orderly manner on the premise of ensuring the safety; (2) Cooperating with educational organizations to conduct nuclear safety science education for students; (3) Establishing nuclear safety science education centers, printing and issuing pertaining materials; (4) Other measures provided for by the laws and administrative regulations." Moreover, the *Law on Prevention and Control of Radioactive Pollution* states that "local governments shall organize propaganda nuclear safety activities, make the public know about related science knowledge." However, what can the operators of nuclear facilities and local governments do specifically about public education on basic nuclear science?

Establishing long-term campaigns and public education on basic nuclear science needs to occur at the right time, with the right content and in the right form. Public education on basic nuclear science should be executed as early as possible throughout the siting, construction, operation, and even decommission of civil nuclear facilities. The content of the public education on basic nuclear science should be objective and cover all questions that the public may ask, including basic knowledge, nuclear industry attributes, environmental protection, and nuclear safety management. The forms of public education can be classified into a "one-way form" and "interactive form." The "one-way form" includes providing science manuals, books, animation, web pages, and other instructive materials about the civil nuclear industry and nuclear safety for the public, and the public can learn basic knowledge of nuclear science through both traditional media and new media such as WeChat and Weibo. The "interactive form" can give the public a greater sense of involvement than the "one-way form." Examples of interactive education include holding face-to-face interviews and video communication in communities and schools between the public and professionals from operators of nuclear facilities; inviting the public to visit civil nuclear facilities; and holding nuclear safety knowledge contests. Media should play a significant role in public education. Thus, it is important to strengthen the neutrality and promote the authority and reliability of both traditional media and new media in providing public education on basic nuclear science with the aim of alleviating the public's nuclear resistance and phobia.

Once receiving sufficient education on nuclear safety and knowing more about the civil nuclear industry, the operation principles of nuclear facilities and related protection measures, the public will truly enjoy its right-to-know and can be better involved in relevant activities during the siting, construction, operation, and even decommission of civil nuclear facilities. Moreover, events such as resisting and boycotting civil facilities will become rarer and may be eliminated one day in the future.

7. Conclusion

China's civil nuclear industry has been developing rapidly in recent years. Meanwhile, more concern is arising about the realization of information disclosure and social involvement. Information disclosure is the basis of social involvement. The *Nuclear Safety Law* and other related legislation and regulations, such as *Measures for Disclosure of Nuclear Safety Information*, stipulate the guarantee of social involvement in nuclear safety issues. However, as demonstrated in past antinuclear cases, the public remains unable to completely realize its right-to-know and right-to-participate, and operators of nuclear facilities and local governments do not propose compensation mechanisms for people living near nuclear facilities. Moreover, the lack of public education on basic nuclear science influences the realization of information disclosure and transparency and social involvement.

This paper proposes several remedies. Firstly, the public's right-to-know and social involvement should also be realized and protected during the siting of nuclear facilities. Only in this way can the public obtain information and be involved in pertinent decision-making during the siting process. Secondly, a preventive compensation mechanism should be established for people living near nuclear facilities in order to satisfy the public's compensation demands for their potential physical and financial losses. Thirdly, great importance should be attached to public education on basic nuclear science, which will eliminate nuclear phobia of people and help them truly realize their right-to-know and right-to-participate. Even though all the suggestions have strong feasibility themselves under today's circumstances in China, it is not easy to judge the effectiveness of these suggestions until they are fully practiced. It is the biggest problem of existing works in this paper.

As information disclosure and public involvement are of great significance for the development of the civil nuclear industry in China and all over the world, the study of this topic will not end after this paper. In the nearest future, this issue will be mainly about the nuclear accident at the Fukushima Daiichi Nuclear Power Plant of TEPCO, its compensation, and legislation renewal, whose influence on public acceptance of civil nuclear power plants is quite strong and cannot be ignored today in China.

Data Availability

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Review Article

Preparation of Drug-Loaded Albumin Nanoparticles and Its Application in Cancer Therapy

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Albumin is derived from plasma and it is the most abundant protein in plasma, which is an ideal material for the preparation of nanoparticles because of its good biocompatibility, noncytotoxicity, nonimmunogenicity, biodegradability, and so on. Besides, albumin can enhance the targeting of drugs, reduce the toxicity of free drugs, and enhance the water solubility of hydrophobic drugs, etc. Drug delivery systems based on albumin nanoparticles are widely used in the medical field. At present, the main methods of preparing albumin nanoparticles are desolvation, self-assembly, thermal gelation, spray-drying, double emulsification, emulsification, Nab-technology, pH coacervation, and so on. Due to the differences of principle and preparation conditions, these methods show different advantages and disadvantages. This review systematically summarizes the latest research progress of albumin nanoparticles about its methods of preparation in past five years, and it also introduces the latest applications in cancer therapy, existing difficulties. Thus, this review can fill the two gaps that few articles focus comprehensively on the application of albumin nanoparticles in tumor therapy and no article clearly points out the difficulties faced in current research of albumin nanoparticles.

1. Introduction

In recent years, new tumor treatment strategies have attracted increasingly researchers' attention. However, most of antitumor drugs are hydrophobic drugs, with side effects and poor targeting, and all the above problems lead to the limited use of antitumor drugs. Thus, it is necessary to develop new therapeutic strategies that can improve drug solubility, targeting, and reduce side effects. Nanoparticles are widely used in the biomedical fields; for example, metal oxide nanoparticles can exhibit better antibacterial or antioxidant potency, such as copper nanoparticles [1], silver nanoparticles [2–4], and zirconium nanoparticles [5]. Meanwhile, protein-based nanoparticles are widely used as drug carriers to deliver relevant substances. Such as natural or chemical drugs, nucleic acids, peptides, and small-molecule protein can be delivered through protein-based nanoparticles. Nanoparticles with appropriate size can enrich in tumor tissue, improve the bioavailability of drugs, and reduce the toxic and side effects of free drugs. Protein-based nanoparticles target tumor mainly by enhancing permeability and retention effect (EPR effect) or receptor-mediated pathways; among these protein-based nanoparticles, albumin nanoparticles are a typical representative. In 2005, the FDA approves Abraxane® for marketing, which is a kind of nanoparticles based on albumin. This kind of albumin nanoparticles with targeting properties has attracted extensive attention. Albumin is the most abundant protein in plasma (30-50 g/L, human serum), and it has many advantages, such as good biocompatibility, noncytotoxicity, nonimmunogenicity, and biodegradability, so albumin is an ideal material for the preparation of nanoparticles. In addition, albumin-binding glycoprotein 60 (gp60) on the surface of vascular endothelial cells and secreted proteins acidic and rich in cysteine (SPARC) overexpressed on the surface of a variety of tumor cells can efficiently bind to albumin and promote the aggregation of nanoparticles loaded with drugs in the stroma of tumor cells (Figure 1).

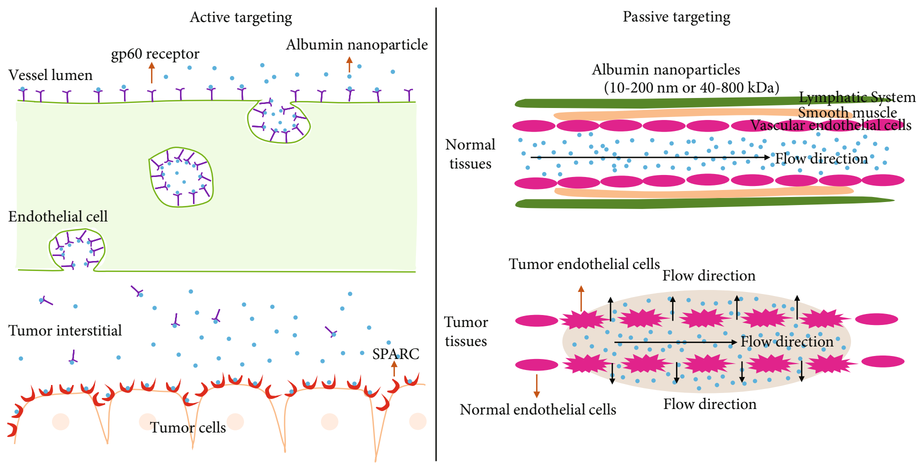


Figure 1: Schematic diagram of the mechanism of albumin nanoparticles targeting tumor tissue. Arrows indicate the flow direction of nanoparticles.

Based on the above advantages and characteristics of albumin, more and more researchers turn their attention to the study of albumin nanoparticles, and albumin nanoparticles have become one hot topic for research in biomedical field, especially in cancer therapy.

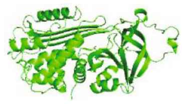
2. Types of Albumin

2.1. Ovalbumin. Ovalbumin is the most abundant protein in egg white, which accounts for 54-69% of total protein in egg white [6]. The isoelectric point of ovalbumin is 4.5, which is composed of 385 amino acid residues, and more than half of the amino acids are hydrophobic amino acids. Ovalbumin is a typical kind of globulin, and it is also the only protein containing free sulfhydryl groups buried in the hydrophobic core in egg white. Ovalbumin is a monomer and globular phosphoglycoprotein, whose molecular weight is about 45 kDa. Ovalbumin contains A1, A2, and A3 domains, whose difference lies in the number of phosphate groups. Glycosylation sites accounted for 3.5% in ovalbumin; 4 free sulfhydryl groups and 1 disulfide bond were buried in the hydrophobic center. In the crystal structure of natural ovalbumin, α-helix protrudes from the reaction center and 5 β-pleated sheets parallel to the long axis of the molecule. Disulfide bonds and sulfhydryl groups in the structure have a great influence on the aggregation structure of ovalbumin. Main functional characteristics of ovalbumin are emulsifying properties [7], foaming properties, water holding capacity, and film forming properties, which can be used as emulsifiers, moisturizer, edible packaging film, gel, and drug carriers [8–10]. It can improve food taste and texture, enhancing product stability and prolonging shelf life [11, 12]. Xiong et al. constructed lipid-soluble nutrient delivery vehicles based on ovalbumin [13]. Ovalbumin nanoparticles also were used to enhance efficiency of antigen uptake [14]. Self-assembled ovalbumin nanoparticles can deliver polyunsaturated fatty acids [15]. Rao et al. fabricated ovalbumin-carvacrol gel nanoparticles which show physicochemical and antibacterial properties [16]. Ovalbumin complex nanoparticles exhibit good encapsulation efficiency [17].

2.2. Bovine Serum Albumin. Bovine serum albumin (BSA) is a globulin in bovine serum, which contains 583 amino acid residues, whose molecular weight is 66.43 kDa and isoelectric point is 4.7. BSA is widely used in biochemical experiments [18]. For example, as a blocking agent in Western blot, BSA was added into restriction endonuclease reaction buffer to protect enzymes by increasing the concentration of protein in solution, and the specific principle is that BSA can block the degradation of enzymes and nonspecific adsorption, and it also can reduce the denaturation of enzymes caused by some adverse environmental factors such as heating, surface tension, and chemical factors. BSA comes from bovine plasma and is very cheap, which is often used to prepare nanoparticles as well as HSA. Chang et al. constructed a kind of complex nanoparticles based on BSA, and it shows high stability, good cell penetrating ability, and potential anticancer activity [19]. Cu^{2+}-BSA complex nanoparticles show better antibacteria activity [20]. BSA complex nanoparticles can be used as biocompatible nanoprobes for super resolution imaging [21]. BSA nanoparticles modified by N-Acetylcysteine can improve its stability [22], and BSA nanoparticles are often used as drug carriers to control the release of drug [23].

2.3. Human Serum Albumin. Human serum albumin (HSA) is the most abundant protein in human plasma, accounting for about 50% of total plasma protein. Its concentration in human plasma is about 30-50 g/L, and human liver can synthesize 12-20 g HSA every day. HSA consists of 585 amino acid residues with a molecular weight of about 67 kDa, whose single-molecule conformation likes a heart-shaped structure [24]. HSA is mainly divided into three domains, I, II, and III, respectively. Each domain is further divided into two substructures, namely, IA and IB, IIA and IIB, and IIIA and IIIB. Because albumin is derived from human plasma, it has good biocompatibility [25, 26]. Because of its good biodegradability, high biological stability, noncytotoxicity, and more drug-binding sites, it is widely used in medicine [27–29], biochemistry [30], and other fields [31, 32]; especially, the development and application of albumin

Table 1: Basic information of four types of albumin.

Types of albumin	Structure	Length (amino acid)	Molecular weight	Half-life	Organism	Main functions	References
Ovalbumin		385	~45 kDa	19 days	Egg white	Noninhibitory serpin, storage protein of egg white	[38–41]
Bovine serum albumin		583	~66.43 kDa	19 days	Bovine serum	Binds water, metal ions, fatty acids, hormones, bilirubin, and drugs and regulates the colloidal osmotic pressure of blood.	[40, 42]
Human serum albumin		585	~67 kDa	14 days	Human serum	Binds water, metal ions, fatty acids, hormones, bilirubin, and drugs and regulates the colloidal osmotic pressure of blood	[40, 43]
Mouse serum albumin or rat serum albumin	Crystal structures of MSA and RSA have not yet been clarified, and the predicted structure is similar to that of human serum albumin or bovine serum albumin by alphafold2	608	68.693 kDa, 68.731 kDa	Not clear	Serum of mice or rats	The same as the functions of serum albumin in bovine and human	[44–47]

drugs-carrier have attracted increasingly researchers' attention. Diethylenetriaminepentaacetic acid- (DTPA-) loaded HSA nanoparticles were used to treat generalized arterial calcification of infancy and pseudoxanthoma elasticum [33]. HSA-functionalized nanoparticles can deliver antitumor drug to HER-2-positive breast cancer cells [34], and HSA-functionalized nanoparticles can also be used as an MRI contrast agent and a potential luminescent probe to detect Fe^{3+}, Cr^{3+}, and Cu^{2+} in water [35]. Voicescu et al. constructed silver-HSA complex nanoparticles which can carry riboflavin [36].

2.4. Mouse Serum Albumin and Rat Serum Albumin. Mouse or rat serum albumin is composed of 608 amino acid residues with a molecular weight of about 68.7 kDa. Its structure is similar to that of other serum protein, and it can be divided into mouse serum albumin (MSA) and rat serum albumin (RSA) according to its source. However, crystal structures of both have not been determined [37], and the predicted structures can be obtained by alphafold2. So far, mouse serum protein is mainly used as a carrier to couple haptens in the process of antibody preparation, and there is no research report on its application in drug delivery.

Table 1 summarizes the basic information of four types of albumin.

3. Main Methods to Prepare Albumin Nanoparticles

3.1. Desolvation Method. A desolvation method means using a dehydrating agent such as ethanol to remove the hydrated membrane of albumin under stirring conditions, so its hydrophobic region is exposed and the solubility of albumin can be reduced; eventually, albumin will precipitate into nanoparticles. Stable albumin nanoparticles can be formed by thermal denaturation or chemical crosslinking and glutaraldehyde is often used as a crosslinking agent. Finally, the residual crosslinking agent and organic solvent were removed to obtain purified albumin nanoparticles. A desolvation method has many advantages such as simple preparation process, rapid reaction, and no need to add surfactants. It is suitable for the encapsulation of a variety of hydrophobic drugs, and it is also the most widely used method for the preparation of albumin nanoparticles at present. Whose disadvantage is that residual crosslinking agents such as glutaraldehyde have certain toxic and side effects on organisms.

The process of traditional desolvation method also has the following disadvantages, such as unstable stirring speed, low efficiency, and friction with bottom of the reaction vessel, which limits its large-scale application. Wacker et al. realized large-scale preparation of albumin nanoparticles by using a two propeller stirring system [48]. Particle size of nanoparticles is in the range of 234.1-251.2 nm, and the polydispersity index (PDI) is lower than 0.2. Nanoparticles can be stored for a long time after freeze-drying, and the resuspended nanoparticles can be further treated, such as adsorbing drugs or covalently modifying targeted ligands on the particle surface. In recent years, nanoparticles prepared by the desolvation method have been studied widely in antitumor applications. Doxorubicin-loaded human serum albumin nanoparticles prepared by the desolvation method show good antitumor activity [49]. Ziaaddini et al. constructed a kind of BSA nanoparticles with the desolvation method which can enhance the efficacy and reduce cytotoxicity of anticancer drug [50]. Folate-decorated HSA nanoparticles acquired by desolvation can target breast cancer cells [51].

Table 2: Advantages and disadvantages of various methods for preparing albumin nanoparticles.

Methods	Main advantages	Main disadvantages	References
Desolvation method	Simple preparation process, rapid reaction, no need to add surfactants and repeatability	Having certain toxic and side effects due to the usage of crosslinking agents, unstable stirring speed, low efficiency, friction with bottom of the reaction vessel	[59]
Self-assembly	No inducer is added	Chemical modification may be needed to increase the self-assembly force	[60, 61]
Thermal gelation	Easy operation, no need to add crosslinking agents, good stability of products	Not suitable for heat-sensitive drug	[62]
Spray-drying	Easy operation, fast speed of production and good dispersion	Denaturation and inactivation of proteins because of high temperature	[62, 63]
Emulsification	Experimental conditions are relatively mild and experimental process is simple	Albumin nanoparticles may be destroyed and degraded because of mechanical shear force and ultrasonic action, and emulsification also has poor efficiency of encapsulation of hydrophilic drugs	[64, 65]
Double emulsification	Efficiency of encapsulation of hydrophilic drugs is improved, and the experimental conditions are relatively mild.	Albumin nanoparticles may be destroyed and degraded because of mechanical shear force and ultrasonic action	[66–68]
Nab-technology	Decreasing the usage of surfactants, simple and safe process	Needing to add toxic solvents such as chloroform and dichloromethane	[69, 70]
pH coacervation	Simple preparation process and repeatability	Crosslinking agents needed to be used, such as glutaraldehyde, which may have potential toxic and side effects	[71, 72]

3.2. Self-Assembly. Increasing the hydrophobicity of albumin molecules can make it self-assemble by certain methods, such as reducing the internal disulfide bond of albumin molecules, heating treatment, or adding denaturants. Then, drug molecules combine with the hydrophobic domains of albumin to mediate self-assembly of albumin into nanoparticles. Common reducing agents include β-mercaptoethanol, dithiothreitol, and cysteine. Some steps of self-assembly method are very similar to that of desolvation. Albumin nanoparticles obtained by self-assembly method can better retain functions of the protein, so which have active targeting properties. For example, Cai et al. constructed a kind of nanoparticles by self-assembly which can target neurons [52].

3.3. Thermal Gelation. Thermal gelation is a continuous process involving protein interactions (such as hydrogen bonding, electrostatic, and hydrophobic interaction) and thermal induced unfolding. Advantages of this method are that it is easy to operate and does not need to use crosslinking agents; the albumin nanoparticles prepared by this method have good stability. However, the disadvantage is that they are not suitable for heat-sensitive drugs. Albumin nanoparticles prepared by thermal gelation are relatively stable, so which often have good mechanical properties. Hughes et al. constructed nanoscale hydrogels based on albumin by thermal gelation, and it exhibits well mechanical properties [53].

3.4. Spray-Drying. Spray-drying is the process of changing the material from liquid to powdery. The typical spray-drying process consists of 4 steps, that is, atomization of materials, drying through gas, particle formation, and collecting particles. Spray-drying has some advantages, for example, the process of production is simple, the speed of drying is fast, and the dispersion of products is well. Thus, it is widely used in medicine, detergents, dairy products, and other fields. However, the traditional spray-drying device is difficult to capture particles whose size is less than $2\,\mu$m, and the hot air drying process is easy to denature and inactivate albumin, so it is not suitable for the preparation of albumin nanoparticles. Steps of spray-drying are relatively simple, and albumin nanoparticles prepared by this method often have high drug loading. Chow et al. utilized spray-drying method to prepare high siRNA loading powders based on HSA [54].

3.5. Emulsification. An emulsification method is aimed at mixing aqueous solution of albumin with the oil containing drugs and emulsifiers, and emulsifying can be achieved by stirring, ultrasonic or high-pressure homogenization; oil in water (W/O) emulsion would be obtained. Albumin bound to drugs is distributed in aqueous droplets of internal phase, and then, the droplets are solidified by thermal denaturation or chemical crosslinking. Finally, albumin nanoparticles are obtained after the organic agents are removed. Size of albumin nanoparticles is affected by shear force, the nature and concentration of emulsifier, and so on. Albumin nanoparticles loaded with hydrophobic drugs can be acquired effectively by emulsification, but its deficiency is that mechanical shear force and ultrasonic action in the process of emulsification may destroy the stability of albumin and degrade albumin. Uppal et al. constructed a kind of albumin nanoparticles using emulsification, and it can deliver benzyl isothiocyanate efficiently [55].

3.6. Double Emulsification. Hydrophobic drugs can be encapsulated effectively by nanoparticles prepared by the emulsification method, but this method has poor efficiency

Table 3: Application of albumin nanoparticles in the diagnosis and therapy of cancer in the last five years (Excerpt).

Title	The preparation method of nanoparticles	Aims	Types of cancer	References
VE-Albumin Core-Shell Nanoparticles for Paclitaxel Delivery to Treat MDR Breast Cancer	Desolvation	Therapy	Breast cancer	[86]
HA/HSA Co-Modified Erlotinib-Albumin Nanoparticles for Lung Cancer Treatment	Desolvation	Therapy	Lung cancer	[87]
Preoperative Albumin-Bilirubin Grade as a Useful Prognostic Indicator in Patients with Pancreatic Cancer	N/A	Diagnosis	Pancreatic cancer	[88]
Preparation and Evaluation of Cabazitaxel-Loaded Bovine Serum Albumin Nanoparticles for Prostate Cancer	Biomineralization	Therapy	Prostate cancer	[89]
In Vivo Efficacy of Bevacizumab-Loaded Albumin Nanoparticles in the Treatment of Colorectal Cancer	Coacervation	Therapy	Colorectal cancer	[90]
Self-Assembled PEGylated Albumin Nanoparticles (SPAN) as a Platform for Cancer Chemotherapy and Imaging	Self-assembly	Therapy	Breast cancer	[91]
pH-Responsive Allochroic Nanoparticles for the Multicolor Detection of Breast Cancer Biomarkers	Self-assembly	Diagnosis	Breast cancer	[92]
Triple-Functional Albumin-Based Nanoparticles for Combined Chemotherapy and Photodynamic Therapy of Pancreatic Cancer with Lymphatic Metastases	Nab-technology	Therapy	Pancreatic cancer	[93]
Precise Cancer Anti-Acid Therapy Monitoring Using pH-Sensitive MnO_2@BSA Nanoparticles by Magnetic Resonance Imaging	pH coacervation	Therapy	Lung cancer	[94]
A Phase II Study of nab-Paclitaxel in combination with Ramucirumab in Patients with Previously Treated Advanced Gastric Cancer	Nab-technology	Therapy	Gastric cancer	[95]
Beta-Carotene-Bound Albumin Nanoparticles Modified with Chlorin e6 for Breast Tumor Ablation Based on Photodynamic Therapy	Nab-technology	Therapy	Breast cancer	[96]
RGD-Conjugated Resveratrol HSA Nanoparticles as a Novel Delivery System in Ovarian Cancer Therapy	Emulsification	Therapy	Ovarian cancer	[97]
Albumin Nanoparticle of Paclitaxel (Abraxane) Decreases While Taxol Increases Breast Cancer Stem Cells in Treatment of Triple Negative Breast Cancer	Nab-technology	Therapy	Triple negative breast cancer	[98]
Nanoparticle Albumin-Bound Paclitaxel Plus Carboplatin Induction Followed by Nanoparticle Albumin-Bound Paclitaxel Maintenance in Squamous Non–Small-Cell Lung Cancer (ABOUND.sqm): A Phase III Randomized Clinical Trial	Nab-technology	Therapy	Lung cancer	[99]
Interstitial Lung Disease Associated with Nanoparticle Albumin-Bound Paclitaxel Treatment in Patients with Lung Cancer	Nab-technology	Therapy	Lung cancer	[100]
Enzyme-Sensitive Gemcitabine Conjugated Albumin Nanoparticles as a Versatile Theranostic Nanoplatform for Pancreatic Cancer Treatment	Conjugation	Therapy	Pancreatic cancer	[101]
Investigation of Different Targeting Decorations Effect on the Radiosensitizing Efficacy of Albumin-Stabilized Gold Nanoparticles for Breast Cancer Radiation Therapy	Chemical reduction	Therapy	Breast cancer	[102]
Tumor Progression of Non-Small Cell Lung Cancer Controlled by Albumin and Micellar Nanoparticles of Itraconazole, a Multitarget Angiogenesis Inhibitor	Gelation	Therapy	Non-small-cell lung cancer	[103]
EGFR Targeted Cetuximab-Valine-Citrulline (vc)-Doxorubicin Immunoconjugates-Loaded Bovine Serum Albumin (BSA) Nanoparticles for Colorectal Tumor Therapy	Desolvation	Therapy	Colorectal tumor	[104]
Efficacy and Safety of Nanoparticle Albumin-Bound Paclitaxel as Neoadjuvant Chemotherapy in HER2-Negative Breast Cancer	Nab-technology	Therapy	HER2-negative breast cancer	[105]
Nanoparticle Albumin-Bound Paclitaxel in Elder Patients with Advanced Squamous Non-Small-Cell Lung Cancer: A Retrospective Study	Nab-technology	Therapy	Non-small-cell lung cancer	[106]

Table 3: Continued.

