

Research Article

Chitosan and Ferrite Nanoparticles Modified Zeolite (ZSM-5) as Adsorbent for the Removal of Acid Red Dye from Water

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The present study involved the synthesis and characterization of nanocomposites (NCs) consisting of $MgFe_2O_4$ -chitosan-ZSM-5 zeolite (MgF-Cs-Ze), NiFe_2O_4-chitosan-ZSM-5 zeolite (NiF-Cs-Ze), and MgFe_2O_4@ NiFe_2O_4-chitosan-ZSM-5 zeolite (MgF@NiF-Cs-Ze). These NCs were investigated for their potential application as effective adsorbents in various environmental contexts. In order to investigate the composition and physical properties of the NCs, XRD, FT-IR, SEM-EDX, and TEM techniques were utilized. The present study is aimed at evaluating acid red (AR) dye adsorption behavior from aqueous solutions onto MgF-CS-Ze and NiF-CS-Ze NCs under different experimental circumstances. The study revealed that the NCs MgF-CS-Ze and NiF-CS-Ze exhibited maximum capacity for adsorption of 55.55 mg g⁻¹ and 41.66 mg g⁻¹, respectively, in that regard when tested with AR dye. These findings underscore the significant adsorption capabilities of these NCs. Examining the adsorption kinetics revealed that AR dye adsorption process followed the pseudo-second-order kinetic model. Resulting from thermodynamic studies, it was discovered that the adsorption of AR dye onto MgF-CS-Ze and NiF-CS-Ze NC process was an exothermic and spontaneous.

1. Introduction

The issue of water contamination that caused the issue of organic and mineral pollution has emerged as a significant social problem in contemporary times. Of significant importance are dyes, which constitute a frequent category of contaminants that may be recognized by the unaided human eye. The utilization of these dyes spans across many industrial sectors, including textile dyeing, paper manufacturing, leather treatment, and pigment development [1-3]. The introduction of these highly pigmented chemical compounds into aquatic habitats presents a significant peril to the entirety of the aquatic biota. The observed adverse effects are frequently associated with a decrease in the concentrations of dissolved oxygen in these ecosystems, hence compounding the issue as a result of their restricted biodegradability [4-6]. Therefore, it is crucial to employ effective treatment techniques for effluents that contain dyes, before releasing them into natural ecosystems. Several primary treatment approaches have been investigated in the field, involving chemical precipitate [7], membrane filtration [8], photocatalysis [9], coagulation-flocculation [10], and adsorption and ion exchange [11–13]. Nevertheless, one notable limitation of the majority of these methodologies is their correlation with considerable operational and maintenance costs, inadequate elimination of contaminants, elevated energy demands, and the production of troublesome pollutant-laden sludge, which presents difficulties in terms of appropriate disposal [14, 15]. On the other hand, the attainment of cost-effective and efficient elimination of contaminants from wastewater is greatly sought for. Adsorption is a treatment option that is well acknowledged in academic literature as a cost-effective and environmentally sustainable strategy [16, 17].

Nanoferrites have garnered significant attention owing to their extensive array of uses. Ferrofluids have been utilized in a diverse range of fields, including focused medication administration, high-density magnetic storage devices, and tumour treatment. The use of nanoparticles as contrast agents in magnetic resonance imaging, their role in

enhancing the magnetic separation of biological molecules such as proteins and enzymes, their potential contribution to tissue healing, and their ability to enable cell separation have been discussed in previous studies [18, 19]. In contemporary times, there has been an expansion in the use of these materials in water treatment applications, specifically in the areas of catalysis and the elimination of pollutants through adsorption [20-23]. Additionally, these materials have been employed in degradation and photodegradation processes for water treatment [24, 25]. Early research efforts were primarily centered around the synthesis and characterization of materials, with a subsequent shift in focus towards the removal of harmful and cancer-causing contaminants from water sources. Chitosan (Cs) exhibits significant attributes such as biocompatibility, biodegradability, nontoxicity, abundance, bioactivity, and high adsorption capacity. These qualities render it a highly promising contender for utilization in water purification and extraction procedures [26, 27]. The Cs molecule has a significant number of amino and hydroxyl groups and significantly augments its adsorption ability for pollutants. The occurrence of this phenomenon may be ascribed to its capacity to establish hydrogen bonds and participate in electrostatic interactions with adsorbates [28]. Many approaches have been used to increase their selectivity and adsorption performance, keep them from dissolving in acidic media, or make the process of separating them from the treated solutions easier [29, 30]. They have been altered to include a variety of functional groups, for instance, to increase their ability to absorb. By cross-linking to the magnetic surface, the magnetic chitosan derivatives were also demonstrated, and after this procedure is completed, they may be readily separated by an external magnet. Since iron oxides (Fe₃O₄ and Fe₂O₃) have substantial magnetic activity, easy production, and good thermal stability, they are typically explored as the magnetic component of magnetic chitosan [31, 32]. In addition, zeolite, a naturally occurring aluminosilicate, is widely recognized for its diverse range of applications, which encompass several fields such as catalysis and water purification [33–35]. The remarkable adsorption capabilities of this substance account for its elevated surface area and porous structure [36, 37]. The adjustment of zeolite porosity can be achieved through the implementation of many procedures, including templating, dealumination, and desilication [38, 39]. Hierarchical zeolites, which possess a combination of micro- and mesopores, exhibit superior adsorption efficiency compared to typical zeolites. The utilization of zeolite-infused polymer composites has demonstrated efficacy in the removal of hazardous pollutants from water sources [40, 41]. Therefore, it is postulated that the combination of zeolite with Cs to create a composite material may improve the thermal and mechanical stability of the resulting adsorbent. The present work explores the utilization of ferrites (namely, MgFe2O4 and NiFe₂O₄) for enhancing the adsorbent's ability to be separated from water, thereby facilitating its regeneration and enabling repeated use.