Title	The preparation method of nanoparticles	Aims	Types of cancer	References
Albumin-Based Nanoparticles Loaded with Hydrophobic Gadolinium Chelates as T 1-T 2 Dual-Mode Contrast Agents for Accurate Liver Tumor Imaging	Coacervation	Diagnosis	Liver tumor	[107]
Doughnut-Shaped Bovine Serum Albumin Nanoparticles Loaded with Doxorubicin for Overcoming Multidrug-Resistant in Cancer Cells	Desolvation	Therapy	Lymphoblastic leukemia	[108]

Table 4: Summary of review papers about albumin nanoparticles in the last decade.

Title of review	Main scope	Year	References
Targeted Delivery of Albumin Nanoparticles for Breast Cancer: A Review	The using of albumin nanoparticles in the therapy of breast cancer	2022	[109]
Hyaluronic Acid and Albumin Based Nanoparticles for Drug Delivery	Preparation of hyaluronic acid and albumin-based nanoparticles and its application in tumors, skin tissue, joints, and vitreum	2021	[29]
Anticancer Nano-Delivery Systems Based on Bovine Serum Albumin Nanoparticles: A Critical Review	Bovine serum albumin nanoparticles for anticancer drug delivery	2021	[110]
Navigating Albumin-Based Nanoparticles through Various Drug Delivery Routes	Discussing various drug delivery routes of albumin nanoparticles and exploring their possibilities in other administration routes	2018	[28]
Treatment Innovations for Metastatic Breast Cancer: Nanoparticle Albumin-Bound (NAB) Technology Targeted to Tumors	Mechanism of action, efficacy, and safety of albumin nanoparticles loaded with paclitaxel	2014	[111]
Challenges, Expectations and Limits for Nanoparticles-Based Therapeutics in Cancer: A Focus on Nano-Albumin-Bound Drugs	Components, characteristics, limits, and clinical efficacy of nanoalbumin-bound drugs	2013	[112]
Albumin-Based Nanoparticles as Potential Controlled Release Drug Delivery Systems	Albumin nanoparticles as controlled release drug delivery systems and methods of surface modification of albumin nanoparticles	2012	[27]
Management of Breast Cancer with Nanoparticle Albumin-Bound (nab)-Paclitaxel Combination Regimens: A Clinical Review	The application of albumin-bound (nab)-paclitaxel nanoparticles in the clinical treatment of breast cancer	2011	[113]

of encapsulation for hydrophilic drugs. To improve the efficiency of encapsulation, a double emulsification method was proposed to prepare albumin nanoparticles containing hydrophilic drugs. Main steps are as follows. First, albumin was dissolved in deionized water and hydrophilic drugs were mixed with the oil containing surfactant to form a primary W/O emulsion. Albumin and medicine are dispersed in the internal water phase, and a surfactant is distributed on surface of the emulsion to stabilize. Then, the primary emulsion was dispersed into the water phase added with another surfactant, and the water/oil/water (W/O/W) composite emulsion was obtained. After evaporation of the intermediate oil phase, nanoparticles with uniform particle size were obtained. Zhang et al. constructed a kind of BSA complex nanoparticles by double emulsification, which can control drug release [56].

3.7. Nab-Technology. Nab-technology (NAB™) developed by American Bioscience is a unique method for preparing hydrophobic drug-loaded albumin nanoparticles. The technology uses albumin as a substrate and stabilizer, mixing nonpolar solvents containing hydrophobic drugs (chloroform, dichloromethane, etc.) and water containing albumin to obtain nanosize emulsions under high shear force (ultrasonic treatment, high pressure homogenization, etc.). After evaporation of nonpolar solvents, albumin nanoparticles loaded with drugs are obtained and particle size is usually the range of 100-200 nm. Compared with traditional preparation methods, NAB™ technology does not need to use other surfactants, which avoids the use of glutaraldehyde that is toxic to the human body. It is a relatively simple and safe method to prepare drug-loaded albumin nanoparticles. The disadvantage is that toxic solvents such as chloroform and dichloromethane still need to be used. Abraxane® (it is also known as NAB-PTX) is the first chemotherapy drug prepared by Nab-technology and approved by the FDA for the first-line tumor therapy, which can effectively treat multiple types of cancer including metastatic breast cancer and non-small-cell lung cancer. In addition, the combined use of this product and gemcitabine has been approved to treat metastatic pancreatic cancer by FDA. Luo et al. used Nab-technology to construct albumin nanoparticles which exhibited antitumor efficacy, good pharmacokinetics, and better drug-safety [57].

3.8. pH Coacervation. Changing pH of the solution can effectively adjust the solubility and ionization of albumin in water. Based on this finding, adding organic solvents such as ethanol can promote the precipitation of albumin into nanoparticles, which is equivalent to an improved desolvation method. Disadvantages of this method are similar to the desolvation method. It also needs to use crosslinking agents such as glutaraldehyde, which may have potential toxic and side effects. Advantages of this method are simple preparation, good repeatability, and mechanical properties. Albumin-based nanoparticles acquired by pH coacervation showed good mechanical features [58].

Various methods for the preparation of albumin nanoparticles have their own advantages and disadvantages, which are summarized in detail in Table 2.

4. Applications in the Diagnosis and Therapy of Cancer

Albumin and its nanoparticles can be used in the diagnosis and therapy of various diseases, such as various kinds of cancer [73–75], diabetes [76, 77], kidney inflammation [78–80], liver diseases [81, 82] and so on [83–85]. In this section, we focus on the application of albumin nanoparticles in the diagnosis and treatment of cancer in recent five years, and specific information can be seen in Table 3.

In the past ten years, there are some reviews that summarize the applications of albumin nanoparticles in cancer therapy (Table 4). However, these reviews rarely summarize the preparation methods of albumin nanoparticles in detail, and this review makes up for some deficiencies to some extent.

5. Challenges

Albumin has good biocompatibility, nontoxicity, and nonimmunogenicity, and its application in novel drug carriers is increasing. Especially for tumor therapy, albumin nanoparticles have shown some unique advantages. However, the development of albumin nanoparticles still faces the following challenges:

(1) In recent years, there are increasingly researchers focusing on albumin nanoparticles, and there are also many articles reporting about various albumin nanoparticles, but few of them are effectively transformed into clinical applications. How to make more research about albumin nanoparticles transform into clinical application, which is still a big challenge to scientists

(2) Organic reagents are almost used in the preparation of albumin nanoparticles nowadays, and albumin has been denatured during the preparation of albumin nanoparticles. If albumin is denatured and inactivated, some of its functions will be lost. Therefore, how to acquire albumin nanoparticles without organic reagents, which is also a challenge to researchers

(3) Although albumin nanoparticles have advantages such as better biocompatibility, nontoxicity, and nonimmunogenicity, there are still some shortcomings in delivering drugs. For example, albumin may react with protein in blood leading to a decrease in number of nanoparticles entering the tumor tissue [114]

(4) Albumin is not sufficiently stable due to its structural properties and the complex environment of the body containing various enzymes and proteins [115]. Appropriate modifications to albumin are still needed to enhance its stability

6. Conclusions

Currently, there are many methods to prepare albumin nanoparticles, and all of these methods have their own advantages. However, these methods have one common disadvantage, which is that albumin nanoparticles will be denatured during the preparation. Proposing a new method to prepare nondenatured albumin nanoparticles, so these nanoparticles will have more biological functions of natural albumin, which is a challenge that scientists should face. Besides, researchers also need to think how to make more albumin nanoparticles available for clinical use and not just limited to research.

Conflicts of Interest

All authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

RM wrote the original manuscript and contributed to the draft design and conception. HZ revised the manuscript. ZW collected some references. SH and BW revised the manuscript and contributed to the draft conception. All authors agree to the final submission of the manuscript.

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Research Article

Comparative Analysis of NOx Emission Reduction in Engines Using $NiCo_2O_4$ Nanoparticles without External Reductant at Low Temperatures: An Experimental Investigation

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Due to increasingly stringent rules, eliminating pollutants (NOx) emitted by diesel engines in the automobile sector remains an intriguing scientific and technological problem. To meet the strict NOx emission restrictions, a catalytic system with a high level of complexity, unit size, and quantity, as well as higher fuel consumption, is required. As a result, for a reduction in individual exhaust gas emissions, an after-treatment system for a diesel vehicle must employ integrated catalyst technology. For selective catalytic reduction of NOx without any external reductant, a highly effective catalyst "spinel nickel cobaltite" ($NiCo_2O_4$) was produced using a polymeric precursor technique. In this work, an exhaust gas treatment system without external reductants using nano-$NiCo_2O_4$ as catalyst was designed and fabricated, for NOx control in diesel and petrol engines at low temperature. In order to determine the NOx conversion efficiency in the selective catalytic reduction system, tests were carried out at different engine loads. The system was supposed to be cost-effective due to the nano-$NiCo_2O_4$ catalyst's ability to work at low temperatures. The findings proved the developed SCR system's potential to reduce NOx emissions. At a high load, the nitric oxide (NO) emissions were reduced by 54 and 96 percent, respectively, without increasing HC, CO, and CO_2 emissions or compromising efficiency.

1. Introduction

NO_x emissions (NO and NO_2) are a significant source of pollution in the atmosphere. They have a wide range of negative consequences for the environment and human health. The main effects of NO_x on the environment include acidification of rain, photochemical smog, greenhouse effect, and ozone depletion, while the most severe effect of NO_x on people's health is respiratory tract disorders [1–3]. Although many sources such as agriculture, thermal plants, and industry have been considered as contributors to NO_x emissions, the transport sector especially diesel-powered vehicles are the main contributor of NO_x emissions. NO_X is principally produced by a high-temperature endothermic reaction between nitrogen and oxygen in the fuel-air mixture.

Around 40% of total NO_x emissions come from road transport, while diesel-powered cars account for 85% of NO_x emissions from the transportation sector. The challenge for vehicle makers and researchers has been to minimize NO_x emissions from diesel engines without sacrificing engine performance.

To obtain optimal conversion rates in NO_x emissions, numerous research and technological advancements have been done [4]. Pretreatment methods reduce NOx emissions before they are sent to the engine's exhaust port, whereas after-treatment methods reduce NOx emissions after they

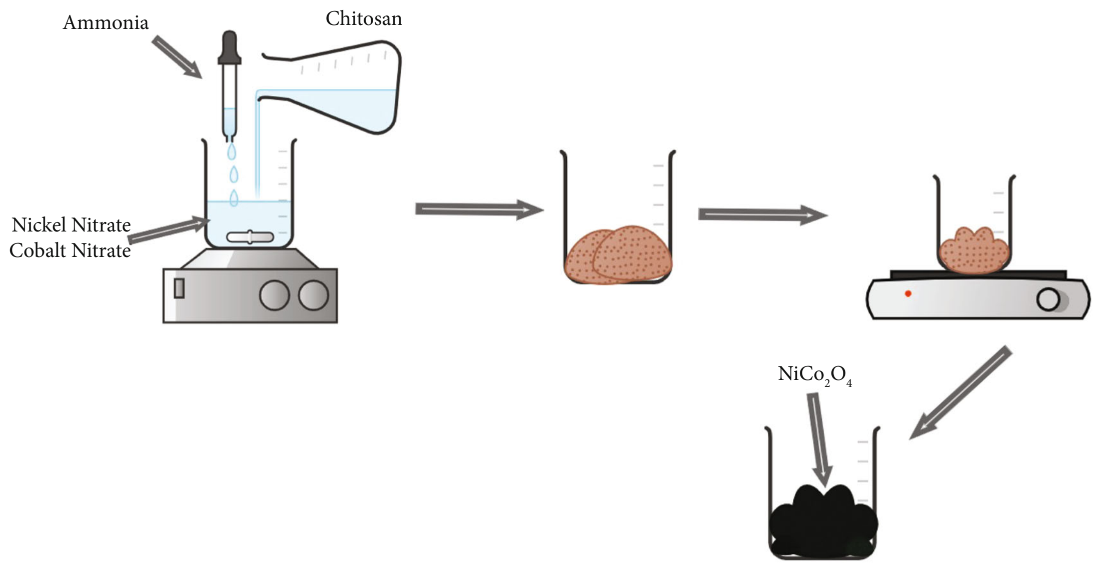

FIGURE 1: Schematic representation of the synthesis of $NiCo_2O_4$ nanoparticle.

have been directed to the engine's exhaust port. Pretreatment methods for decreasing NOx emissions include exhaust gas recirculation (EGR), electronically controlled fuel injection, engine modification, increased injection time, water spray in the combustion chamber, improved fuel characteristics, and the use of fuel additives. After-treatment technologies including the use of lean NOx trap (LNT) catalysts and the selective catalytic reduction (SCR) systems, which were developed to reduce NOx emissions and are widely used in diesel engines, are the subject of this research [5].

SCR (selective catalytic reduction) of NO_x emissions is a common technique nowadays. With a reductant and catalyst in an SCR system, NO_x emissions from diesel engines can be reduced significantly [6]. The most common reductant and catalyst used to reduce NO_x emissions at high exhaust gas temperatures are ammonia (NH_3) and V_2O_5–WO_3/TiO_2. However, conversion efficiency remains low at low exhaust gas temperatures below 250°C, and NH_3 builds up on the exhaust line and catalyst surfaces. This phenomenon, known as NH_3 slip, has a significant detrimental impact on SCR conversion efficiency and can lead to catalyst degradation [7].

Many catalysts, such as Cu zeolites or Mn oxides, have been created with superior low-temperature SCR activity; however, they are all ineffective in most off-gas circumstances because the active sites are substantially destroyed by sulfur dioxide poisoning [8, 9]. Yu et al. created a Cu-SSZ-13 zeolite-metal oxide hybrid catalyst that has improved SO_2 tolerance by preferring producing Zn sulfate over Cu sulfate [10]. Unfortunately, commercialization in the field is problematic due to the sophisticated catalyst preparation procedure and the requirement for a very high temperature (650°C) to regenerate inactive catalysts [11].

For SCR NOx reduction, a variety of catalysts have been studied, including platinum group metals (PGM), perovskite-type oxides, spinel-type oxides, and mixed transition metal oxides [12–15]. In a low-temperature selective catalytic reduction, low-cost spinels were used [16].

However, in this work, the catalyst used is capable of reducing NOx at low temperatures less than reported temperature of ABS [17] without any external reductant. Further, $NiCo_2O_4$ was chosen as the preferable catalyst in this investigation because of its high activity at low exhaust temperatures, environmental benefits when compared to conventional catalyst toxic effects, and great performance in NOx reduction [18, 19]. NOx conversion efficiency was studied using $NiCO_2O_4$ as a catalyst at two different engines with various loading conditions. Furthermore, using a basic physical mixing strategy is a cost-effective and practical option that can be quickly implemented in the industry. This catalyst reduces additional fuel expenses and carbon dioxide emissions by operating at low temperatures without the use of an external reductant. As a result, it provides enormous economic and environmental benefits.

2. Materials and Methods

2.1. Synthesis of Nano-$NiCo_2O_4$. The polymeric precursor technique [20] was used to make $NiCo_2$O4. The starting components, nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), and chitosan, were employed exactly as purchased. 14.5 g cobalt nitrate and 7 g nickel nitrate were dissolved in distilled water and stirred continuously for 20 minutes. Then, 5% of the chitosan solution was added, and the mixture was stirred constantly at 80°C until it formed a gel, which was then heated at 80°C for 4 hours at a rate of 5°C/min to generate a black powder. The black powder was pounded in an agate mortar and then calcined for 6 hours in an air environment at 300, 500, 700, and 900°C. The schematic representation of synthesis of nano-$NiCo_2O_4$ is shown in Figure 1.

2.2. Engine. The process begins by choosing the engine. Here, a twin-cylinder diesel engine, three-cylinder petrol engine, is used for testing the emission. The twin-cylinder diesel engine

Figure 2: Fabrication of SCR catalytic converter.

Figure 3: Experimental setup of diesel and petrol engine with fabricated SCR.

Table 1: Specifications of engines.

Specification	Diesel engine	Petrol engine
Make	Comet	Maruti-Suzuki S-presso
Cylinder	Two cylinders	Three cylinders
Fuel type	Diesel	Petrol
Engine cubic capacity	1107 cc	999 cc
Cooling agent	Water-cooled	Water-cooled
Speed	1500 RPM	5500 RPM

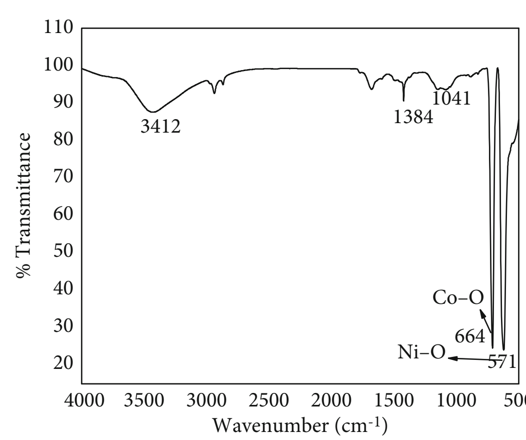

Figure 4: FTIR spectra obtained for $NiCo_2O_4$ nanoparticle.

is a stationary engine with constant speed at different load conditions. The various emissions like HC, CO, NOx, CO_2, and O_2 are noted down at different load conditions.

2.3. Fabrication of SCR System. The honeycomb structure is brought in and the synthesized catalyst (nickel cobalt oxide ($NiCo_2O_4$)) is coated into it using a binder solution of polyvinyl alcohol (PVA). The honeycomb structure is then welded around the edges of a cylindrical metal (Figure 2).

2.4. Experimental Setup. Figure 3 shows a schematic illustration of the experimental setup used to determine the effectiveness of NOx conversion utilizing fabricated SCR systems. A specially designed exhaust system and a generator motor that can be operated at various loads makes up

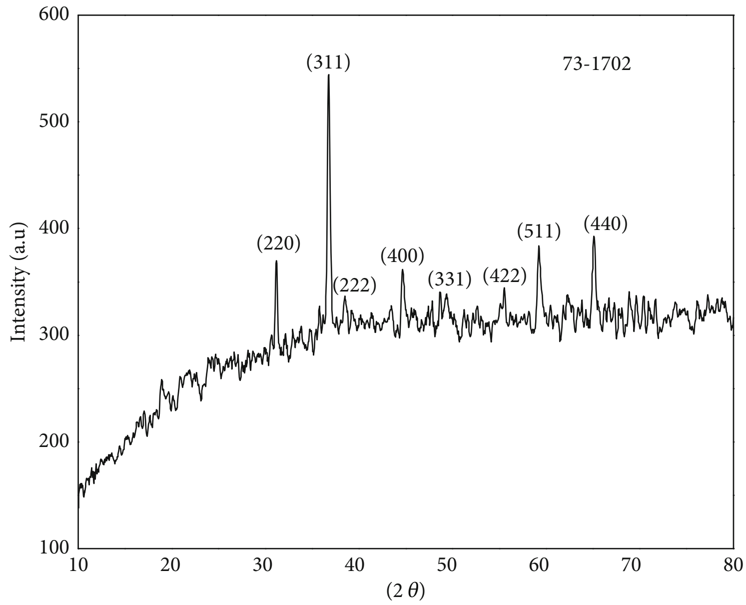

FIGURE 5: XRD pattern of $NiCo_2O_4$ nanoparticle.

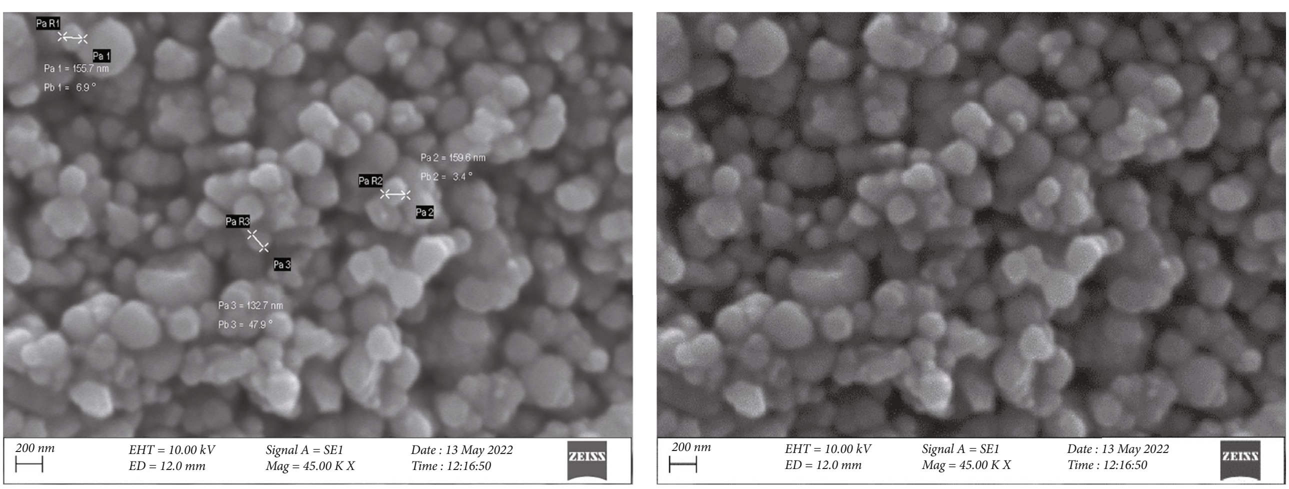

FIGURE 6: SEM images of $NiCo_2O_4$.

TABLE 2: Diesel engine reading without using SCR catalyst.

Load	Without SCR catalyst				
	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO2 (ppm)
0	94	160	11	0.03	1.63
4	116	287	5	0.02	3.05
8	133	351	5	0.01	2.63
12	144	441	11	0.02	2.71

TABLE 3: Diesel engine reading using $NiCo_2O_4$ SCR catalyst.

Load	With $NiCo_2O_4$ SCR catalyst				
	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	99	98	5	0	1.15
4	122	184	4	0.01	1.68
8	142	189	4	0.01	1.51
12	152	200	1	0.01	1.28

the test setup. Experiments were carried out at different engine loads (0 kW, 4 kW, 8 kW, and 12 kW, using two different engines). We chose a twin-cylinder diesel engine and s-presso three-cylinder petrol engine to test the fabricated SCR system with a speed rate of 1500 rpm. The specifications of the engines are given in Table 1. NOx conversion ratios were determined in the tests to determine the performance of the catalyst generated at low exhaust gas temperatures.

2.5. Characterization. X-ray diffraction (XRD) was used to determine the crystalline structure and phase purity of the products using an X-ray diffractometer (Bruker Instrument

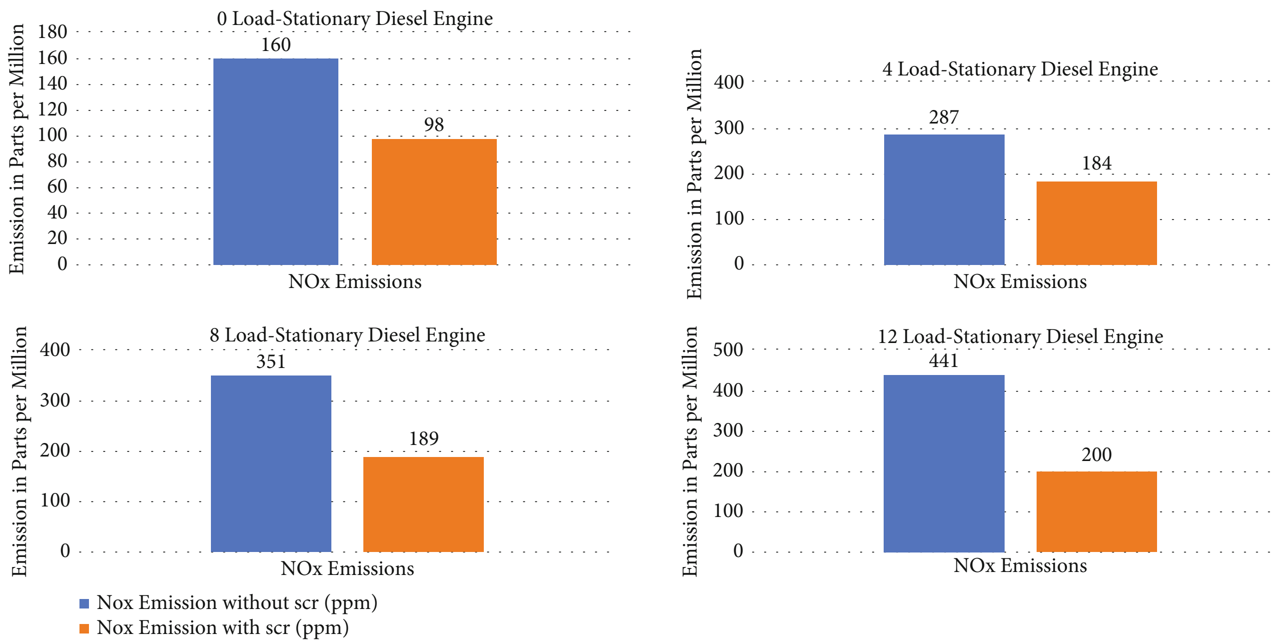

FIGURE 7: NOx reduction on various loads with and without $NiCo_2O_4$ catalyst in diesel engine.

(D8 Advance)) with Cu-Kα ($\lambda = 1.5418\,Å$) radiation ranging from 10 to 80° at ambient temperature. The sample's formation and morphology were studied using scanning electron microscopy (SEM) (FEI QUANTA FEG 200 HR) and Fourier transform infrared spectroscopy (FTIR spectrometer, JASSCO Model 4100). The fabricated catalytic converter is put through its paces with different loads on an emission analyzer. The base readings and the final readings are made as a graph, and from the graph, we can identify the NOx reduction percentage and reduction of other emissions.

3. Results and Discussion

3.1. Characterization of $NiCo_2O_4$. The synthesized $NiCo_2O_4$ sample's FTIR spectrum is shown in Figure 4. The spectrum of $NiCo_2O_4$ spinel exhibits two separate sharp bands in the region of 550 to 650 cm^{-1}, as indicated in the previously published literature. The presence of a metal–oxygen bond in a metal oxide spinel is shown by these two bands. The stretching vibrations of Ni–O bond were assigned to the band at 571 cm^{-1}, while the stretching vibrations of Co–O bond were attributed to the band at 664 cm^{-1} in $NiCo_2O_4$ spinel [21–23].

The XRD spectrum of the as-synthesized $NiCo_2O_4$ nanoparticle is shown in Figure 5. The synthesized sample's XRD pattern is indexed to spinel $NiCo_2O_4$ (JCPDS card no. 73-1702). No other peaks corresponding to NiO or CoO was found which indicates the formation of pure phase $NiCo_2O_4$ [24].

The surface morphology of synthesized $NiCo_2O_4$ nanostructures was examined using SEM. The SEM image in Figure 6 clearly shows the formation of hexagonal-shaped nanostructures of $NiCo_2O_4$ [25].

3.2. NOx Reduction Analysis. The NOx emissions acquired from two different types of engines at different engine loads are illustrated below. The temperature of combustion has a big impact on nitrogen oxide production. At high engine load and high combustion temperature, the highest production of NOx occurs [26–28]. When the engine is under maximum load, high combustion temperatures are reached. High engine load produces more NOx than low engine load. The temperature is the key factor for the highest NOx reduction at higher loads.

In the case of a twin-cylinder diesel engine, the engine rpm was fixed as 1500 rpm but its load is varied from 0 to 12 kW. NOx emissions before and after the SCR catalyst are shown in Tables 2 and 3. There is a considerable reduction in NOx after treatment with $NiCO_2O_4$-modified SCR without an external reductant. On varying load conditions, the catalyst $NiCo_2O_4$ showed superior NOx conversion at all loads, particularly at 12 kW load conditions. Similarly, the overall conversion percentages of HC, CO, and CO_2 were affected by the load. If the temperature of the SCR catalytic converter is between 120°C and 200°C, the most efficient NOx reduction is achieved. The reason for the NOx reduction at low temperature is due to synthesized nano-nickel cobaltite which possesses higher oxygen vacancies in the surface-active site of the catalyst $NiCo_2O_4$. As reported by Trivedi, our catalyst showed good redox property in reducing the NOx at low temperatures due to the surface-active sites [18]. Figure 7 clearly depicts the reduction in NOx with and without SCR catalyst on varying loads.

Similar reports are observed (Tables 4 and 5) when the same SCR catalyst was examined in petrol engine. The efficiency of the SCR catalyst (synthesized nickel cobaltite) was studied using s-presso GDI petrol engine. The engine was run with 1500 rpm speed, but the load is varied from 0 to 16 kg. On varying the load, the NOx reduction occurs maximum at lower temperature from 250 to 320°C. Similar to diesel engine study, HC, CO, and CO_2 also reduced drastically. This further confirms that the catalyst $NiCo_2O_4$

Table 4: Petrol engine reading without using SCR catalyst.

Without SCR catalyst					
Load (kg)	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	253	1	5	0.04	13.52
4	296	2	5	0.15	14.01
8	333	5	36	0.15	14.05
12	354	13	25	0.13	14.07
16	430	25	12	0.32	14.39

Table 5: Petrol engine reading with using SCR catalyst.

With SCR catalyst					
Load (kg)	Exhaust temperature (°C)	NOx (ppm)	HC (ppm)	CO (ppm)	CO_2 (ppm)
0	240	0	5	0	0.55
4	258	1	5	0	1.03
8	278	1	5	0	1.89
12	301	2	5	0	2.31
16	322	1	5	0.01	4.58

(nickel cobaltite) has surface-active sites which is more effective in reducing NOx at low temperatures.

Since NOx is a key pollutant for many environmental issues, even though other pollutants are also significantly reduced in both engines, our focus is on NOx reduction. The catalyst's ability to reduce NOx without H_2 may be caused by redox couples of $Ni^{3+/}Ni^{2+}$ (0.58 V/0.49 V) and Co^{3+}/Co^{2+} (0.53 V/0.51 V) as well as oxygen vacancy-rich $NiCo_2O_4$ nanoparticles, which boost the catalyst's reactivity and number of active sites [29].

4. Conclusion

The spinel catalyst $NiCo_2O_4$ was successfully synthesized and fabricated on alumina monolith for NOx reduction study. Two types of engines have been selected, and NOx reduction efficiency was investigated. In the studies, no external reductant was added but the reduction was maximum at lower temperatures. This may be due to the surface-active centers of nanospinel $NiCo_2O_4$ and its morphology. After further investigations over lengthy periods of time on stream from CNG cars, such as water vapors and S-based chemicals, the spinel catalyst $NiCo_2O_4$, which is affordable, highly active, and thermally stable, may be suggested for use as a noble metal alternative in emission management.

Data Availability

All data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Research Article

Fabrication of High-Performance $MgCoO_2$/PEDOT:PSS@Nickel Foam Anode for Bioelectricity Generation by Microbial Fuel Cells

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We report the fabrication of cost-effective, biocompatible, and high-performance anode made of nickel foam (NF) modified with magnesium cobalt oxide ($MgCoO_2$) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as active components. Modified electrodes were prepared upon addition of each component to NF which formed PEDOT:PSS@NF, $MgCoO_2$@NF, and $MgCoO_2$/PEDOT:PSS@NF. These electrodes were compared for their electrocatalytic activity in dual-chambered microbial fuel cells (MFCs). Sewage wastewater was used as feed stock while exoelectrogenic microbes present in wastewater served to generate bioelectricity upon utilizing organic waste and glucose as an electron donor. The maximum power and current density values were found to be 494 mWm^{-2} and 900 $mA\,m^{-2}$ using $MgCoO_2$/PEDOT:PSS@NF anode. It was ~2.5 times higher than that of unmodified NF anode. Electrochemical impedance spectroscopy (EIS) analysis exhibited reduction in charge transfer resistance for $MgCoO_2$/PEDOT:PSS@NF anode (25.26 Ω) compared to the unmodified NF anode (61.34 Ω). Thus, with the enhanced electrocatalytic activity and biocompatibility, $MgCoO_2$/PEDOT:PSS@NF anode offered better stability and porosity for dense biofilm formation which helped in the efficient generation of bioelectricity.

1. Introduction

Over the past decade, microbial fuel cells (MFCs) have been recognized as a competent technology in the treatment of wastewater in terms of generating reusable irrigational/portable water and renewable energy such as bioelectricity [1]. At this pace of dual benefit, generation of electricity is catalyzed by the exoelectrogenic microorganisms adhering onto the anode in a MFC system where the waste organic matters are degraded or metabolized under anaerobic condition to form electrons, protons, and CO_2 [2]. At the cathode, protons and electron equivalents combine with oxygen to form water, which completes the charge balance. As they pass through an external circuit, electron equivalents released during oxidative microbial metabolism can be used to generate a useful electromotive force [3]. In this established mechanism of electron transfer, anode plays a significant role in adhering the oxidizing microbial cells onto it and in transferring produced electrons to cathode [4]. Albeit studies suggest an increase in MFCs magnitude power density up to

10,000 orders during the past years, an efficient extracellular electron transfer upon oxidation of chemical bonds between organic components by the exoelectrogenic microorganisms remains a challenge [5].

Since anode materials have significant role in MFCs, there are numerous studies on the development, modification, and designing of the anode materials in order to subside the challenges in the construction and operation of MFCs [6–9]. The most common materials used in the construction of anode involve carbon-based materials [10, 11], metal/metal oxides, and conducting polymers [12]. However, in the case of conventional materials starting from carbon-based materials such as carbon paper, fibers, sheets, and rods; graphite-based sheets, brushes, fibers, and cloth; metal/metal oxide-based materials involving Fe, Ag, Au, Al, Cu, Co, and CuO; and other conducting polymers such as polyaniline and polypyrrole have been found not efficient in MFCs [6, 13, 14]. The drawbacks laid by these materials have poor stability, low mechanical strength, lesser surface area, larger pore size, corrosiveness, poor biocompatibility, and high cost [15]. To overcome the above-mentioned drawbacks, there is a need to construct an anode that remains stable and offer large surface area for microbial cell adhesion, unclogged pores, better electron transfer, and efficient generation of bioelectricity.

One promising method is to improve the anode's surface properties, and also prepare nanomaterials with complex structures and use them as anodes [16]. Synthesis of modified and doped forms of carbon materials [17], metal/metal oxides, and conducting polymers either in individual or composite forms have been put forward by various researchers to improve the power density, stability, surface area, microbial adhesion, electron transport, biocompatibility, conductivity, corrosion resistance, and electrochemical performance [18] along with cost-effectiveness [4, 19, 20]. Beside this, recently 3D-nickel (Ni) foam has drawn attention in the construction of anode by being base substratum. Among other transitional metals, Ni has remarkable abundance in nature; in addition to that, Ni is less toxic and economically feasible for application on large scale [21–23]. Ni usually exists in +2, +3, and +4 valence states; however, stable valence state in most of the conditions tends to be Ni(II). Ni ions at high valence state (Ni(III) and Ni(IV)) are suggested to execute strong oxidizing properties especially in electrochemical oxidative degradation (EOD) of organic compounds [24]. This property of Ni extends the application of 3D-Ni foam porous network towards designing an anode that would in turn have good conductivity and provide large specific area for efficient EOD of organic matters.

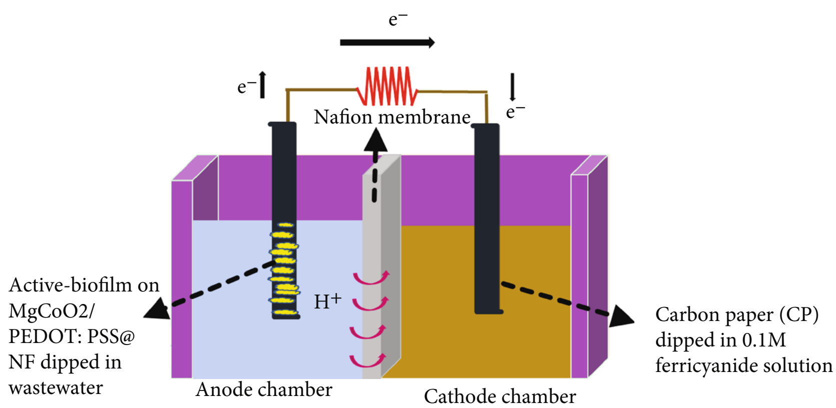
In the present study, an effective anode for a MFC is designed based on the above EOD properties of nickel, where nickel foam serves as the base substratum and enhances the EOD of organic matters present in the wastewater. In order to further improve conductivity and electrochemical properties of the anode, nickel foam was modified with a magnesium cobalt oxide ($MgCoO_2$) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). As that of Ni, $Mg(OH)_2$ is also abundant in nature and has significant characteristics such as high negative standard potential (−2.3 vs. RHE), high melting point (649°C), low cost, and less toxic with an interesting electrochemical storage capacity [25], while PEDOT:PSS was reported to be a potential conducting polymer with influential characteristics such as high electrical conductivity, stability, durability, and ability to form thin homogenous layers [26]. Thus, this study investigated the fabrication of $MgCoO_2$/PEDOT:PSS@ nickel foam anode to set up simple, efficient, biocompatible, and cost-effective MFC with the capability of generating bioelectricity using sewage wastewater as feedstock (Scheme 1).

2. Experimental

2.1. Chemicals and Reagents. Magnesium sulphate heptahydrate ($MgSO_4 \cdot 7H_2O$) (99%) was purchased from Thermo Fisher Scientific, India. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) (99%), 3,4-ethylenedioxythiophene (EDOT) (97%), poly(sodium 4-styrene sulfonate) (PSS) (Mw ~70,000), and N-Cetyl-N,N,N-Trimethyl Ammonium Bromide (CTAB) (98%) were acquired from Sigma-Aldrich, India. Sodium dihydrogen phosphate monohydrate ($H_2NaPO_4 \cdot H_2O$) and sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) were obtained from Spectrochem Pvt. Ltd., India. Dextrose anhydrous was purchased from Loba Chemie, India. Ammonium persulphate ($(NH_4)_2S_2O_8$) (98%) and hydrochloric acid (HCl) were purchased from Finar Limited, India. Dimethyl sulfoxide (DMSO) was acquired from Sisco Research Laboratories Pvt. Ltd., India. Without further purifications, all of the chemicals were used as received.

2.2. Instrumentation. The Fourier transform infrared spectrometer from Shimadzu, IRTracer-100, was used to analyse the functional groups of the samples using the attenuated total reflectance (ATR) technique. CuKα radiation of wavelength ($X = 1.5406$) was utilised in the X'Pert Pro high-resolution X-ray diffractometer from BRUKER, USA, D8 Advance, Davinci, to perform the X-ray diffraction scans in the 2 theta range of 20°-80°. A Thermo Scientific Apreo S was utilised to analyse the morphological and microstructures of the samples ($MgCoO_2$, PEDOT:PSS, $MgCoO_2$/PEDOT:PSS composite, nickel foam, and microbial growth on the anode surface) using a high-resolution scanning electron microscopy (HR-SEM).

2.3. Preparation of the $MgCoO_2$. Synthesis of magnesium cobalt oxide ($MgCoO_2$) was carried out in a cost-effective manner by a sol-gel synthesis process as described by Maitra et al. [19]. Briefly, 0.5 M MgO and 0.12 M $Co(NO_3)_2 \cdot 6H_2O$ were used to prepare 50 mL of the reaction mixture to which triethanolamine ($C_6H_{15}NO_3$) was added dropwise as a chelating agent until the solution turned to pale pink. This was followed by agitating the reaction mixture at 150°C for 12 h or until the solution formed gel. Later, the formed gel was dried for 12 h at 60°C, powdered coarsely, and calcinated for 6 h at 850°C. The possible mechanism behind this sol-gel process was, initially, MgO dissociated to Mg^{+2} ions while dissolving in HNO_3^- and $Co(NO_3)_2 \cdot 6H_2O$ dissociated to Co^{+2} and NO_3^- ions while dissolving in H_2O. Next, agitation



Scheme 1: Schematic representation of microbial fuel cell (MFC) set up to generate bioelectricity from sewage water.

at 150°C in the presence of $C_6H_{15}NO_3$ yielded hydrolysed forms of $C_6H_{15}NO_3^-$ radicals, in addition to Mg^{+2}, Co^{+2}, and H^+ ions. At this condition, several $C_6H_{15}NO_3^-$ radicals along with metal ions formed oligomeric clusters gradually resulting in a gel formation. Following this, drying and calcination processes evaporated the organic fractions present in the gel to form small $MgCoO_2$ crystallites that continuously nucleates to form larger grains.

2.4. Preparation of the PEDOT:PSS. PEDOT:PSS was prepared as per the method described by Ghosh et al. [27] with few modifications. Initially, 50 mL of the solution was prepared using 0.5 M aqueous HCl and 0.05 M CTAB to which 0.15 M ammonium persulphate ($(NH_4)_2S_2O_8$) was added dropwise. To this reaction mixture, 0.05 mM PSS was added followed by the addition of 0.15 M EDOT monomer. The reaction was carried out for 24 h at 60°C. During this reaction, $(NH_4)_2S_2O_8$ dissociates to form NH_4^+ and $S_2O_8^{2-}$ ions that homogenously disintegrates along with sulphate radicals oxidizing EDOT monomers to EDOT cations. The dopant PSSs are also reacted with EDOT during the polymerization process to form a dark blue PEDOT:PSS which is collected and washed with DI water to remove the unreacted monomers or ions. Later, the resulted PEDOT:PSS was dried for 24 h in a vacuum oven at 80°C.

2.5. Preparation of $MgCoO_2$/PEDOT:PSS Composite. 25 mg of $MgCoO_2$ was dispersed in a 5% PSS aqueous solution. Then, the mixture was kept stirring using a magnetic stirrer for 30 min and ultra-probe sonicated for 30 min. To prevent the oxidation via the dissolved oxygen, nitrogen gas (99.999%) was purged into the mixture for 30 min. Subsequently, 0.15 M EDOT monomer was added and again stirred for 24 h at ambient temperature. It resulted in a black colored $MgCoO_2$/PEDOT:PSS composite which was collected and washed with DI water to remove the unreacted monomers or ions. Finally, the $MgCoO_2$/PEDOT:PSS composite was dried in a vacuum oven at 80°C for 24 h.

2.6. Fabrication of Anode and Cathodes. To prepare the anode, nickel foam (NF) was cut into 1 cm × 5 cm pieces. Then, the NF pieces were subsequently treated with ethanol (99.99%), acetone (99.99%), and distilled water in a bath along with sonication, each phase lasting for 30 min. Pretreated NF electrodes were oven dried at 80°C for overnight. After that, each NF was coated with $MgCoO_2$, PEDOT:PSS, and $MgCoO_2$/PEDOT:PSS composite dispersions, which resulted in $MgCoO_2$, PEDOT:PSS, and $MgCoO_2$/PEDOT:PSS@Nickel foam anodes for MFC. Following this, cathode was prepared using a carbon paper (CP) which was also cut into 1 cm × 5 cm pieces. Similar to the above steps, CP pieces were consequently treated with ethanol (99.99%), acetone (99.99%), and distilled water in a bath sonication, each phase lasting for 30 min. Finally, the obtained CP electrodes were oven dried for overnight at 60°C and used as cathode in MFC. To prepare dispersions, 5% DMSO was used to disperse each individual and composite materials.

2.7. Inoculum Preparation. In the present study, wastewater was collected from a nearby lake at SRM Institute of Science and Technology, Kattankulathur, Tamil Nadu, India. After the collection of wastewater, it was kept undisturbed to obtain sludge sediment, later stored at 4°C for further analysis. The pH (10.5) and conductivity (2230 μS/cm) of the obtained wastewater were measured. In addition to the above prepared cost-effective anode, the use of wastewater sludge as an inoculum in bioelectricity generation makes the process more simple, feasible, and environmentally friendly approach. This method offered exoelectrogenic bacterial cultures in an inexpensive manner for the development of high-performance MFC [28].

2.8. Construction of MFC System and Measurements. Plexiglas chambered beakers were used to construct dual MFC chamber with a working volume of 100 mL each. Nafion 117 membrane (DuPont™ Nafion®) served as proton exchange membrane which was initially treated with distilled water at 80-90°C, followed by 5% H_2O_2 and 0.5 M H_2SO_4 for 1 h at 70-80°C. Later, the pretreated membrane was washed with distilled water and stored. Before installation and addition of inoculum to the anodic chamber, completely MFC system was sterilised. Experiments were carried out at room temperature (25±2°C); throughout the experiment, anaerobic condition was maintained in the anode chamber while aerobic condition at the cathodic chamber. In the anodic chamber, sewage sludge was inoculated along with 55 mM glucose as the electron donor. Ferricyanide solution (50 mM) in 0.1 M PBS (pH 7) was used as catholyte. Electrochemical workstation with three-electrode cells (CHI-760E, CH Instrument, USA) was used to perform all of the electrochemical measurements such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). $MgCoO_2$/PEDOT:PSS@NF and CP were used as anode and cathode, respectively. Ag/AgCl (3 M KCl) and platinum wire served as reference and counter electrodes.

Energy generated by MFCs was calculated using polarization calculations and varied external loads. Following the power output stabilization, polarization and power density curves were generated by changing the external resistance (from 10 to 465 kΩ) applied to the circuit.

$$I = \frac{V}{R}, \tag{1}$$

where I represents the current, V represents the anticipated voltage, and R represents the applied resistance used to compute the current, while the formula $P = IV$ was used to calculate the power density. Anode surface area used to standardise the current and power densities [29].

3. Results and Discussion

3.1. Characterization of $MgCoO_2$/PEDOT:PSS@NF Electrode. The band energy red shifted due to the p-d exchange by the interaction between the localised d-electrons of Co^{2+} ions with that of Mg^{2+} cations. At the Fermi level of the valence band (VB), strong p-d (CoO) hybridization led to the VB maxima to migrate higher, which resulted in band gap bending. When Co is integrated into the MgO host lattice, the absorbance of MgO rises (up to its solubility limit). As a result, the enhanced UV emission intensity and redshift observed, both indicated that Co^{2+} ions are occupied the Mg^{2+} site in the MgO host lattice (data not shown) [30, 31]. Fourier transform infrared (FT-IR) spectroscopic analysis revealed the extent of EDOT polymerization in the presence of PSS and the incorporation of $MgCoO_2$ into the formed PEDOT:PSS nanocomposite matrix (Figure 1(c)). Synthesised PEDOT exhibited IR bands at 1360, 1433, and 1480 cm^{-1} due to C-C and C=C stretching of the quinoidal structure of the thiophene ring. Additional vibrational bands observed at 1244, 1141, and 1068 cm^{-1} corresponded to the ethylene oxide, and C-O-C bond stretching were observed (Figure 1(b)). PEDOT:PSS was also exhibited C-S bonds due to thiophene ring bands at 940, 902, and 826 cm^{-1}. In Figure 1(a), peaks at 1120, 1360, and 1630 cm^{-1} are ascribed to the presence of sulfonic acid group of PSS, C-C, and C=C bonds of the thiophene ring, respectively. Characteristic IR band of MgO bond vibration was observed at 510 cm^{-1}, while O-H due to surface water molecules and CoO in polymer matrix showed bands at 3429 and 421 cm^{-1}, respectively [19, 32, 33] (Figure 1(a)).

XRD spectra were further used to characterize the synthesised PEDOT:PSS, $MgCoO_2$, and $MgCoO_2$/PEDOT:PSS

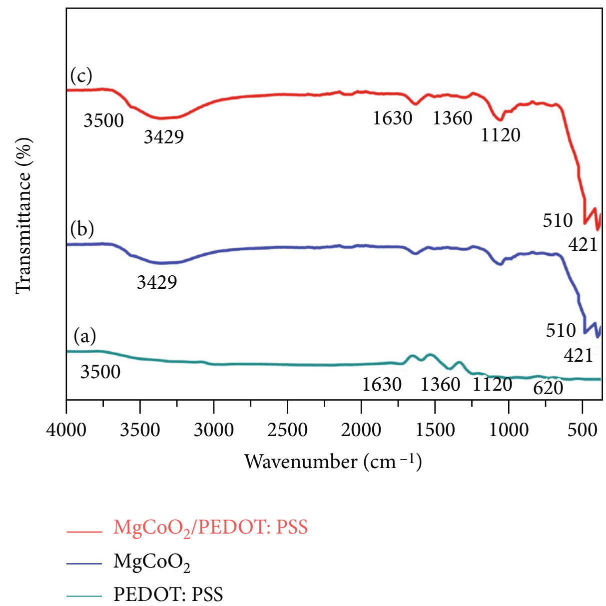


Figure 1: FT-IR spectra of (A) $MgCoO_2$, (B) PEDOT:PSS, and (C) $MgCoO_2$/PEDOT:PSS composite.

nanocomposite samples (Figures 2(a)–2(c)). It was reported that PEDOT:PSS has four characteristic peaks at 2θ of 3.7° and 6.6° attributed to low diffraction while bands at 17.7° and 26.0° were attributed to high diffraction which in turn reflects the lamella stacking and interchain stacking of PEDOT:PSS, respectively [34]. However, it also suggested that all polymers have the characteristic peak at 2θ of 26.0° which is related to interchain planar ring stacking [35]. In agreement to this statement, in the present study, PEDOT:PSS had revealed the peak at 2θ of 26.0°. In the case of $MgCoO_2$, the diffraction peaks found at 2θ of 36.79°, 44.79°, 64.21°, 74.31°, and 77.79°, corresponded to (111), (200), (220), (311), and (222) planes, respectively, which were found to match with the standard card number (JCPDS card no: 04-002-2875). However, in the case of PEDOT:PSS/$MgCoO_2$ composite, additional characteristic peak of PEDOT:PSS at 2θ of 26.0° was confirmed with the binding of $MgCoO_2$ into the polymer matrix (Figure 2(a)).

To ascertain about the surface morphology of the materials, HR-SEM images of nickel foam, $MgCoO_2$, PEDOT:PSS, and $MgCoO_2$/PEDOT:PSS composite were recorded (Figure 3). HR-SEM image of nickel foam revealed the 3D structure of numerous pores in the size ranging between 200 and 500 mm (Figure 3(a)). This unique network of porous structure suggested the increase in contact area between the collector and active material which in turn shortening the diffusion and migration of electrolyte ions, resulting in improved electrochemical performance [36]. PEDOT:PSS polymer matrix was found to have nanorod-like structure with CTAB molecules aiding as surfactant (Figure 3(b)). After the sample calcinated, $MgCoO_2$ was found to be in irregular globular form (Figure 3(c)). Finally, HR-SEM image of $MgCoO_2$/PEDOT:PSS composite confirmed the presence of irregular-globular $MgCoO_2$ coated onto PEDOT:PSS nanorods (Figure 3(d)).

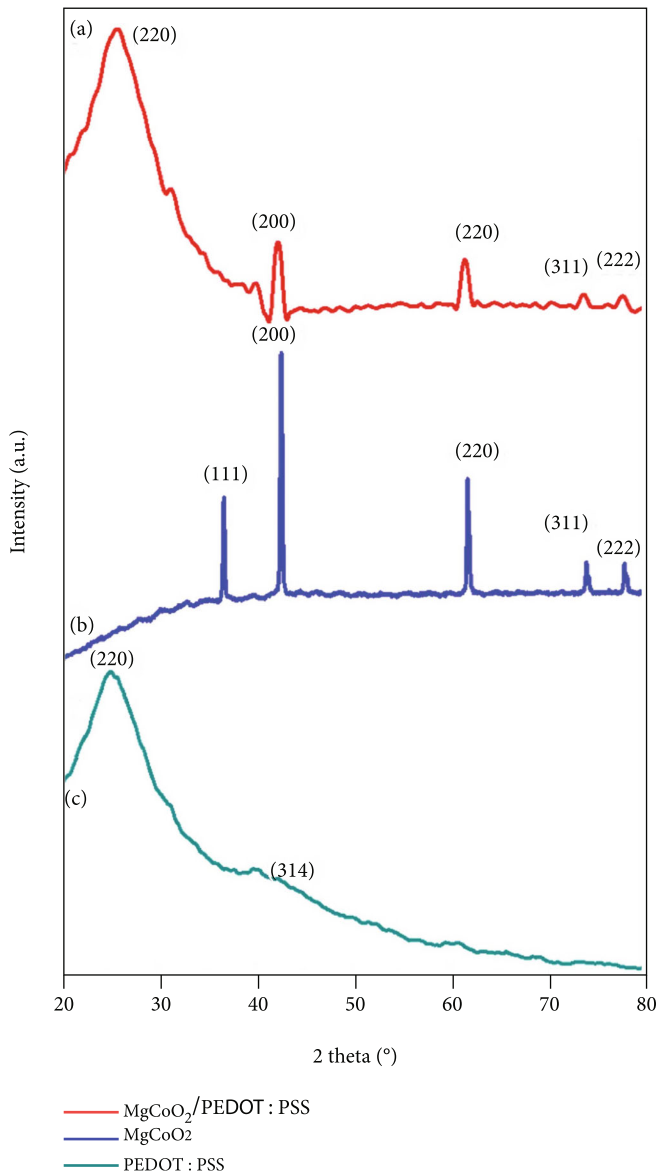
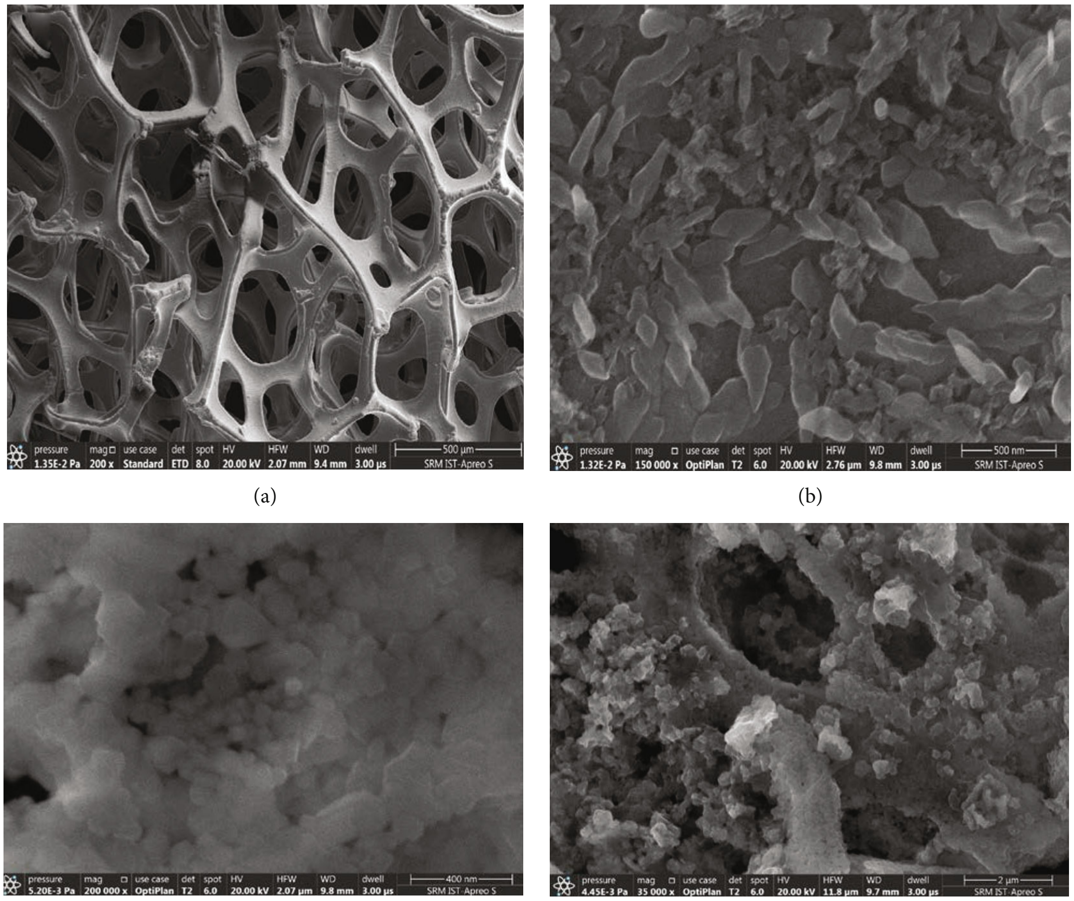


Figure 2: XRD spectra of (A) $MgCoO_2$/PEDOT:PSS, (B) $MgCoO_2$, and (C) PEDOT:PSS composite.

Furthermore, morphological characterizations of PEDOT:PSS@NF, $MgCoO_2$@NF, and $MgCoO_2$/PEDOT:PSS@NF composite were carried out after they have been used in MFCs system for ten days (Figure 4). Comparison of pretreated NF electrode surface before and after installation into a MFC system revealed the biofilm formation upon utilization of organic waste present in the wastewater by the microorganisms (Figure 4(a)). Biofilm formation was also observed on both the PEDOT:PSS@NF and $MgCoO_2$@NF matrix surfaces (Figures 4(a) and 4(b)). However, microbial population adhering onto $MgCoO_2$/PEDOT:PSS@NF composite was relatively high when compared to the above-mentioned individual matrixes (Figures 4(c) and 4(d)). This confirmed the biocompatibility of the $MgCoO_2$/PEDOT:PSS@NF anode for bioelectricity generation and wastewater treatment. This also revealed low cytotoxicity and biocompatibility of the fabricated anode which can be used in microbial cells.

3.2. Bioelectricity Generation. Electrode potentials, polarization curves, and power density were studied at each external resistance throughout the stabilization phase to assess the performance of anodic materials such as PEDOT:PSS@NF, $MgCoO_2$@NF, and $MgCoO_2$/PEDOT:PSS@NF in MFCs. Operation of MFC in the presence of $MgCoO_2$/PEDOT:PSS@NF as anode revealed that 85 h was required to reach a steady voltage output. Meanwhile, this time interval was sufficient for the microbial inoculum to multiply and form highly dense biofilm onto the anode surface. MFC installed with $MgCoO_2$/PEDOT:PSS@NF anode generated a stable voltage output of 0.9 V (Figure 5(a)). At the end of each cycle, utilized medium was replaced with the fresh growth medium, i.e., sewage wastewater. In the present study, electrocatalytic behaviour of $MgCoO_2$/PEDOT:PSS@NF anode towards glucose oxidation with increased long-term stability was found to be appealing with potential applications.



(a) (b) (c) (d)

Figure 3: HR-SEM images of (a) NF, (b) PEDOT:PSS, (c) $MgCoO_2$, and (d) $MgCoO_2$/PEDOT:PSS composite.

Polarization and power density curves were evaluated when the voltage output remained constant to better understand the efficiency of the MFC. The changes in the external resistance were used to test the system, and the polarization and power density curves were extracted. In terms of the highest power density (494 mW/m^2) and current density (~900 mW/m^2), $MgCoO_2$/PEDOT:PSS@NF anode's performance was found to have been high (Figure 5(b)). Thus, the nickel-foam-based $MgCoO_2$/PEDOT:PSS anode was revealed to have high specific surface area that in turn reduces charge transfer resistance (R_{ct}) and allowed better electron transport between the biofilm and anode surface.

3.3. Electrochemical Performance. Anodes such as $MgCoO_2$/PEDOT:PSS@NF, $MgCoO_2$@NF, PEDOT:PSS@NF, and NF individually showed enhanced CV anodic peak currents in the potential ranging from -1 to 0.6 V. In terms of morphological characteristics such as porosity, physical and chemical stability, biocompatibility, large surface area, and efficient transport of electrons in the cathodic cell, $MgCoO_2$/PEDOT:PSS@NF is one of the best anodes that can be used to boost anodic peak current with high performance. It is suggested that as there is an increase in voltage scan rate, the interaction between the metallic oxide and conducting polymer could improve the activity of the electrodes. Since anode plays a significant role in electron transport, the decrease in overpotential could be associated with acceleration of electron supply to cathode or due to enhanced electron transfer kinetics from exoelectrogeneic microbes to anode [37]. Cyclic voltammetry (CV) analysis of NF, PEDOT:PSS@NF, $MgCoO_2$@NF, and $MgCoO_2$/PEDOT:PSS@NF was performed at a scan rate of 50 mVs^{-1} to further understand the bioelectrocatalytic behaviour towards anodic biofilms and electron transfer mechanism towards cathode. Both the anodic and cathodic peaks indicated that the MFCs contained dissolved redox species which are hypothesized to serve as electron transporters [38]. From the CV curves, it is evidenced that $MgCoO_2$/PEDOT:PSS@NF showed a higher anodic limiting current density (2.1 mA) which was nearly three times higher than the current obtained using unmodified NF (0.8 mA) (Figure 6). On the other hand, bare NF anode electrode exhibited wide rectangular CV curve which revealed a potential electrochemical double layer capacitive behaviour in comparison with $MgCoO_2$/PEDOT:PSS composite. This suggested that the efficiency of additional anodic components such as metal oxides and conducting polymers could improve the surface area and charge potential.

3.4. Evaluation of Electrocatalytic Activity of Fabricated Anode. Electrocatalytic activity of the $MgCoO_2$/PEDOT:PSS@NF electrode was evaluated by electrochemical

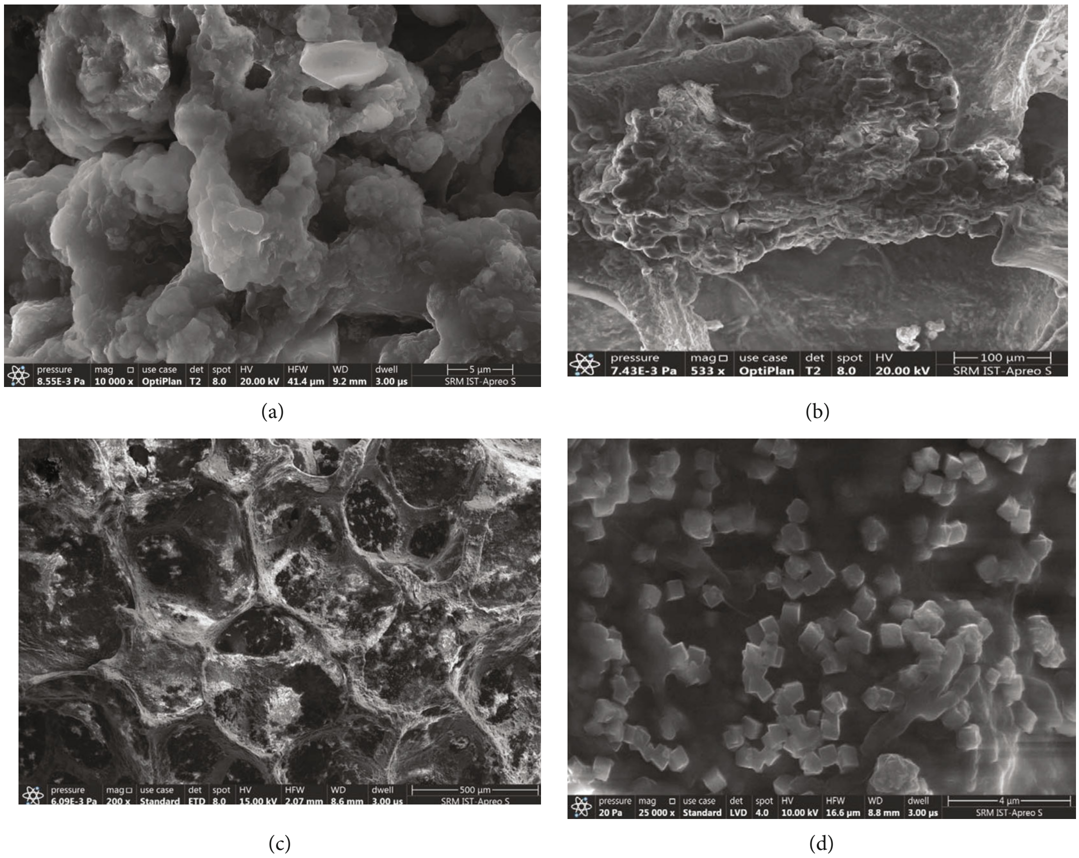


FIGURE 4: HR-SEM images of biofilm formed onto (a) PEDOT:PSS@NF, (b) $MgCoO_2$@NF, and (c, d) $MgCoO_2$/PEDOT:PSS@NF.

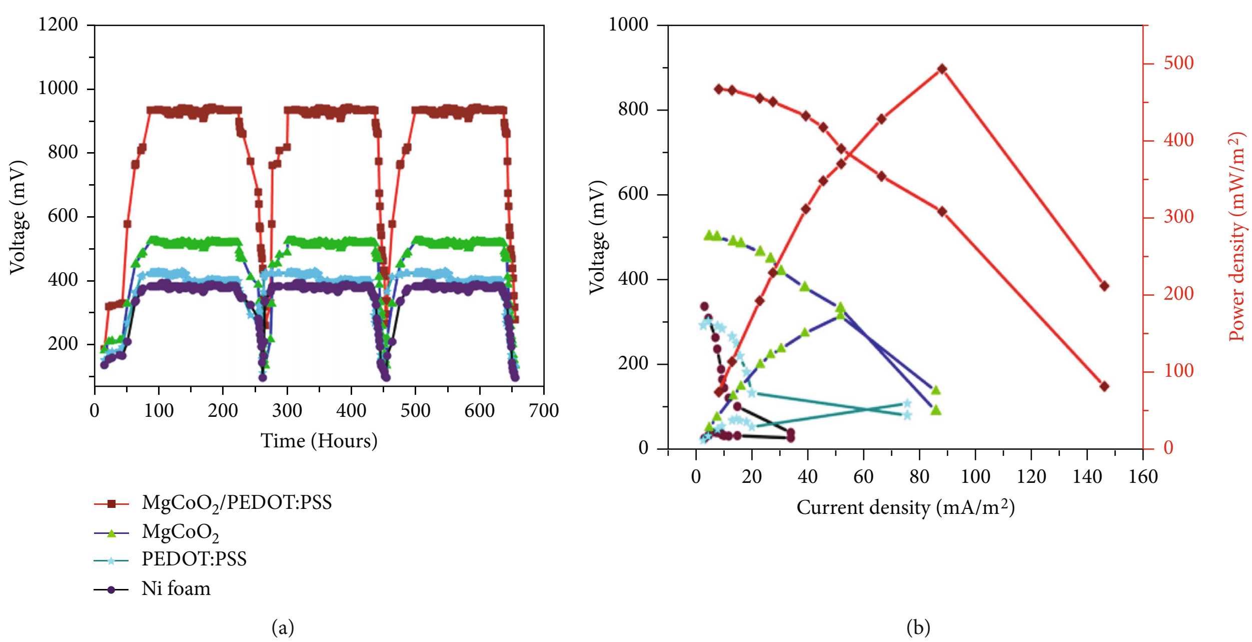


FIGURE 5: (a) Electricity generated using a dual-chambered MFC and (b) current and power densities generated while functioning MFC system in the presence of sewage wastewater using NF (black color), PEDOT:PSS@NF (green color), $MgCoO_2$@NF (blue color), and $MgCoO_2$/PEDOT:PSS@NF (red color) as anodes.

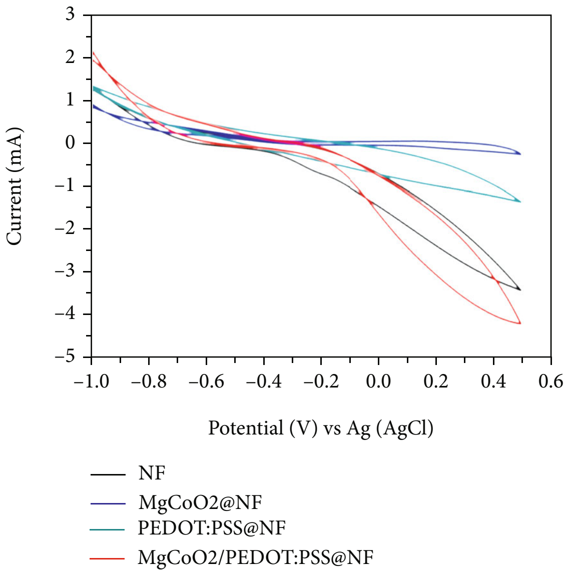


FIGURE 6: Cyclic voltammograms of the NF (black color), PEDOT:PSS@NF (green color), $MgCoO_2$@NF (blue color), and $MgCoO_2$/PEDOT:PSS @NF (red color) as anodes in a MFC system at a scan rate of 50 mV/s.

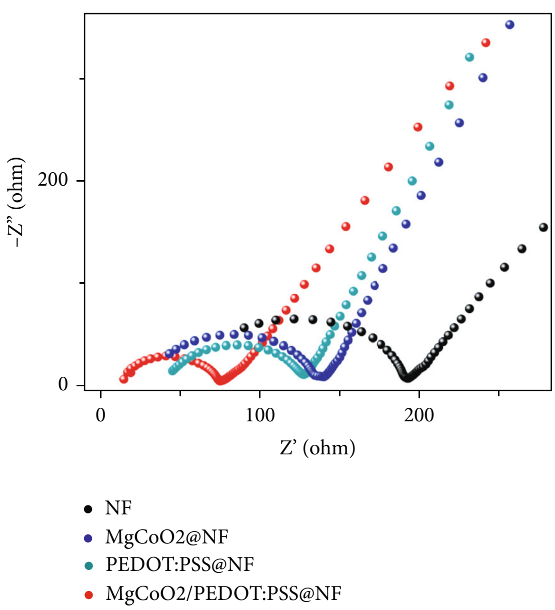


FIGURE 7: The Nyquist curves were recorded for NF (black color), PEDOT:PSS@NF (green color), $MgCoO_2$@NF (blue color), and $MgCoO_2$/PEDOT:PSS @NF (red color) as anodes in MFCs.

impedance spectroscopy (EIS) using a typical three-cell electrode apparatus (Figure 7). In general, charge transfer resistance (R_{ct}) of the working electrode is related to the diameter of semicircle which can indicate the interfacial processes of charge transport between the electrode surface and electrolyte ions [38]. In the study, EIS plots are represented by straight lines at lower frequency range whereas semicircles at higher frequency range [39]. The semicircle is formed due to charge transfer and capacitive resistance, while straight line indicates the diffusion resistance characterized by Warburg mass transfer resistance [40]. The internal resistance including polarization resistance of the cathode, ohmic resistance, and double layer capacitance were accounted to be constant [41]. $MgCoO_2$/PEDOT:PSS@NF anode (25.26 Ω) exhibited the shortest semicircle with the low charge transfer resistance when compared to the $MgCoO_2$@NF (39.09 Ω), PEDOT:PSS@NF (55.78 Ω), and NF anode (61.34 Ω) (Figure 7). The decrease in R_{ct} value indicated the higher electroactivity of the $MgCoO_2$/PEDOT:PSS@NF anode which was directly related to an improved adherence of microbial cells (biofilm formation) onto the electrode compared to that NF anode.

4. Conclusion

In summary, we have demonstrated an anode material using nickel foam modified with $MgCoO_2$ and PEDOT:PSS that had significantly improved porosity, biocompatibility, and conductivity. When compared to unmodified NF, $MgCoO_2$/PEDOT:PSS nanocomposite-coated NF had great influence on the adhesion of microbial cells which may be due to the large surface area offered by irregular globular structures of calcinated $MgCoO_2$. The dense biofilm formed in combination with PEDOT:PSS had improved the anodic reaction, in turn transferring electrons to the cathodic chamber in an efficient manner. Thus, the $MgCoO_2$/PEDOT:PSS-based anode developed in the present study can be used to setup MFC to generate bioelectricity at a lower cost. This new anode material has to be further studied in order to implement at large scale in combination with wastewater treatment system to produce bioelectricity.

Data Availability

Data will be provided upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Brahmari H. Shetty and Raji Atchudan contributed equally in this study.

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Review Article

Environmentally Conscious Manufacturing and Life Cycle Analysis: A State-of-the-Art Survey

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Research on developing new methodologies on environmentally conscious manufacturing and way of reducing environmental impacts on product design was started over two decades ago. Environmentally conscious manufacturing has become a challenge to the environment and to the society itself, enforced primarily by government regulations and the customer expectation on environmental issues. In both industry and academics, there is a sizable following for environmental-related issues which are aimed at finding answers to the problems that arise in this newly emerged area. Problems are widespread including the ones related to the life cycle of products, disassembly, material recovery, and remanufacturing and pollution prevention. Only very few researchers have concentrated on ecofriendly products. This paper investigates the literature by classifying more than 200 published references into four categories, viz., design for environment checklist, environmentally conscious manufacturing, life cycle analysis, and material selection.

1. Introduction

Increasing customer demands has led to the present manufacturing industries to continuously evolve in meeting all the needs of end customer due to factors like competition and profit. But in this evolution process, environmental issues were neglected. This has resulted in serious environmental disputes like global warming, acid rain, changes in weather, and water shortages around the world. As a result of these environmental consequences from fast-paced industrial evolution, the ecofriendly Industrial Revolution has begun. While developing a product, the environmental performance of these products has become a vital issue. Bearing 5this issue in the mind, some industries are investigating ways to minimize their effects on the environment by providing products with high-level reusability. In recent scenario, a manufacturing facility was specifically designed in solar energy sector by a unique manner for utmost efficiency in terms of production and energy. The global earth warming is being mitigated by providing solar panels developed by NASA that utilizes sun energy. In another scenario, novel invention of a product, ecoconscious-based materials, reusable packaging products, etc. to name a few pave a good way for eradicating environmental pollution and maximizing resources. Remanufacturing is an economically viable and environmentally friendly way to achieve many of the goals of sustainable development. Remanufacturing forms an essentially closed-loop manufacturing system by concluding ends of the material use cycle. It primarily focuses on value-added recovery, rather than just material recycling. There are estimated to be in excess of 73,000 firms engaged in remanufacturing in the United States directly employing over 350,000 people (Lund, 1998). Environmentally conscious remanufacturing is fundamentally an industrial process wherein worn-out products are restored to like-new condition. The discarded product is completely disassembled through a series of industrial processes in a factory environment. The reusable parts are cleaned, refurbished, and put into inventory based on product development.

In another study, it was revealed that major hindrances faced by Western Europe are waste management and landfill space. The overseas manufacturers are incorporating more and more postlife considerations into their product design and development process. Both in industries and academia, under the influence by European governments, a considerable attention has been drawn towards material recycling. The material recycling focuses on leading constituent materials from the disposal of the product or its associated value into a new cycle of usage. Arguably, a drastic reduction in impact on environmental factors can be attained by reuse of product and remanufacture by which geometrical aspect of the product is retained and is reutilized for the same purpose as during its original life cycle for secondary purposes. With remanufacturing, the energy and matter consumption during manufacture is eliminated as the existing components are facilitated. The monetary expenditure incurred for producing or acquiring new product components are reduced elastically with remanufacturing. On the other side, the disadvantages incurred in remanufacturing are as follows: requirement of channels for collecting worn-out products, identification of product design and restructuring of product design for remanufacturing, need to redistribute and retail reprocessed products, etc. The four categories, design for environment checklist, environmentally conscious manufacturing, life cycle analysis, and material selection, play a vital role in sustainable manufacturing.

1.1. Design for Environment Checklist. Several researchers have given an overview on environmental design checklist as a method or tool to help manufactures to achieve an optimized design for ecofriendly development. A sustainable environmental design also contributes towards development of green manufacturing disciplines in the world. The primary objective of ecofriendly manufacturing process is to minimize environmental degradation effects in the product development perspective, viz., taking recyclability, reusability, and degradability into account, rather than to boost economic benefits. The design methodology for environmental design and development is attributed to energy efficient lighting, heating, and cooling systems. This energy-reliable manufacturing as an element of environmental design check suits lower operating costs as well as longevity in the product lifetime. In day-to-day scenario, the constructions of buildings in accordance with environmental principles provide enhanced occupant productivity and sense of wellbeing. Recycling and waste management are another aspect of environmental design.

1.2. Environmentally Conscious Manufacturing. Environmentally conscious manufacturing abbreviated as ECM is associated with producing methods for manufacturing new products from conceptual design to final delivery as well as ultimately to the end-of-life (EOL) disposal with respect to environmental standards and requirements. Product recovery, on the other hand, is aimed at minimizing the amount of waste sent to landfills by recovering materials and parts from old or outdated products by means of recycling and remanufacturing. ECM is driven by the escalating deterioration of the environment. With the aftereffects of both fast depletion of the raw materials and an increasing number of various forms of waste, viz., solid waste, air, and water pollution, in order to design and develop a product which is environmentally benevolent, the life cycle of the product should be very well understood. Figure 1 shows the flow process of environmentally conscious design.

1.3. Life Cycle Analysis. Life cycle assessment (LCA) stands as the preeminent tool for estimating environmental impacts caused by products from "cradle to grave" or "cradle to cradle." It exists in multiple forms, claims a growing list of practitioners, and remains a focus of continuing research. Presently, this system of LCA is often used by decision-makers to study an entire product system in a very detailed way and still remains the focus as if the whole products were a single process. Therefore, LCA is started to prove that it is an excellent guidance tool for the industrial world to make their processes environmentally friendly. In LCA, useable parts are cleaned; then, the new product is reassembled from the old and, where necessary, new parts to produce a product that is fully equivalent and sometimes superior in performance and expected lifetime to the original product. Life cycle analysis (LCA) spans over the development, manufacturing, use, and disposal stages of the product. At these stages individually, decisions based on environmentally friendly techniques need to be made and have prompted methods like design for environment (DFE), design for disassembly (DFD), and design for recycling (DFR). LCA has proven to provide most important solution to environmental problems; its adjacent effect is with the birth stages of novel product development. However, the greatest impairment to nature occurs when the product completes its lifetime utility. Therefore, understanding and developing innovative techniques for end-of-life management of the products by means of product/material recovery would be a suitable solution for eradicating environmental or natural degradation. LCA is extremely crucial considering the millions of products that have already been developed without incorporating their undesired effects on the environment.

Recovery of products can be done in binary methods as discussed in the former sections, viz., remanufacturing and recycling. The difference between recycling and remanufacturing is based on recovering ability of material content. Recycling is aimed at recovering the material content of retired products by performing the necessary disassembly, sorting, and chemical operations. On the other hand, remanufacturing preserves the product's (or the part's) identity and performs the required disassembly, sorting, refurbishing, and assembly operations in order to bring the product to a desired level of quality. Disassembly has proven its role in material and product recovery

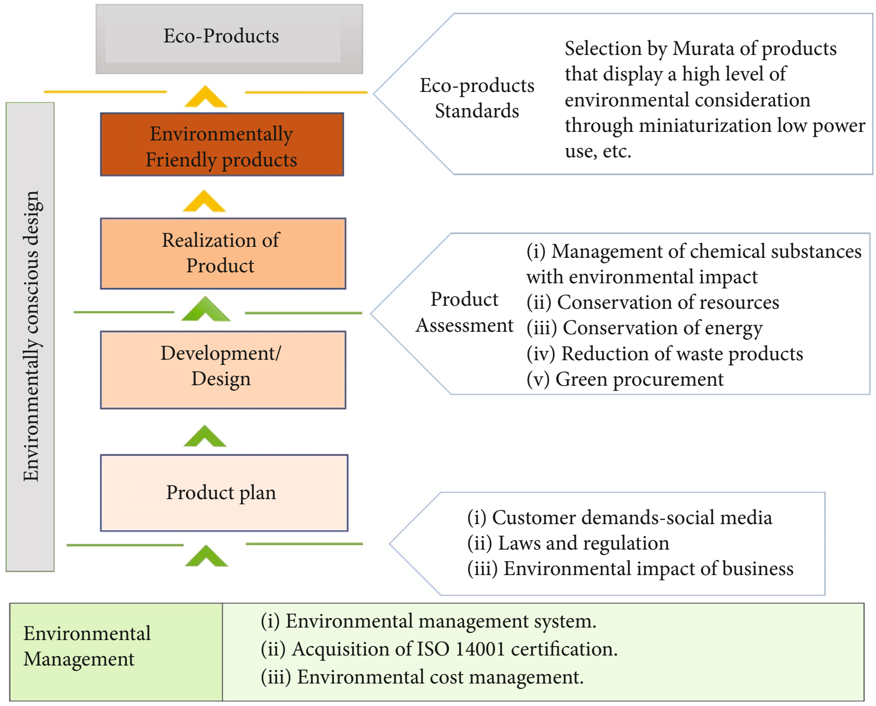

Figure 1: Flow process of environmentally conscious design.

by allowing selective separation of desired parts and materials. Besides being able to recover valuable precious materials by material recovery, good component removal via disassembly could provide parts for discontinued products and reduce the lead times in the assembly of new products. Life cycle analysis (LCA) spans over the development, manufacturing, use, and disposal stages of the product as depicted in Figure 2.

1.4. Materials for Environmentally Friendly Usages. Two common primary objectives arise as a momentum with the result of fast depletion of the raw materials and an increasing number of different forms of waste (solid waste, air, and water pollution). They are creating environmentally friendly materials (i.e., green products) and developing techniques for product recovery and waste management. Ecofriendly materials pave their way to the top among other class of materials. The primary reason for this ranking is due to its recycling and biodegradation aspects as well as zero degradation on disposal. The green materials are taking huge strides replacing toxic waste in the market place with organic materials. The trend of this green or ecofriendly materials has been escalating drastically to meet the demand of consumers for renewable and reusable resources. The materials used for environmentally friendly needs are diversified and spread in various regimes like constructions, waste water treatments, biodegradable materials, manufacturing, and packaging to name a few.

In this review article, many issues have been captured based on environmental issues with the attention of industries, academia, and manufacturing sectors. This article comprises detailed review about the effects of product design and development on ecofriendly aspects. Our objective is to offer an up-to-date literature review on product development based on environmental aspects, materials for recycling and reusable purposes, design for environment, etc. Basically, our surroundings have limited resources, viz., materials that convert into product, energy, water, and air supply. The areas for waste disposal and treatments are scarce in the society. The thrust for providing a sustainable environment for the next generation is of utmost privilege as the resources available in the globe are used for raising the living standard. This paper focuses on various literatures associated with the former mentioned aspects as the need to cultivate a viable solution for ecofriendly aspects related to product design development and manufacturing as well as recycling is of greater importance. The identification of extent of product issues and corrective actions given on research articles are also summarized in this paper. Moreover, the problems or issues sorted by the researchers in various dimensions affecting environmental degradation are also explained in this literature review article. The material selection criteria based on environmentally friendly aspects, degradation, and reusability are also given primary importance, for a better future. Lots of review researches have been carried out on green materials for environmentally conscious manufacturing aspects involving design and production.

Material selection should be a crucial consideration when building a product with environmental benefits. The environmental features of a product are very much fixed once the design decisions are made and the materials used to make it are known. In order to accomplish a complete ECM concept, concerns such as energy source selection, cooling systems, and handling of hazardous byproducts, among others, must be regulated during the production process.

When the product structure is large and complex and the number of components to examine expands, the LCA problem becomes more complicated. LCA demands contributions from all parts of society, including public pressure organizations,

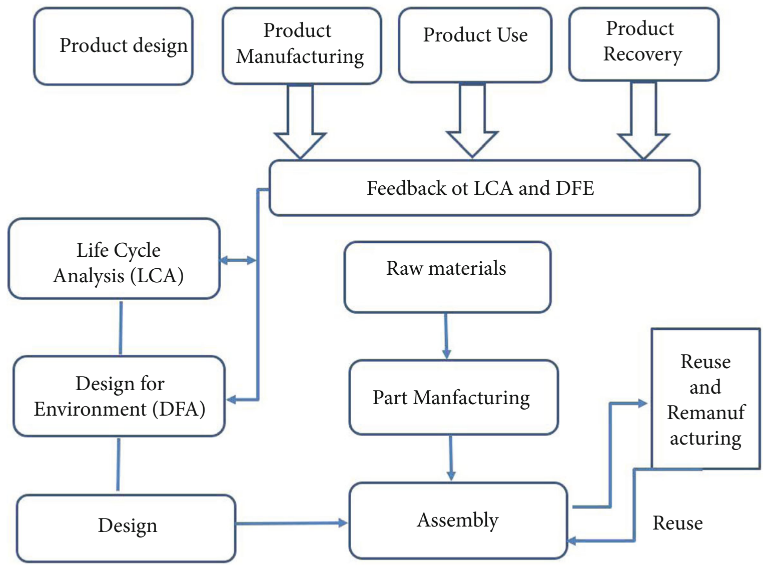

Figure 2: Flowchart representing LCA.

educational institutions, companies, and government agencies, according to a number of LCA-related researches.

2. Review Status of the Ecofriendly-Based Manufacturing Process

2.1. Design for Environment Checklist. DFE checklists are widely used tools for supporting product analysis at the design stages. Some checklists are intended for certifying ecolabels such as Ecomark [1]. By using a checklist, the designer can design good-quality, desirable, and cost-effective products to reduce the impact on the environment. Preparation of ecodesign checklist adds value or supports the designer for designing ecofriendly products. One of the most prevailing checklists called "the ecodesign checklist" covers the entire life cycle of a product from need analysis to the recovery and disposal stage [2]. Japanese manufacturers adopted the use of checklists and LCA for assessing the environmental aspects of their manufacturing products [3]. Many researchers have done lots of work with the help of the ecodesign checklist, and some of the findings are described below. Kishita et al. [4] framed a checklist that reduces CO_2 by 8% for a digital duplicator.

Ketchatturat [5] developed a self-evaluation checklist with each set consisting of 3 check points, 14 subcheck points, and 70 items to increase the value of educational provision processes. The author analyzed the data by employing content analysis, cross-case analysis, and analytical description methods. The PDCA cycle was used in the implementation of the self-evaluation checklist. "The ten golden rules," which is a powerful tool for integrating realistic environmental demands into the product development process, was introduced by Luttrop and Lagerstedt [6]. The product developers/designers can use these general guidelines as a base and guideline for the development of situation-specific product design challenges. Wimmer [7] developed an ecochecklist method that supports engineers in product development to produce ecofriendly products. The checklist is prepared based on a holistic view of the product in three analysis levels, namely, part, function, and product. Checkpoints show where the weak points of a product are and how to reuse and recycle the parts, where to integrate, omit, or create functions, and where to increase efficiency and reduce consumption and the usability of the whole product.

A method for incorporating ecodesign into product design and development in an automobile company was proposed by Wimmer and Zust [8]. The application of the twelve-step approach of ecodesign is implemented for the fuel tank unit of a car. This indicates that the approach can be a viable ecodesign method for manufacturers to integrate the environmental aspects of their products into their product design and development processes.

A variety of ecodesign checklists presenting a system to assist product designers in selecting the appropriate ecodesign checklist for product development were investigated and analyzed by Masoudi et al. [9]. Byggeth and Hochschorner [10] proposed that ecodesign tools can be used in both product development and purchasing, i.e., to prescribe design alternatives, assess environmental impacts, or compare environmental improvement alternatives. In this study, the authors analyzed 15 different ecodesign tools to ascertain whether a valuation is included in the tools, in what way the tools give support in different types of trade-off situations, and whether the tools provide support from a sustainability perspective. And it is concluded that nine of the 15 tools analyzed provide support in trade-off situations, but the support is not sufficient. The authors suggest that an ecodesign tool should contain a valuation if it is designed to support a user in a trade-off situation. The valuation should include a life cycle perspective and a framework for sustainability to give an accurate result from a sustainability perspective.

For industrial designers, Lofthouse [11] developed a more holistic framework for building ecodesign tools. The author has provided his result that "information/inspiration" makes ecodesign much more accessible to designers who intend to consider ecodesign strategies within their design work. It is a more user-friendly, design-specific service to designers, guidance providers, supplier information, and educators and allowed browsing source-specific data for interesting ideas. Two handbooks with recommendations and procedures for developing environmentally friendly vending machines were created by Vezzoli and Sciana [12]. To achieve these results, an LCA has been developed and a system to prioritize guidelines has been adopted. Finally, these tools have been integrated within the company procedure to consistently reduce the overall environmental impact of products throughout their entire life cycle.

Telenko et al. [13] made a compilation of designs for environmental guidelines. A total of 6 DFE strategies and 76 DFE guidelines were reconciled from 20 sources, and a subset was illustrated with examples. The guidelines are intended to be used in the early stages of design to reduce the environmental impacts of products and systems. The guidelines can be used as prompts for ideation, as expert knowledge in automated design guidance, and as criteria for evaluating early-stage design alternatives.

2.2. Environmentally Conscious Manufacturing. Environmentally conscious manufacturing involves producing products with minimized environmental effects [14–17] [16, 17]. ECM consists of two important issues. The first one is described that it understands the life cycle of the product and its impact on the environment at each of its life stages. Next, it will make better decisions during product design and manufacturing so that the environmental impacts of the product and the manufacturing process are kept at a minimum level. The issues in environmentally conscious manufacturing were addressed by Gungor and Gupta [18]. During the design stages of the product, there are different objectives that the designers should focus on. ECM designs the product which increases recyclability ([19][19–25], manufacturability [26, 27], and disassemblability ([28–30]; Lambert & Gupta 2005) in order to minimize the effect on the environment.

Ayes et al. [31] discussed the role of government regulation as a driver of change by reviewing several specific cases from European firms, with emphasis on the potential for internalizing the product by recovery, remanufacturing, and material recycling. The authors conclude with the views that the economics, the regulatory environment, and the organizational and management aspects are the problem. In light of environmental concerns, Brennan et al. [32] explain why manufactured parts must be disassembled. The authors emphasize the important point that the products and machines are to be designed in terms of disassembly and part recycling. The increased awareness of the state of the environment by both the consumer and the producer, recycling regulations, and resource conservation needs are leading to new challenges and dictate a fundamental reappraisal of the traditional manufacturing paradigm. A heuristic algorithm, referred to as the Acyclic Assembly Time (AAT) algorithm, which is based on the asynchronous model for concurrent machines in electronic assembly was developed by Moyer and Gupta [33]. The developed AAT algorithm increases the utilization of the individual mechanisms, and the efficiency of the overall system is naturally improved. The ultimate goal of reducing the total assembly time is achieved.

Mittal and Sangwan (2014) stated that the reliable, valid, and tested model has three types of drivers—internal, policy, and economic. It has been found through hypothesis testing that internal drivers for the implementation of ECM are positively related to policy and economic drivers, and policy drivers are positively related to economic drivers. This research is expected to help the government and industry in developing policies and strategies for the successful implementation of ECM. Argument et al. [34] examine academic research and industrial requirements in the area of environmentally conscious design. The authors wish to explore the perceived gap that exists between academic research and industrial requirements. Duhan et al. [35] in their paper on environmentally conscious manufacturing have used an analytical network process (ANP) decision tool in ECM and have concluded by saying that the manufacturing control process plays the most important role for environment-conscious manufacturing, and then, waste control comes next in the priority while quality control and research and design process comes next in hierarchy, and packaging control is the least important among the factors selected.

Yusuff et al. [36] have discussed the importance of the manufacturing process and environmental considerations which must be in place, from the design, production, use, and disposal. It is no longer viable to consider reduction measures of environmental problems after it has been produced.

The authors have found a way of strong disagreement, by suggesting the existence of a gap, and conclude that the most significant gaps are in the area of environmental concerns and research preferences. Many other researchers have also provided their perspectives and scope on environmentally conscious manufacturing which have been tabulated in Table 1.

2.3. Life Cycle Analysis. LCA is a process for assessing and evaluating the environmental and occupational health and resource consequences of a product through all phases of its life, i.e., extracting and processing raw materials, production, transportation and distribution, use, remanufacturing, recycling, and final disposal [44, 45]. To reduce ecological burdens, Alting and Legarth [46] introduce a conceptual framework of integrating life cycle engineering into designing low energy consumption in the use phase of a product. An economic input-output life cycle analysis model which was used to generate a large array of indicators for analyzing the economic and environmental impacts of a product was developed by Maclean and Lave [47].

The assessment was investigated in the application of a midsized automobile. Focusing on the manufacture and the use stage, Joshi [48] performed a life cycle inventory analysis by presenting a new model for performing product life cycle assessment. The proposed model is a matrix, which consists of environmental impact categories in conjunction with about five hundred economic inputs and outputs. The scope of LCA involves tracking all the materials and energy flows of a product from the retrieval of its raw materials to the disposal of the product back into the environment [49]. Most of the

Table 1: Author scope on ECM.

Author review	Scope
Lisa et al. (1998)	Environmentally conscious design
Bras & McIntosh [37]	Remanufacturing
Zhang et al. [38]	Environmentally conscious design and manufacturing
Guide et al. [39]	Production planning and control for remanufacturing
Guide [40]	Production planning and control, inventory management and control, disassembly, reverse logistics
Tang et al. [41]	Disassembly modeling, planning, and application
Williams [42]	Electronic demanufacturing processes
Kim et al. [43]	Disassembly scheduling
Duhan et al. [35]	Analytical network process (ANP)
Yusuff et al. [36]	Disassembly design, production planning, and application

researchers use LCA within a DFE methodology as a tool to measure the environmental impact of a product design [38, 50–53] [50]. LCA is a powerful tool chosen from a large number of available tools for their suitability of product assessment (Finnveden & Moberg 2004). Several authors have applied LCA to different case studies in automotive [54], [55], construction (Banaitiene et al. 2006), and computer industry [56, 57], [57], to target the individual evaluation of technical, economic, and environmental aspects of products or systems.

Most of the literature on LCA focuses on the second stage of the study, namely, the selection and evaluation of various, noncomparable environmental consequences ("chalk vs. cheese"), according to Ayres [58]. This problem is, indeed, very difficult and may well be impossible to solve convincingly—even at the conceptual level. However, the only approach that can make progress utilizes monetization to the limits of its applicability, rather than one that seeks to bypass (or reinvent) economics. Nevertheless, the evaluation problem is second in priority, for the simple reason that LCA has utility even if the evaluation technique is imperfect. On the other hand, LCA has no (or even negative) utility if the underlying physical data is wrong concerning critical pollutants.

2.3.1. Environmental Life Cycle Assessments. The idea of comprehensive environmental life cycle assessments (LCA) was conceived in the U.S.A. in the late 1960s and early 1970s. The first study of the life cycle perspective was focused on environmental impacts from different types of beverage containers [59], [60]. However, the formal analytical scheme to become LCA was first conceived by Harry E. Teasley, Jr. in 1969. At that time, he was managing the packaging function of the Coca-Cola Company. One of the interesting findings of the Coca-Cola Company is switching from glass bottles to plastic bottles [61], [62]

After the Coca-Cola study, there was a steady flow of resource and environmental profile analysis (REPA) studies at Midwest Research Institute (MRI). In the early 1970s, the driving force became solid waste issues. People were very interested in the total life cycle manufacturing system aspects of solid waste in comparison to postconsumer solid waste. The role of recycling and the use of reusable products to reduce solid waste were of particular interest. The inclusion of energy and other environmental emissions was not considered as important as solid waste. The second REPA study to be completed at MRI was sponsored by the Mobil Chemical Company [61], [63].

In the 1970s, the various calculations for performing an LCA were done without the aid of electronic computing equipment. The umpteen numbers of calculations were done on a mechanical calculator that did not even have a paper tape printout. It consisted of electric motors and rotating wheels [61], [61]. In 1973, the first LCA computer program was funded by an MRI client. The data filled several boxes containing many hundreds of punched cards. The information on the cards had to be loaded into the computer with a mechanical feeder at any point in time we wished to do calculations. Often the feeder would not read one or two cards correctly, and we had to start all over. The computer would often just indicate the error "somewhere," which meant the people would have to hand sort through the boxes of cards and try to find the card error. From 1970 to 1974, the modern concept of REPA/LCA took shape. Also, during that time, a framework for impact assessment was developed [62], 1973)[59].

In 1985, the major report was completed for Goodyear Tire and Rubber Company [60], [64]. The purpose of this report was to provide a database that the container presented no more threat to the environment than competitive containers. This was a study on 2-liter plastic (PET) soft drink containers and played a pivotal role in the initial marketing of that container. In 1992, there was a dramatic reawakening of environmentally consciousness, and it did not have a single source, but rather several factors were converged to create national debate and extensive media attention. Several consecutive international Society of Environmental Toxicology and Chemistry (SETAC) working groups moved the methodology development and international consensus building to a good step forward [65–67].

Presently, many automotive and manufacturing industries lead their research and developmental activities in response to the negative environmental developments. The new European Ford model, Mondeo, is designed to be 85% recyclable [68], [68]. Mercedes Benz implemented a total vehicle recycling program with vehicle design and vehicle recycling [69]. The highlight of the recycling program is reducing the variety and volume of plastics used, avoiding composite materials, and making logos with plastic parts. Mercedes and Swatch jointly designed a prototype car with vegetable fibers instead of metals. BMW announced a pilot program to test the feasibility of recycling BMW automobiles under the compulsion of German laws for recycling [70], [70]. Similar contributions were made by General Motors [69], Volkswagen [71], Nissan Motors [19], and Volvo Car Corporation [72]. The manufacturing industry adopted this technique to perfect their processes to make them more productive and environmentally friendly. Many researchers have worked on ecodesign for product development through the implementation of various tools and techniques. Table 2 presents various authors dealing with the application of life cycle analysis of various product designs and manufacturing processes and the results achieved.

From the above literature review process, a detailed study has been envisaged about life cycle analysis. LCA-based studies have been focused on development of performance-based manufacturing process suitable for reducing environmental degradation. Several researchers have also reported about LCA related to welfare assessment works. A prototype-based LCA has also been incorporated to estimate rapid assessment of conceptual design for environment.

2.4. Material Selection. The main concern in today's manufacturing industries is to bring out the products that are ecofriendly, and therefore, ecodesign is widely incorporated in the material selection [132]; [112]. Material selection influences more while designing a product. To reduce the environmental burdens of products, ecodesign is incorporated with material selection [113]. Tseng et al. [114] performed a green material cost analysis to recommend materials that cause less environmental impacts. The enormous types of materials are available for engineering application which makes the designer complexity in deciding the most appropriate materials. Several systematic methods have been proposed to help the designers in the selection of materials and processes [115, 116].

One of the most commonly used quantitative selection methods introduced by Ashby and Cebon [117] was based on the definition of the material index, and it consists of sets of physical-mechanical properties to maximize some performance aspects of the components. Defining the indexes, it is possible to produce selection charts reviewing the relation between properties of materials and engineering requirements [118]. Environmental information about materials is a must for the completion of product LCI. The different industrial sectors have developed environmental profile database for material based using the LCA approach [119, 120].

Holloway [121] introduced material selection charts called Ashby's method and shows how this methodology can be extended to take environmental factors into account. By implementing these charts and extending their range to include environmental concerns, designers may consider them the same way they consider the other material and process properties. A new life cycle cost analysis methodology with the goal of building a new sustainability model to quantitatively evaluate the overall direct cost of a vehicle over its complete product life cycle was proposed by Ungureanu et al. [122]. Evaluation of environmental impacts caused by a lightweight material and aluminum alloy used for autobodies was presented. Implementation of a life cycle engineering approach was done by Ribeiro et al. [123] to determine the material selection for a fender. The authors evaluated the best choice of material from mild steel to ultrastrength steel and aluminum alloys for the automobile fender. Three different methods—LCC, LCA, and a conventional approach—were applied for the sustainability performance of the product. The study by Zhou et al. [124] depicts that optimal material with the highest total fitness value was selected for a drink container. Genetic algorithms (GA) and artificial neural networks (ANN) were used to achieve the optimized mechanical, economic, and environmental properties.

Zarandi et al. [125] emphasize life cycle engineering (LCE), and it is one of the best approaches of material selection for sustainable products. The authors proposed a new methodology that supports the preliminary filtering of alternatives from an environmental viewpoint. Moreover, a prototype hybrid expert system based on the proposed methodology called material selection expert system for sustainable product design is developed to support the task of preliminary filtering. Five distinct life cycle effect assessment methods to study the use of different polymer materials used for packaging reasons were employed by Bovea and Gallardo [112]. He concluded that during material selection for a product design, decisions are based on a variety of factors such as cost, properties, performance, and environmental aspects. Katsukiya and Kevin (2001) presented guidelines for the ecological design of engineering products and processing of iron and steel through the application of automobile manufacture and its use. They concluded that the improved application of iron and steel enables the environmental burden to be reduced.

Zuo-ren et al. [126] introduced several representative case studies such as life cycle analysis of civilian buildings and metal production in China by reviewing the recent developments of LCA methods and application of materials via life cycle assessment. The possibility of reducing environmental effect for automobile components by adopting alternative materials and production procedures was investigated by Vinodh and Jayakrishna [127]. Sustainability Xpress evaluates the environmental impact and the mean percentage reduction in carbon footprint, water eutrophication, air acidification, and total energy consumed estimated at 43.68, 99.58, 48.38, and 52.19, respectively, which are meant as a drastic reduction.

Jeya Girubha and Vinodh [79] used VIKOR (VlseKriterijumska Optimizacija I Kompromisno Resenje in Serbian, which means Multicriteria Optimization and Compromise Solution) as an MCDM tool for the selection of alternate material for instrument panel used in an electric car. The authors finally concluded that polypropylene can be used as a suitable alternative material for ABS instrument panels. A structural optimization technique to determine the best foams to use as the core material for sandwiches with aluminum alloy faces that would be used as floor panels in a concept car's bottom structure was employed by Ermplaeva et al. [128]. In future minimization, a problem for the weight of the entire bottom structure under static load conditions, including stiffness, strength, and buckling constraints, is formulated and solved for the material application. More analytical tools should be developed for estimating environmental degradation effects

Table 2: LCA of various product designs and manufacturing process or overview of applied case studies in LCA.

Authors	Application	Achieved result
Rosa et al. [73]	Life cycle assessment of a composite component for automotive using SimaPro 7.2 software	A panel made of hemp fiber and processed through vacuum bag infusion reduces the environmental impact at the production phase due to the use of plant-based materials and the impact reduction in the use phase due to the weight reduction of 280 g
Premrudee and Naruetep [73]	Life cycle assessment of lead-acid battery using Eco-indicator 95	An assessment of the entire life cycle of the battery found that a calcium maintenance-free battery had 28% less impact on the environment
Song et al. [74]	Environment performance of Chinese TV sets using SimaPro software version 7.2	Increases the energy efficiency within the various life cycle stages which reduces the environmental impact of TV sets. It also reduces overall energy consumption
Andersson et al. [75]	Life cycle assessment of tomato ketchup using CML provisional method	Packing and food processing were found to be hot spots, and the critical parameter was found to be the storage time in a refrigerator
Paris & Museau [76]	Quantification of environmental impacts of self-vibratory drilling (SVD) over traditional drilling (TD) using CML 2 baseline 2000 V2.04	Self-vibratory drilling is an innovative technology that increases productivity without coolant. Lifespan increases for twist drill to 200 m could contribute to the reduction of the environmental impact of the SVD process by 25% to 30%
Mayyas et al. (2012)	Life cycle assessment-based design approach to assess the performance of vehicular body-in-white is an analysis of the material to be used in the vehicle	It shows that magnesium and aluminum are used because of less energy consumption; however, advanced high strength steel (AHSS) has very less energy consumption than both of the above
Curran [73]	Life cycle assessment-based design approach to assess the performance	Ten important often overlooked or misunderstood aspects of LCA methodology and descriptions of what users should be aware of when setting out to conduct an LCA or when reviewing an LCA conducted by someone else
Vinodh & Rathod [77]	Integration of environmentally conscious quality function deployment (ECQFD) and life cycle assessment (LCA)	The analysis of the response of executives indicates that the suggested tools/techniques are practically feasible and compatible for sustainable product development
Eliceche et al. [78]	Minimization of environmental life cycle impact as a tool for process optimization of utility plants	Significant reduction in the environmental impact, operating cost, natural gas, and electricity consumption has been achieved simultaneously, increasing the efficiency of the plant
Vinodh et al. [79]	Application of life cycle assessment on the instrument panel of an electric car using CML methodology	The sustainability index of the instrument panel has been computed before and after implementing the EIA methods, which has shown a notable improvement level from 6.09 to 7.73. Also, the improvements have been statistically validated and found to be 90% satisfactory after the implementation of EIA into practice
Kharel & Charmondusit [80]	Ecoefficiency evaluation of iron rod industry in Nepal using LCA	It is noteworthy to mention that the ecoefficiency of the iron rod industry has been improved in all respect of energy intensity, material consumption, water use, waste generation, and CO_2 emission

Table 2: Continued.

Authors	Application	Achieved result
Monteiro & Freire (2012)	Life cycle assessment of a house with alternative exterior walls using CML 2001 and EI'99	To sum up all results, the wood wall has been pointed out as the preferable solution by the three methods and the results for the remaining exterior wall scenarios are influenced by the life cycle impact assessment method applied, in particular for the toxicity categories
Marco et al. [81]	Validation of recycled materials using life cycle assessment methodology for the injection molding process	The study underlined the effective improvements of the environmental aspects by substituting the actual product with the one made of recycled PET (RPET). The research demonstrated a useful interaction between life cycle assessment and the conceptual design phase with the design supporting software packages used in the injection molding field
Li et al. [82]	Ecoefficiency approach to evaluating energy as well as resource efficiency of manufacturing processes in grinding case	The evaluation process shows the dynamic nature of the unit manufacturing process, whose ecoefficiency can be improved by accounting for all aforementioned aspects. The current application faces challenges to gather reliable data, such as life cycle inventory data for grinding wheel and coolant consumption/loss
Gonzalez-Garcia et al. [83]	Life cycle assessment of eucalyptus TCF pulp manufacture using CML baseline 2000 V2.1	The main contributors to the environmental impact are not related to the wood paper pulp manufacture that takes place inside a mill, the background process such as the upstream production of chemicals and fuels has been identified as the main contributor to impact categories related to toxicity and abiotic resource depletion
Puettmann & Wilson (2005)	Life cycle analysis of wood products: cradle-to-gate approach	The environmental performance of these products is measured by total energy and major emissions. LCI findings for the production of wood products, by the nature of the industry, show that the use of biomass as major fuel will decrease the environmental impacts
Duflou et al. [84]	Life cycle assessment of manufacturing process	Significant environmental impact (CO_2 PE!) reductions are identified in the manufacturing unit process
Frenette et al. [85]	Life cycle assessment of light-frame wood wall assemblies using IMPACT 2002+, Eco-indicator 99, and TRACI	The results of the case study, which are consistent with all the methods considered, show the relatively small contribution of the wood framing and other wood-based products on the total embodied impact
Cherubini & Jungmeier (2010)	LCA of a biorefinery concept that produces bioethanol, bioenergy, and biochemicals from switch grass using CML 2 baseline 2000 V.2.03	Significant GHG and fossil energy savings are achieved when the biorefinery system is compared with a fossil reference system. In the first 20 years of activity, 79% of GHG emissions and 80% of fossil energy were saved. After 20 years, the soil is in new equilibrium and atmospheric CO_2 is no longer sequestered; CO_2 emissions of the biorefinery system increase by 65 kt/a
Kaebernick et al. [86]	Life cycle assessment of product development using various tools	Environmental requirements must be considered as equal partners to the traditional requirements of cost and quality. Several tools and methodologies are available, and some others are still being developed

Table 2: Continued.

Authors	Application	Achieved result
Pecas et al. [87]	Life cycle assessment of plastic injection molds using Eco-indicator 99	The comparison of two alternative molds reveals that the “best mold” is the STM mold in terms of economic and environmental aspects, while conventional mold (CM) mold has a better technical performance
Zufia &Arana [88]	The life cycle of tuna with tomato food products using LCA-TEAM 4.0	Improvements are established for the concept of product, the reduction of the use of material, a material with less impact, transport efficiency, and replacement of raw material
Lombardi [89]	Life cycle assessment and energetic life cycle assessment (ELCA) of a semiclosed gas turbine cycle using SimaPro	The results show that the major energy destruction is due to the SCGT/CC cycle operating phase because of the conversion of chemical energy into thermal energy during the combustion process. The energy of all phases is negligible when compared with these terms
Wang & Sun (2012)	Life cycle assessment of CO_2 emissions from wind power plants	Sensitivity tests show that the measures taken to increase the CP would result in a significant reduction of emissions. The use of wind to produce electricity constitutes an environmental improvement, and more research on this technology is needed
Erol &Thoming (2005)	Ecooptimization of pretreatment processes in metal finishing	From this process, 74% improvement can be attained in terms of environmental indicators depending upon the weighting ratio; it represents the impact factor and cost objective
Andrae et al. [90]	Life cycle assessment of electronic products assessed using a generic compact model	The model has successfully been applied to a digital system telephone (DST) to partly quantify technospheric greenhouse gas emissions from the intermediate unit processes (IUPs) of the DST, in the upstream life cycle. The need for data gathering is great but not as extensive as it would be whereby the data collection can be reduced for silicon-containing electronic components
Busi et al.	Environmental sustainability evaluation of innovative self-cleaning textiles	This paper shows the whole “gate-to-gate” analysis; the innovative material shows decreased impacts
Cottle and Cowie	Allocation of greenhouse gas production between wool and meat in the life cycle assessment of Australian sheep production	This paper proposes PMA as a simple, easily applied allocation approach for use when attributional life cycle assessment (LCA) is undertaken
Manda et al. [91]	Prospective life cycle assessment of an antibacterial T-shirt and supporting business decisions to create value	This paper supports LCA-supported decision-making of business functions to create sustainable value
Go et al. [92]	Multiple generation life cycles for product sustainability: the way forward	In this paper, design for multiple life cycles is defined as a combination of ecodesign strategies including design for environment and design for remanufacture, which leads to other design strategies such as design for upgrade, design for assembly, design for disassembly, design for modularity, design for maintainability, and design for reliability
Matsuyama et al. [93]	Simulating life cycles of individual products for life cycle design	This paper defined two types of information of products: nominal information and entity information. To support the design of such a product life cycle, this paper proposed a method for modeling the product life cycle by simulating the entity information at its design stage

Table 2: Continued.

Authors	Application	Achieved result
Miranda de Souza and Borsato [94]	Combining Stage-Gate™ model using set-based concurrent engineering and sustainable end-of-life principles in a product development assessment tool	Their paper presents a development example using the proposed tool and compared it with a product designed with normal Stage-Gate
Scheepens et al. [95]	Two life cycle assessment- (LCA-) based methods to analyze and design complex (regional) circular economy systems. Case: making water tourism more sustainable	The conclusion from this paper is that the approach of ecoefficient value creation helps to avoid many pitfalls of the design of circular business models
Wiedemann et al. [96]	Application of life cycle assessment to sheep production systems: investigating coproduction of wool and meat using case studies from major global producers	This paper provides a functional BA method based specifically on protein requirements for application in attribution to LCA studies
Hicks and Theis [97]	A comparative life cycle assessment of commercially available household silver-enabled polyester textiles	The paper discusses the lifetime environmental impact of the three textiles considered varied as a function of the silver content and environmental impact category
Piontek and Muller [98]	Literature review: life cycle assessment in the context of product-service systems and textile industry	Analysis of the literature focused on the following aspects: The impact categories: while some categories appeared quite often (e.g., global warming potential, energy usage, and water depletion), others are less common and therefore difficult to compare to other studies
Roman et al. [99]	Development of LCA benchmarks for Austrian torrent control structures	This paper determines the range of LCA results, where an estimate of environmental impacts in early planning stages becomes possible
Morales-Gonzalez et al. [99]	Life cycle assessment of vitamin D_3 synthesis: from batch to photo-high p, T	This paper explains how continuous manufacturing of vitamin D3 is faster, requires fewer steps, and uses fewer solvents compared with the industrial synthesis using LCA
Joyce [99]	Computer vision for LCA foreground modeling—an initial pipeline and proof of concept software, Icopt–cv	This paper demonstrates that it is possible to generate a fully functional LCA model from a picture of a flowchart This has potentially important implications not only for LCA practitioners as a whole but also in particular for the teaching of LCA
Budzinski et al. [100]	Consequential LCA and LCC using linear programming: an illustrative example of biorefineries	This article shows that linear programming can be used to extend standard LCA in the field of technological choices
Gediga et al. [101]	Life cycle assessment of zircon sand. The international journal of life cycle assessment	In this paper, the LCA has quantified the potential environmental impacts associated with the production of the zircon sand ($ZrSiO_4$). With this study, a sound dataset for downstream users of zircon sand has been provided
Peters et al. [102]	A Swedish comment on review: the availability of life cycle studies in Sweden	Rather than being a review of the available data, the article lists a tiny sample of the many Swedish LCAs available from the included sources and provides some descriptive statistics and comments on this particular sample
Crenna et al. [99]	Global environmental impacts: data sources and methodological choices for calculating normalization factors for LCA	This paper discusses the quantification of the current levels of environmental pressures that entails the critical aspects, as it consists of an accounting of emissions and resources, relying on data often incomplete or based on modeling

Table 2: Continued.

Authors	Application	Achieved result
Heijungs et al. [103]	Everything is relative and nothing is certain. Toward a theory and practice of comparative probabilistic LCA	This paper puts the elements discussed in a structure that provides a research agenda for dealing with comparative uncertainties in LCA
Pelletier et al. [104]	Interpreting life cycle assessment results for integrated sustainability decision support: can an ecological economic perspective help us to connect the dots?	This paper supports a reinterpretation of LCA as a true sustainability decision support tool, in particular by enabling unification of historical development/practice with recent methodological developments
Vrasdonk et al. [105]	Reference situations for biodiversity in life cycle assessments: conceptual bridging between LCA and conservation biology	The paper recommends that reference situations for biodiversity in LCIA models should be developed based on biodiversity targets aligned with society's conservation frameworks
Corona and San Miguel [99]	Life cycle sustainability analysis applied to an innovative configuration of concentrated solar power	The methodological approach described in this investigation provided flexibility in the selection of objectives and analysis tools, which helped to quantify the sustainability effect of the system at a micro- and mesolevel in the three sustainability dimensions
Borridon et al. [106]	Development of LCA calculator to support community infrastructure codesign	A prototype version of an LCA calculator software tool has been developed to enable rapid assessment of the conceptual design of engineering systems
de Laurentlis et al. [64]	EATS: a life cycle-based decision support tool for local authorities and school caterers	This article focuses on the potential offered by the public food sector for a transformative reduction in the environmental impact of urban food consumption
Loppolo et al. [107]	Integrating strategic environmental assessment and material flow accounting: a novel approach for moving towards sustainable urban futures	The proposed SEA-MFA framework has the potential to unify and standardize the processes of categorizing and quantifying data to improve the understanding of urban metabolic principles and scale effects
Allacker et al. [108]	Energy simulation and LCA for macroscale analysis of ecoinnovations in the housing stock	The authors concluded that LCA integrated with dynamic energy simulation may help to unveil the potential improvements and burdens associated with ecoinnovations
Tallentire et al. [99]	The challenge of incorporating animal welfare in a social life cycle assessment model of European chicken production	In this paper, a methodology that incorporates animal welfare indicators into S-LCA was developed that is both scalable and related to welfare assessment frameworks
Prathap and Senthilkumaran [109]	Reduction of environmental impact by incorporating performance-oriented life cycle analysis	This paper discusses how incorporating performance-oriented life cycle analysis can impact environmental reduction
Prathap and Senthilkumaran [110]	Quantitative evaluation for reduction of environmental impact in the product life cycle of a monoblock pump	In this paper, the authors have given insight into how selective materials for a monoblock pump can have an impact on environmental evaluation
Prathap and Senthilkumaran [73]	Production life cycle studies based on design for environmental checklist for product enhancement	In this paper, the authors have studied the various environmental checklists for product enhancement
Prathap and Senthilkumaran [111]	Environmental cautious design of subassemblies in 0.5 hp pump	This paper discusses how various materials selected for subassemblies of pumps have an impact on the environment

during manufacturing. Ecofriendly manufacturing process should be projected towards development of recyclable products. Also, develop strategic models for the analysis of eco-friendly products concerning technological and organizational dynamics.

3. Conclusions

This paper presented a view of the state-of-the-art literature on environmentally conscious manufacturing of products published during 1999-2018; the following general conclusions could be drawn from the literature review.

(i) Environmental issues are gaining acceptable popularity among society, government, and manufacturing industries due to the negative environmental influences

(ii) Researchers proved that the manufacturing of environment friendly products is crucial to minimize the use of virgin resources, which can be achieved by studying the life cycle tool implementation. Reclamation of materials and parts from outdated products is equally crucial in fighting against environmental issues

(iii) The firmer implementation of environmental laws and regulations globally will bring our society to think of our environment as a global issue rather than an individual nation's problem. Although the modern development in environmentally conscious manufacturing of products research is encouraging, researchers' collaboration is highly needed to develop interrelationships and determine the global effects of this sphere

Data Availability

There are no relevant data to be made available.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Research Article

Petroleum Exploration System Based on Main Migration Pathway and Nanohydrocarbon

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Nanohydrocarbon is a new concept for oil accumulation mechanism, and oil can be found in nanosized pore throats. At Qikau Sag, the source and reservoir are found coexisting along the slopes of this basin. It is a complex process for nanopores to converge into the reservoir. Source-control theory and multiple oil-gas accumulative zone theory are the efficient petroleum exploration theories in the areas of low-middle developed exploration degree in the continental basin, but they are not suitable for middle-high developed exploration areas. For this reason, in this research work, the theory of the Petroleum Exploration System based on main migration pathway and nanohydrocarbon is proposed. In complex middle-high developed petroleum exploration area, we focus on the premise of determining the source and use the abundant data of seismic, logging, coring, analysis and testing, production performance, and a large number of research results of predecessors, to detect the geometry of the main migration channels of oil and gas and to make clear migration trajectory of oil and development history of traps, track clues, and dig the optimization exploration areas based on the assessment condition. The risk for petroleum exploration in a new area can be minimized and led to the utmost advantage of exploration by using this option.

1. Introduction

Recently, nanohydrocarbon has become an important area of research. Oil and gas are exhibited in nanosized pore throat, especially for the coexisted source with reservoir. A more detailed hypothesis for framework accumulation of nanometer hydrocarbon was put out. It is considered that the migration of nanohydrocarbon may be similar to the mineralization of solid nano-ore-forming materials, that is, the effect of structural mineralization and accumulation. Hence, we can research it by systematically thinking, such as Metallogenic System Theory, tied with resource, transportation, channel, and storage. The ability to transport nanoparticles has interesting applications [1]. The nanosized pore throat is a new view for the source [2], but the channel is more important. Therefore, Petroleum Exploration System is based on the main migration pathway and nanohydrocarbon.

Vertical pathways and migration paths are the two most common components of shallow plumbing systems [3]. Faults provide the best potential vertical migration routes in many petroleum basins, but the same faults must also provide lateral migration obstacles for reservoirs to form legitimate traps. This duality of fault behaviour was examined [4, 5], and one proposed explanation was that vertical leaking may be temporary and limited to active faulting periods, whereas static 60 lateral sealing would be the norm during inactive fault activity. In terms of migration and accumulation properties, a PS can be classified into several petroleum migration–accumulation systems [6].

Alipour et al. [7] discussed the concept of the Petroleum System. In recent years, a lot of studies pay attention to investigating the Petroleum System [8–13]. But, some questions are in suspense, such as the hydrocarbon accumulation process is challenging [14]. The issue of accumulation and migration of oil and gas in carrier systems is always a difficult subject in petroleum research [15–17]. Petroleum exploration technologies made an important contribution to the development of the Chinese petroleum industry, but they are not aiming at the direct target of petroleum exploration—the oil-gas reservoir. Source-control theory and multiple oil-gas accumulative zone theory are the efficient petroleum exploration theories in the areas of low-middle developed exploration degree in the continental basin. They have played very important roles in the enhancement of exploration efficiency and the addition of oil-gas reserves and output in the development history of the Chinese petroleum industry, but they have a lot of limitations and nonadapt abilities in the areas of middle-high developed exploration degree. In light of the characteristic of oil-gas exploration in the areas of middle-high developed exploration degree in the continental basin, the authors put forward a new theory "Petroleum Exploration System Based on Main Migration Pathway and Nanohydrocarbon." The theory connotation is that the spatial distribution location and the scale of oil and gas reservoir are controlled by the type, location, and transition ability of the main migration path. The theory is relatively systematically discussed in this paper; the plane distribution model scheme of the oil-gas main migration path's origination and the seven types of oil-gas reservoir models' formation are all based on the "main migration path controlling hydrocarbon theory." So long as to ascertain the oil gas main migration path, people can find out the oil-gas reservoirs located near or in the main migration path and select a proper target oil-gas reservoir to drill. In this way, the oil-gas exploration risk will be reduced greatly, the successful ratio of oil-gas exploration boosted maximally, and the oil and gas exploration effect enhanced.

2. Nanohydrocarbon

Nanohydrocarbon is tied with unconventional hydrocarbon; it is focusing on nanosized pore throats. Nanohydrocarbon exists in poor phase separation and percolation; they are controlled by pressure and subjected to pervasively and continuously coexisting. Considering the accumulations, there are coexisting sources and reservoirs in Qikau Sag, Bohai Bay. Nanohydrocarbon accumulated between nanosized pore throats. Pore-throat diameter of oil and gas is even locally developed micrometer-sized pores. Nanohydrocarbon consists of four features, including a few industrial production capacities for a single well, coexisting source and reservoir, nonbuoyancy accumulation, and short-distance migration.

An in-depth understanding of nanohydrocarbon resources, the invisible trap, and the main migration pathway is the key idea through the theoretical research on the gas accumulation mechanism and hydraulic fracturing. The trap is the most favorable enriched position for the gas and results closely from the tectonic stress, regional structural background, and petrological properties. Under the action of the tectonic stress, the strata of the shale and low permeability sandstone have no significant deformation and only structural fractures are produced. The oil and gas reservoir is accumulated in the formed interconnected fractures and pores in the above microsize opening. The shale gas reservoir is generated from the action of the buoyancy on the above pores; on the contrary, the nanopores are not connected and are unable to accumulate into the reservoir and are not needed to fracture. There are no essential differences in the accumulating mechanism between the shale gas reservoir and conventional oil and gas reservoir. The power of the oil and gas enrichment in the reservoir pores is the buoyance generated from the density differential of the liquids.

2.1. Distribution Regulations of Effective Hydrocarbon Source Rock. Effective hydrocarbon source rocks are known as rocks that may not only generate but also expulse hydrocarbon. The rocks with especially enriched organic matter are called high-quality source rocks. Previous studies focused on the content of hydrocarbon generation but ignored the action of hydrocarbon expulsion. Quantitative evaluation of hydrocarbon expulsion action and distribution rules in abundance bed of organic matter is required in modern reservoir forming theory. Thus, the study of the effective and high-quality hydrocarbon source rock is growing vigorously. According to the recent study combined with literature investigation, effective source rock is considered to be formed in an overlay area with the prospering organism and anoxic environment. Geochemical measures of the actual profile, simulation experiments of source rocks with various organic contents, and lithology should be done to recognize it. Effective and high-quality source rocks make a tremendous contribution to hydrocarbon reservoir forming despite a few thicknesses and special distribution.

Normally, it is common that hydrocarbon source rocks depend on basin type in the continent basin, focusing on the sediment center, hydrodynamic conditions, sedimentary facies, provenance, thermal evolution, and charging process. Based on mass well-logging data, the effectiveness of source rock of Qikou Sag has been studied on the whole wells, which overcomes the difficulty to hold the distribution of source rock restricted from unsystematically geochemical data and discontinuous single-well data. We analyzed a ratio, of source volume of high-quality to effective, as the evaluation criteria for distribution quality. With the ratio criteria, we can evaluate source effectiveness and quality in the different oil-bearing beds of Qikou Sag and can more objectively reveal that the distribution of source rock in the study area is dominated by a sedimentary environment. With this study, it is found that the main developed area for high-quality sources developed in deep-lacustrine and semi-deep-lacustrine facies near the basin center and predicted the main exploration area for conventional and unconventional petroleum in the study area.

2.2. Migration of Nanohydrocarbon. Nanooil and gas are mainly distributed in source rocks and near the source, tight reservoir systems in close contact with a large area, including shale oil, shale gas, coalbed methane, tight sandstone oil, tight sandstone gas, and tight limestone oil. The pore throat diameter of the reservoir is generally nano. The seepage capacity of oil, gas, and water in the nanopore throat is poor, and the phase differentiation is difficult. It is mainly driven by overpressure. Oil and gas are retained and adsorbed and continuously distributed in a large area in the source reservoir symbiotic tight formation.

Hydrocarbon migration is a series of processes that drive oil and gas from an effective source rock to the surface of the Earth. With the progress of diagenesis, organic matter generates hydrocarbons, inorganic minerals transform and dehydrate, and rock structure changes accordingly. The results of this series of changes will lead to the discharge of hydrocarbons. Therefore, the hydrocarbon expulsion power is mainly the inner fluid pressure of source rocks formed by the combined action of compaction, geothermal stress, and fluid generation, but the size of various actions is different in different evolution stages. Generally, in the early stage of diagenesis, the porosity of source rock is high, and a large amount of hydrocarbon fluid can be discharged. In the late stage of diagenesis, the change of porosity is not much. When to start hydrocarbon expulsion and the main hydrocarbon expulsion period can be studied by basin simulation. The contour map of hydrocarbon expulsion intensity of effective source rocks is an important map to reveal the quantity of oil and gas transported by the main migration channel and the location and scale of oil and gas reservoirs. In millimeter-scale-sized pores, the fluids flow unrestrictedly, in micrometer-scale-sized pores, fluid flows are restricted by capillary resistance; in nanoscale pores, let alone pore throat diameter less than 1 μm, fluid flows lead to “retention” [18].

3. Accumulation

The migration path of hydrocarbons in the petroliferous basin is confirmed by the 3-D spatial distribution of the discontinuous sealing surface. Under the sealing surface, oil and gas choose the path with the most favorable structure and the least migration resistance—the main migration channel. Among them, the structural form, long-term or multistage active faults or fractures, high permeability and porosity reservoirs, and unconformities act as key actions facing the main migration channel [19].

3.1. Main Migration Pathway. In petroliferous basins, faults, sand bodies of the framework, and unconformities are the key elements. Generally, oil and gas migrate laterally along the framework sand body, laterally along the unconformity surface, and vertically along the fracture and fault system. The main migration channels of hydrocarbons mainly appear in the form of composite, especially the two or even all combinations of faults, skeleton sand bodies, and unconformities. From source rocks to traps, the main migration channels gradually diverge to converge, from fine to coarse and from more to less, in the shape of “inverted branches.”

3.2. Faults and Fractures. The faults often cut through source rocks and reservoir rocks in different horizons. They are the main vertical migration channel. Generally, active faults act as channels for oil and gas. If the fault is not active, it will block oil and gas. The channel action and sealing action of faults are relatively complex [20–25]. Faults and fractures have the characteristics of penetrating layers, vertical migration, and periodic migration for long distance. When Sibson [26] put forward “seismic pump” theory of hydrothermal migration along the fault, he believed that the migration of hydrothermal fluid along the fault was caused by the earthquake. The fault pumped the hydrothermal fluid from the deep part and lifted it into the shallow part above like a pump. Hooper [27] introduced this principle into oil and gas migration and pointed out that when the fault layer is inactive, the fault section is closed. When the fault is active, oil and gas migrate along the fault in a short and rapid form. In addition, according to Losh et al. [28], the analysis of the structure of a scientific exploration well core and the vertical and horizontal flow of fluid relative to the growth fault in the 330 block of Eugene Island in the south of Louisiana coast shows that the growth fault plays a very important role. In the analysis of the relationship between the fault activity period and oil-bearing property, it shows that the fault activity period is the same as the generation and migration period of oil and gas. The fault is conducive to the migration of hydrocarbons along the fault and fracture, and a lot of fluid accumulated along the fault trend is complex, indicating that the section shape plays an important role in controlling hydrocarbon migration. Therefore, fractures and faults are an important part of the main migration channel of hydrocarbons, especially those that cut through effective source rocks. Studying oil migration from the clastic sediments, Cordell [29] pointed out that the frequent sand and mud interstratification and pressure were the reasons for the long-distance vertical migration of the impending oil and gas from the clastic rocks.

3.3. Skeleton Sand Body. Magara [30] believed that the discharge capacity of hydrocarbons in source rocks usually increases with the increase of contact area with sandstone, and the content of sandstone in the formation is 20%~60%, with a median of 30%~40%; Xin et al. [31] believed that the migration channels of hydrocarbons are selective, and the migration channels are very limited, accounting for only 1/10 of the reservoir; Rhea et al. [32] believed that oil and gas enter the framework sand body from the source rock, and its migration direction is controlled; It can be seen that the channel, delta, and other framework sand bodies with good porosity and permeability are the main migration channels of lateral short-distance oil and gas[33]. Generally, the framework sand body with lateral migration and the fault (oil source) with vertical migration constitute the main ladder oil and gas migration channel of the fault framework sand body.

3.4. Unconformity. Unconformity, as the oil and gas migration pathway, has the following characteristics: (1) long-term weathering and erosion increase porosity; (2) plane of unconformity is usually the oil and gas migration pathway for long distances; and (3) unconformity is the “bridge” between the source rocks and reservoir rocks. The unconformity is the main lateral migration pathway on the slope and plays a considerable role in onlap hydrocarbon reservoirs. Because of long-term weathering and erosion, it often forms a permeable formation, along which oil and gas can migrate horizontally for a long distance and accumulate. Unconformity and incise waterway filling complex are both the main hydrocarbon migration pathways. The unconformity is beneficial to the oil and gas accumulation and migration, and it is the main lateral migration pathway for a long distance. It connects the faults and sand bodies of the framework, a long-distance network of main oil and gas migration pathways, which benefits forming erosion oil fields and interior reservoirs.

In addition to the scouring unconformity, there are also incised channel filling complexes on the sequence boundary, which can be used as the main migration channel of oil and gas. It is the main channel of lateral and long-distance migration of oil and gas [33]. It connects faults and skeleton sand bodies of different ages, forms a regional and long-distance main migration channel network of oil and gas, and is conducive to the formation of large corrosive oil and gas fields and insider oil and gas reservoirs [34, 35].

3.5. Space of Vertical and Horizontal Migration. The structure contour map of fault morphology is one of the main results of the accurate hydrocarbon exploration methods (Figure 1), which reflected the convex is the main migration pathway location. Section shape description is useful. The seismic technology is used to find out the shape, occurrence, and combination relationship of faults.

Thus, it provides a powerful tool for implementing the main migration channel of oil and gas. The contour map of section shape and structure is one of the main achievement maps of important maps of accurate oil and gas exploration methods. It can express various properties of deposition, stratigraphy, structure, and oil reservoir, to understand the enrichment characteristics of oil and gas, and determine favorable exploration direction, well placement position, and oil and gas field development plan. When oil and gas migrate from the sag to the shallow layer, the migration path has the characteristics of divergence to convergence, and the dominant migration direction of different section shapes and stratigraphic occurrence strokes is different. The shape of the section forms the dominant convergence point of vertical migration of oil and gas, and the relationship between the shape of the section and the occurrence of the formation controls the lateral dominant migration path of oil and gas. According to the analysis of the configuration relationship between the fault plane and the strata, the convex surface of the downside of the fault forms the dominant migration direction of oil and gas and converges to the low-potential area.

The description of sand bodies of the framework. In areas with more drillings, the description can directly be taken through log data, while in areas with fewer drillings, there is a need to use the logging data, the GLOG inversion, and logging constrained inversion of seismic wave impedance inversion, as well as neural network technologies to predicate the porosity. The top surface structural map and the contour map of physical properties are the important result maps with accurate oil and gas exploration methods, in which the areas with high porosity and permeability are the important positions of the main migration pathway. In Figure 1, the framework sand bodies with the high porosity and permeability and the faults run nearly east-west and are north trending, forming the ladder-shaped main migration pathway.

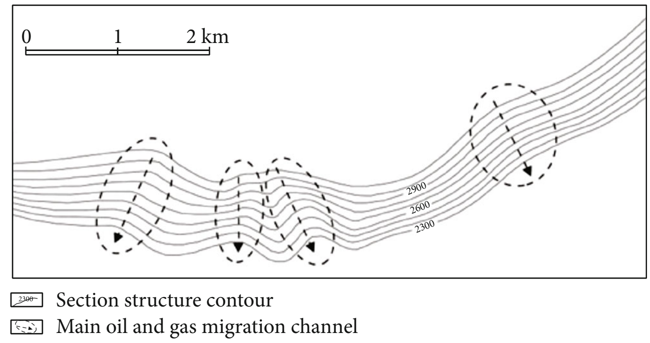

Figure 1: Sketch map of main migration paths in the fault cross-section structure contour.

The description of unconformity. In addition to the regional unconformity, the unconformity during the formation and evolution of continental basins is usually found in the nonsedimentary province around the source sag and has good porosity and permeability within a certain thickness. The structure ridges on the top of unconformity are important migration paths. The description of the unconformity is mainly the structure description which can be studied according to 3-D seismic data and logging data. The top surface structural contour map of unconformity is the important result map of the geometrical description of the main migration pathway, in which the distribution area of the structure ridges is the main migration pathway.

Based on the geometrical description of the fault, unconformity, and sand bodies of the framework, the distribution map of the main migration pathway for oil which consists of the morphology of fault, the structural contour map of unconformity, and the physical properties contour map of sand bodies of the framework is an important result while in accurate oil and gas exploration. According to the maps combined with hydrocarbon expulsion intensity contour map, oil-source correlation, and other information, several possible and most likely main oil and gas migration pathways can be identified.

3.6. Transmission Capacity of Main Hydrocarbon Migration Pathway. Studies show that when it has vertical expulsion direction, fixed length, and volume, the buoyancy of the oil neck is several orders of magnitude than that when the expulsion direction is low-angled and horizontal. At the same time, the volume of the rock through which oil and gas migrate horizontally is several orders of magnitude than that when the expulsion direction is vertical; that is, the loss when oil and gas migrate horizontally through the reservoir is much greater than that when the migration is vertical through faults and cracks. Through theoretical calculations, Liu et al. [36] suggested that the transporting capacity of the large fault zone is much larger than that of reservoirs. Zeng and Wang [37] suggested that the sands with high permeability are the main migration path. Thus, in general, the horizontal migration with a low angle is less efficient than vertical migration and the long-term active systems of the faults and fracture are the highly efficient vertical migration paths of oil and gas. And due to the high efficiency in oil and gas migration through faults and cracks, we should pay close attention to the study of the main migration pathway related to faults or cracks.

As a migration channel of oil and gas, it has the following characteristics: (1) long-term weathering and erosion enhance porosity; (2) unconformity is often the channel of long-distance hydrocarbon migration; and (3) unconformity is the "bridge" between source rock and reservoir rock. The unconformity is an important channel for lateral migration of oil and gas under the slope background and plays an important role in hydrocarbon reservoirs in the overbreak zone of the basin. Due to long time weathering and denudation, permeable layers with certain porosity and permeability are often formed, and hydrocarbons can migrate and form reservoirs laterally and remotely along the unconformity surface (Figure 2).

Figure 2 detailed descriptions are illustrated in (a–g). (a) Reservoir controlled by paths which consists of faults, framework sand bodies, and planes of unconformity; (b) reservoir controlled by paths which consists of faults and planes of unconformity; (c) reservoir controlled by paths which consists of faults and framework sand bodies; (d) reservoir controlled by paths which consists of framework sand bodies and planes of unconformity; (e) reservoir controlled by fault-type paths; (f) reservoir controlled by paths with type of framework sand bodies; (g) reservoir controlled by paths with type of unconformity.

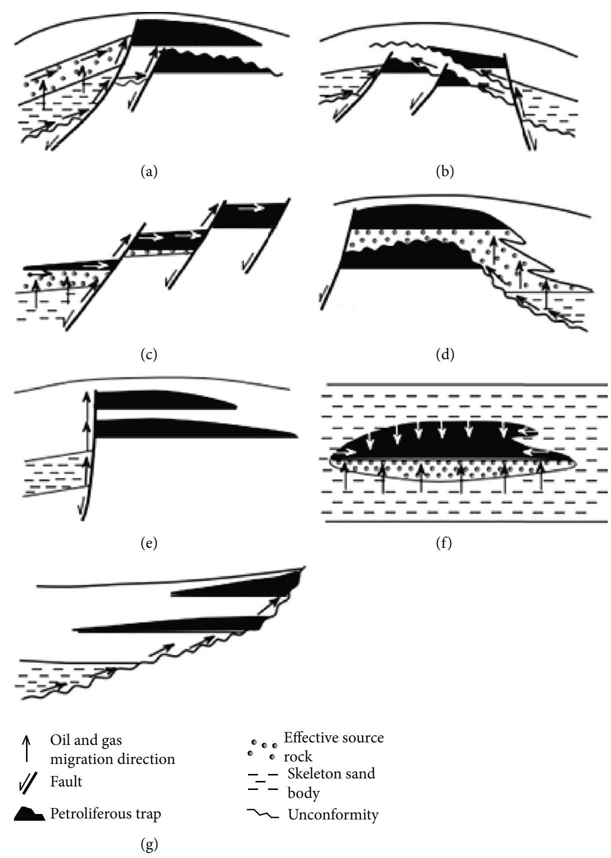

Figure 2: The resource-migration-reservoir sketch map.

4. Storage for Oil and Gas

We make use of the existing data of drilling, well logging, and seismic record. The hydrocarbon generation of effective source rocks is a continuous process with peak hydrocarbon generation, but the discharge of hydrocarbons is not continuous. Episodic hydrocarbon expulsion is usually related to periodic tectonic activities. Among the basic elements of the main migration channel, only faults have the characteristics of episodic activity. Therefore, the period of fault activity is the main period of episodic hydrocarbon expulsion and oil and gas migration of source rocks, and faults or fractures are the main migration channel of large-scale and efficient hydrocarbon migration. The hydrocarbon migration of skeleton sand body and unconformity surface in contact with effective source rock usually changes with the change of hydrocarbon generation process of source rock.

Above all, effective source rocks as well path and geometric description of main migration channels and the formation and evolution of traps are basic elements; we can further determine the target with the most oil and gas exploration potential in or near the main migration channels—oil and gas reservoirs, and carry out drilling [38, 39]. According to the "source transport reservoir" model map in the accurate oil and gas exploration method, in the practice of oil and gas exploration, the "source transport reservoir" under different geological backgrounds will be studied, which will minimize the risk of oil and gas exploration in the medium and high exploration degree area of the continental basin and improve the benefit of oil and gas exploration to the greatest extent. The comprehensive map including effective source rock top structure contour map, section shape, unconformity surface and skeleton sand body structure contour map, skeleton sand body physical property contour map, and trap top structure contour map is a valuable map of accurate oil and gas exploration.

We got a successful test by the use of this theory, at the Qikou Sag, the Es2 member in the Gangdong fault's downthrow side could also be a good place for Es2 source rock to accumulate. At this sag, the faults and unconformities together form the main migration channel of oil and gas, so that the oil and gas generated by the lacustrine source rocks in each sag up to 60 km away can migrate over a long distance and accumulate in the large-scale reef trap, forming 100 million-ton large oil field.

5. Conclusions

For previous exploration theories in China's oil and gas exploration enterprises, such as "fixed concave selection" and "progressive exploration and development," the problem of oil and gas exploration in continental basins with petroleum characteristics cannot be solved, such as "one source multilayer," "one layer multisource," and "multisource, multilayer, and multireservoir," and cannot effectively guide the oil and gas exploration in continental basins.

We propose the main migration pathway to study oil-gas migration. It is focusing on the premise of determining the source, detecting the geometric spatial distribution of the main migration channels of oil, making a clear migration trajectory of oil and development history of traps, tracking clues, and digging for the best of all targets for the oil-gas reservoir. This method is based on the fact that the source of oil and gas has been "determined" in early and midterm exploration and uses the abundant data of seismic, logging, coring, analysis and test, production performance, and a large number of previous research results in the middle and high exploration degree areas to make a detailed description and distribution study of faults, sand bodies of framework, and unconformity surface, to clarify the type and main migration pathway. Combined with trap forming time and spatial distribution, the favorable oil and gas exploration target is accurately located and drilled. The role of the oil exploration method is obvious. It will minimize the risk of exploration in higher exploration degree areas of the continent basin and benefit oil exploration. At the same time, we need to pay attention to some more performance metrics to strengthen the research work, such as a comprehensive resource evaluation of various oil accumulating units in the depression.

Similar to Metallogenic System Theory, tied with source, transportation, channel, and storage, Petroleum Exploration System has the same elements, source, main migration pathway, and storage. The new concept focuses on nanohydrocarbon for source. Nanohydrocarbon in coexisting sources and reservoirs becomes easier to understand. Nanosized pore throats have been paid attention to. Once nanopores are not connected, there is inability to accumulate into oil, so nanohydrocarbon needs a channel or pathway.

Data Availability

Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Research Article

Removal of Toxic Metal Presence in the Wastewater and Production of the Biomass from Microalgae *Chlorella* sp.

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Removal of high toxic metals from the wastewater was one of the mandate options to avoid the environmental pollution caused by the wastewater plant. Microalgae cultivation on the wastewater was one of the hopeful methods to convert the waste into useful by-product. In this study, the *Chlorella* sp. was used to remove the presence of the total nitrogen (TN) and total phosphorous (TP) in the wastewater. Added to the above, the biomass and lipids of the *Chlorella* sp. were examined with respect to the incubation time. *Chlorella* sp. was cultivated using BG11 medium. Here, two different types of wastewater had been used, one from leather industry and other priggery waste. The respective ratio of leather and piggery wastewater used in the current study was 0 : 100, 25 : 75, 50 : 50, 75 : 25, and 100 : 0. The total percentage of the nitrogen and phosphorous removal by the microalgae within 14 days was determined. Based on the findings, it is clear that *Chlorella* sp. L33 was highly efficient to absorb the nitrate and phosphorous content in the wastewater. With regard to the biomass production, the priggery wastewater treated reported the maximum biomass for 100 μmol/L with 0.55 g/L. However, the 100 μmol/L has higher pH content than other test samples. By varying the ratio of the wastewater, the removals rates can be improved.

1. Introduction

The environmental pollution is one of the talking points for decades. Hazardous metals in the wastewater damage the earth ecosystem massively [1, 2]. Over the years, many notable works had been carried out to reduce the toxic metals' presence in the wastewater (WW) [3, 4]. Microalgae are one of the promising methods to remove these toxic metals from the wastewater. Typically, microalgae absorb the toxic metals in the wastewater as nutrient for its growth. Microalgae are also used as the substitute candidate for the fossil fuel and other vital applications [5, 6]. Biodiesel from the microalgae is believed to be the next-generation fuel, since they are easy to grow at faster rate in cost-effective methods. However, the algae oil produced very minimum due to the less lipid content [7, 8]. Microalgae can also be cultivated in both indoor and outdoor areas. For instance, microalgae grow in both photo autotrophically and heterotrophically in wastewater [9–11]. The presence of heavy metals in the water poses a great threat to the human health due to its toxicity. Extreme concentrations of the heavy metals in wastewater result in lung insufficiency, bone damage, cancer, and other worse effects. Hence, application of the suitable method to remove these toxic metals is highly indispensable [12–14]. Algae are one of the biosorbents of the toxic metals owing to its ubiquitous nature. Microalgae growth on the wastewater neutralizes the carbon and environmental sustainability [15, 16]. Many notable works related to the microalgae were published recently. Leong et al. reviewed the removal of the heavy metals from the microalgae. The review has been performed with removal rates of the arsenic, cadmium, chromium, lead, and mercury. In addition to the removal rates, the potential of the value-added products was also examined [17]. Ahmed et al. reviewed the challenges in removing the toxic contents using microalgae strains. From the review, it is understood that growing the microalgae in the wastewater removes the toxic presence, it is due to the reason that microalgae absorbs nutrients present in the wastewater.

Introduction of these systems in real-time scenario was challenging due to the costing factors and filtration techniques [18]. In addition to the above, complexity in operations also occurred owing to HRT, pH, light, and temperature limitations. Singh et al. reported the sustainable approaches for remediation of the toxic metals in the contaminated water. Based on the study, they identified the removal rates of the metals which were nitrogen (90–98.4%), phosphorous (66%–98%), Pb (75%–100%), zinc (15.6–99.7%), chromium (52.54%–96%), mercury (77%–97%), copper (45%–98%), and cadmium (2–93.06%). In addition to the toxic metals, the microalgae remove the presence of complex pesticides also in the wastewater. On the other hand, the value-added products produced from the microalgae are biofuel, lipids, and proteins. Based on the above literature, it is evident that the use of microalgae for the removal of toxic metals in wastewater is possible and it is sustainable [19, 20]. Hence, this study is mainly engrossed to observe the removal rates of both phosphorous and nitrogen from the wastewater. In addition to the heavy metals, the biomass production for biofuel productions is also examined.

2. Materials and Methods

2.1. Cultivation Method. The microalgae used in the study are *Chlorella* sp. which is the freshwater algae which can effectively grow in BG11 medium [21]. BG11 has a major composition of $NaNO_3$ 1.5 g/L and K_2HPO_4 0.04 g/L. Here, two types of the wastewater had been tested, leather wastewater and piggery wastewater at various concentrations as follows: L0:P100 (0% leather industry and 100% piggery), L25:P75 (25% leather industry and 75% piggery), L50:P50 (50% leather industry and 50% piggery), L75:P25 (75% leather industry and 25% piggery), and L100:P0 (100% leather industry and 0% piggery). The 500 mL of the wastewater was collected and treated with 100 mL of the BG11 at 25°C and allowed to shake continuously in the presence of the 6000 Lux white fluorescent light illumination for 28 days. The flasks were shaken manually two times in a day to eliminate the uncertainty. The measured uncertainty is within the acceptable limit.

2.2. Parameter's Measurement. The collected biomass was filtered through 0.45 μm Millipore filter and dried under the constant temperature of 25°C for 24 hours. Biomass was pre-weighted before the drying process. Lipid content in the microalgae has been determined using colorimetric method [22]. The pH level was determined by PHS-25. The total phosphorous was determined by ammonium molybdate spectrophotometry. The heavy metals are determined according to Changlei Xia et al. [8].

Basic formulas used to derive are the following [8, 9],

$$\text{Dry biomass weight (g/L)} = 0.1836 * OD_{600}, \tag{1}$$

$$\text{Biomass productivity}(g/L/d) = \text{Biomass concentration}\left(gL^{-1}\right)/\text{Time}(\text{days}), \tag{2}$$

$$\text{Lipid productivity}(g/L) = \text{mass of lipid}(g)/\text{Volume (L)}, \tag{3}$$

$$\text{Lipid content}(\%) = \text{Mass of lipid}(g)/\text{Mass of culture}(g) * 100. \tag{4}$$

3. Results and Discussion

The series of the test was conducted using different combinations of the leather industry and piggery. Both leather and piggery wastewater controlled at the portions of 0%, 25%, 50%, and 100% with respect to each other. Herewith, the test combinations are L0:P100 (0% leather industry and 100% piggery), L25:P75 (25% leather industry and 75% piggery), L50:P50 (50% leather industry and 50% piggery), L75:P25 (75% leather industry and 25% piggery), and L100:P0 (100% leather industry and 0% piggery).

3.1. Removal of Total Nitrogen. The contents of the total nitrogen removal in the different cultures are depicted in Figure 1. Based on the procured results it is identified, the total nitrogen removal rates vary based on the incubation time and the wastewater combination. The maximum concentration of nitrogen in the leather and piggery wastewater was 1160 mg/L and 810 mg/L, respectively. These rates were dropped massively when the incubation period increased. Initially at day 3, the nitrogen rates of the samples L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0 were 1150 mg/L, 1055 mg/L, 965 mg/L, 872 mg/L, and 790 mg/L, respectively. Due to the increase of the incubation period, the removal rate after 3 days witnessed the reduction of 0.8%, 1.5%, 1.5%, 2%, and 2.5% of the total nitrogen content in the wastewater compared to the initial day. As the incubation time increases, it is typical to witness all the samples reported reduction of the nitrogen content. At the 15th day, the total nitrogen present in the wastewater was 1005 mg/L, 905 mg/L, 801 mg/L, 701 mg/L, and 610 mg/L. The lowest levels of the nitrogen were reported for the neat leather wastewater. Furthermore, the total nitrogen removal in the span of 15 days incubation time 14%, 16%, 18%, 20%, and 23% nitrogen has been removed from the wastewater. Incubation time needs to be optimized for the better cultivation and superior removal rates. When the incubation time increases, more nutrient uptake leads to reduced metal contents in the wastewater. In the perspective of the better removal rate, leather industry wastewater grown microalgae absorb more nitrogen content compared to the piggery wastewater. With regard to the combination, the second-best removal efficiency was witnessed for L25:P25 combination [23, 24]. Although the removal rates were different, addition of the leather wastewater and piggery wastewater exhibits better total removal efficiency than neat 100% piggery wastewater.

3.2. Removal of Phosphorous. In general, the presence of P in the wastewater will be in different forms like phosphate, poly-phosphate, meta-phosphate, and some other organic complex. These phosphates are very influential to the acid and alkaline environment. Some notable work predicted that

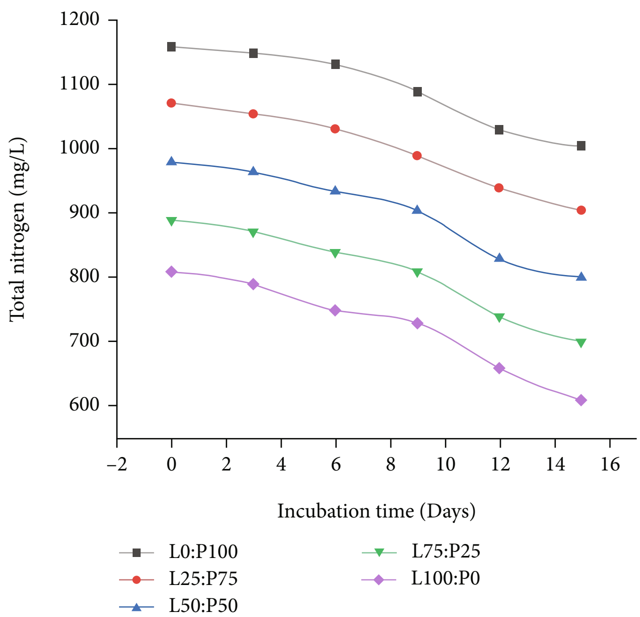

Figure 1: Removal of total nitrogen from the wastewater.

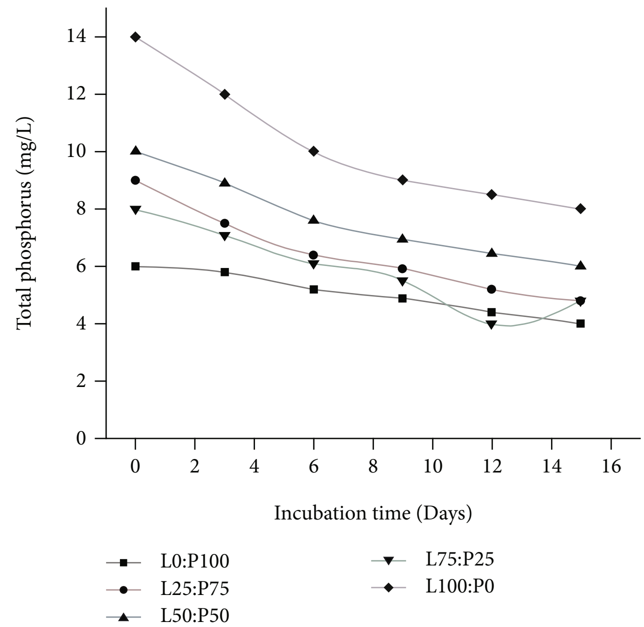

Figure 2: Removal of total phosphorous from the wastewater.

P will vary based on the pH levels of the wastewater. Basically, the microalgae absorb the phosphorous content in the wastewater and utilize them as one of the nutrients. Here, the study has been conducted on two different wastewaters [21, 23]. Compared to the piggery wastewater, the leather industry wastewater has more phosphorous content in them. Both the samples are combined with the configuration of L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0. The maximum phosphorous reported for piggery and leather wastewater was 6 mg/L and 14 mg/L. Compared to the several combinations, L75:P25 recorded lowest levels of phosphorous at the end of day 15 according to Figure 2. As the incubation time increases, the concentration of the phosphorous has been dropped significantly for leather compared to piggery wastewater. Based on the findings, it is more evident that mixing both the wastewater can improvise the removal rates. At day 3, 3.5%, 18%, 11.5%, 11.9%, and 15.3% reduction in the phosphorous has been noticed for the samples L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0. The total removal rate on day 9 was 1.1 mg/L, 3 mg/L, 3 mg/L, 2.5 mg/L, and 5 mg/L; from these stats, it is very evident there is massive reduction in the phosphorous presence in the wastewater. On the incubation period of day 15, the total difference in the phosphorous was 40%, 60%, 50%, 51%, and 54% for the respective samples L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0. The major reduction in the phosphorous has been witnessed for L25:P75 test sample and the second best was reported by L75:P25.

3.3. Effects of Wastewater Concentration on Microalgae Growth. Figure 3 presents the dry biomass productive of the microalgae at different incubation time in different wastewater combinations. The maximum dry biomass produced was 1.75 g/L. As the incubation time increases, the dry biomass increased massively. At day 3, 0.45 g/L, 0.6 g/L, 0.5 g/L, 0.4 g/L, and 0.33 g/L dry biomass were produced for the wastewater samples L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0. Compared to day 3, day 9 reported massive growth in the microalgae 21%, 15.3%, 18.1%, 22%, and 30.7% [8, 9]. From the findings, it is clear that industry leather wastewater produced higher dry biomass compared to the piggery wastewater. With regard to the combination, L75:P25 reported higher cultural growth. For instance, at day 12, the dry biomass procured from the culture was 1.2 g/L, 1.34 g/L, 1.1 g/L, 0.9 g/L, and 0.75 g/L, respectively. Incubation time of day 15 has witnessed the higher biomass productivity; the respective values are 1.5 g/L, 1.75 g/L, 1.3 g/

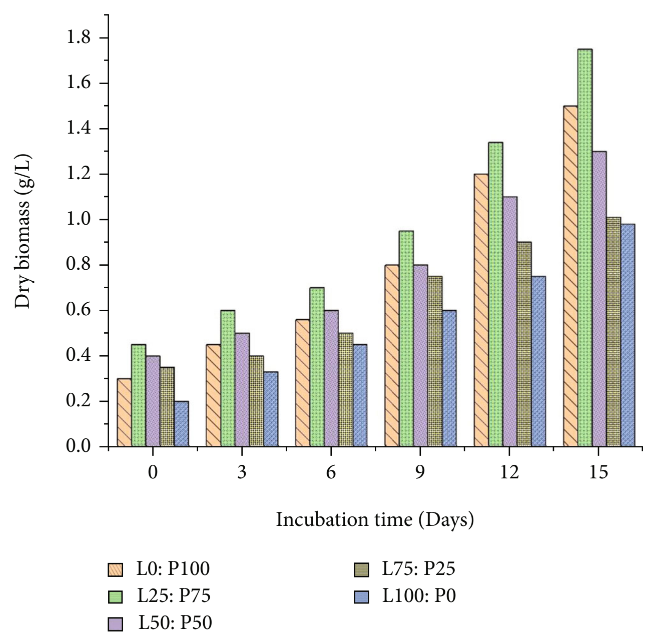

Figure 3: Dry biomass production from the microalgae.

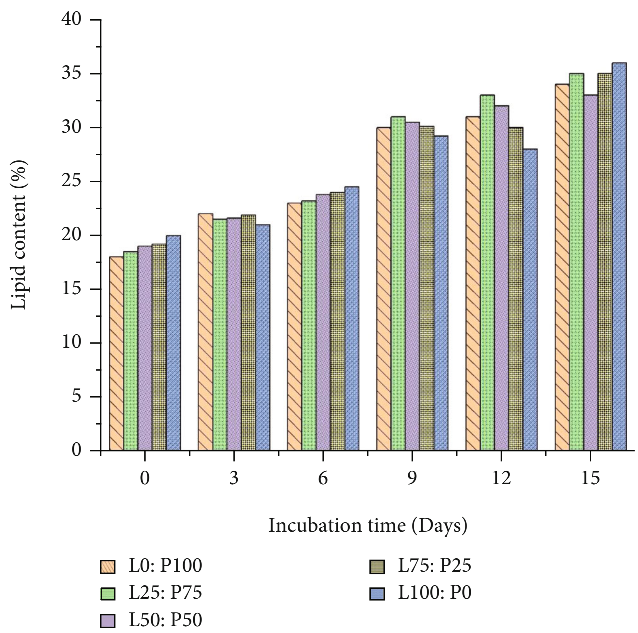

Figure 4: Lipid content presence in the cultivated microalgae.

L, 1.01 g/L, and 0.98 g/L. There is a rapid increase in the production of the dry biomass for the L25:P25 that has been observed irrespective of the incubation period. Unlike above, the specimen L50:P50 also showed some positive effects on the dry biomass accumulation. Compared to the leather wastewater, piggery wastewater microalgae growth is 42% higher due to the presence of high nitrogen and less phosphorous.

3.4. Lipid Content in the Cultivated Microalgae. Microalgae lipids are the value-added resource for the production of biodiesel, chemicals, and cosmetics. Figure 4 shows the lipid yield of the microalgae at different cultivated conditions. Based on the procured results, it is identified that the lipid content in the leather wastewater is higher. As the incubation time elevated, the lipid content was increased irrespective of the WW sample. Initially, on day 3, the sample L0:P100 reported 22% of the lipid content which is 1% higher than the piggery cultivated microalgae. Although the increase is minimal, as the incubation time increases, the difference between the lipid from leather WW and piggery WW intensely increased [25, 26]. The samples such as L0:P100, L25:P75, L50:P50, L75:P25, and L100:P0 reported the lipid content of 22%, 21.5%, 21.6%, 21.9%, and 21% on day 3. Samples of day 3 between every sample are marginally different. However, as the incubation time increases, there was a very notable change that had been observed. At the final moment of day 15, the respective lipid content of the samples is 1.5%, 1.75%, 1.3%, 1.01%, and 0.98%, respectively. Lipid content was dramatically improved when they are cultivated in the leather wastewater than piggery [9, 22]. The main reason for the better lipid productivity for the leather WW was absorbed nutrients. With regard to the type of the specimen, at day 9, L25:P25 reported the marginal increase in the total lipid content than the other samples. After the 9th day, there is no massive improvement in the lipid content that has been noted.

4. Conclusion

The cultivation of microalgae with leather industry and piggery wastewater under various dilution ratios was conducted to remove the heavy metals in the wastewater and derive the value-added products. A set of experimental calibrations were done for the samples and to determine the removal rates of total nitrogen and total phosphorous. In addition to the removal rates of heavy metals, the microalgae growth on the biomass production and the lipid content was also measured. Based on the findings, it is clear that the total nitrogen content was higher for piggery WW compared to the leather WW. The respective concentrations were 1160 mg/L and 810 mg/L. As the incubation time increases, the total nitrogen absorbed by the *Chlorella* sp. augmented. On the other hand, the removal rates of the leather industry WW was 14% higher compared than piggery WW, since the microalgae cultivated by leather WW uptake higher amount of the nitrogen as the nutrient than the leather WW based microalgae. With regard to the phosphorous, the identical behavior has been witnessed. Similar to the total nitrogen, the phosphorus removals rates were larger for the leather WW than piggery WW. The cumulative difference between both the WW was 15%, hence mixing both WW to reduce the total nitrogen and phosphorous content in the wastewater in reasonable pace. Among the different concentration, L75:P25 sample reported 25% of the total nitrogen removal rates and 50% reduction in the total phosphorous. On the other hand, the dry biomass and lipid content were also higher for the leather WW than piggery WW. The maximum dry biomass was obtained for L25:P75 and lipid content for the sample L75:P25. Based on the various results, L75:P25 is more sustainable and it can be a viable solution for WW treatment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

No conflict of interest and no funding received. All the data were presented inside the manuscript and readers can have them according to request. No animals and humans are involved in the study.

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