Due to the environmental responsibility associated with the removal of dye from textiles, tannery effluents, and other industries, the current study has been conducted and published in order to address the environmental challenges. The synthesis of $MgFe_2O_4$ and $NiFe_2O_4$ nanocomposites for the elimination of AR dye is described in this study. The nanocomposite materials were subjected to XRD, FTIR, SEM, TEM, and BET investigations. Additionally, the dye adsorptive ability was assessed in relation to a range of parameters, including the adsorbent's mass, the contact time, the pH level, and the temperature. Additionally, the outcomes were evaluated and associated using thermodynamics and kinetic features. Also, genuine wastewater samples and natural water samples were used to investigate the AR dye removal from them.

2. Experimental

2.1. Chemicals. The compounds $Ni-(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Mg-(NO_3)_2 \cdot 6H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ obtained from BDH were used in their original states. A solution of egg white in water was generated by dissolving 60 g of freshly extracted egg white in distilled water, using vigorous stirring for a period of 30 minutes. The ZSM-5 zeolite was obtained from EHBC Chemicals Pvt, Ltd., a company located in Weifang, China. Chitosan with a low molecular weight, acid red (AR), hydrochloric acid (67%), and acetic acid were obtained from Sigma-Aldrich Chemical Co. Ltd., located in Milwaukee, Wisconsin, USA. The dye solution was prepared through the dissolution of an accurately determined amount of the dye in distilled water.

2.2. Synthesized of NiF NCs. To make an egg-white aqueous solution, dissolve 60 g of freshly extracted egg white in 30 mL of distilled water with vigorous stirring. NiF produced was utilizing the autocombustion technique, which entailed the utilization of fuel made from metal nitrates and egg whites. Specifics of the procedure of the preparation method have been recorded in previous research investigations [21, 42]. In summary, the synthesis of NiF involved the dissolution of a suitable amount of metal nitrates (with a Ni/Fe ratio of 1:2) in 100 mL of distilled water, with the intention of producing Ni2O4 via autocombustion.

Simultaneously, specifically, mix 60 ml of freshly extracted egg white with 40 ml of distilled water to make the aqueous solution. Following this, nitrate-containing solution was gradually added to egg-white-containing solution, with continuous and vigorous stirring. After stirring for a duration of 30 minutes, the gel that developed was left to mature at an approximate temperature of 80°C until it transformed into a dry gel precursor. Subsequently, the precursor underwent autocombustion through additional heating on a hot plate, resulting in the liberation of highly concentrated gases. The loose powder that was obtained after undergoing complete combustion was referred to as the "in-process precursor." The in-depth approach elucidating the creation of ferrites using this technology has been previously covered in existing literature. To facilitate a comparative analysis, the synthesis of MgF was carried out with an identical methodology as outlined in the study conducted.



SCHEME 1: Illustration of the fabrication procedure of ternary ferrite-Cs-Ze NCs and proposed mechanism of dye removal.

2.3. Synthesis of NiF-Cs-Ze NCs. The NCs were made using a simple and direct method. At the outset, approximately 1g of Cs was solubilized in a 100 ml solution of acetic acid with a concentration of 0.1 mol. Following that, a 5% concentration of NiF was added to the solution and agitated for a period of one hour. In an isolated manner, a quantity of 1g of Ze particles was disseminated inside a volume of 100 ml of distilled water and subjected to stirring for an approximate duration of 1 hour. The suspension that ensued was subsequently mixed with the Cs solution. The mixture was subsequently exposed to efficient homogenization using an advanced magnetic stirring system for a duration of 12 hours. Subsequently, the product underwent filtration, underwent meticulous washing to minimize the potential influence of any remaining acetic acid, and was subsequently dried delicately at 60°C overnight. In order to facilitate a comparative analysis, the synthesis of MgF-Cs-Ze NCs and MgF@NiF-Cs-Ze NCs was conducted using an identical process, with the only variation being the utilization of MgF and MgF@NiF in place of NiF.

2.4. Instrumentation. X-ray diffraction (XRD) was used to figure out how good the NCs were. The study was carried out on a D8 Advance Diffractometer manufactured by Bruker AXS. To find out about the surface shape of the nanocomposites, we utilized a JEOL JSM-IT200 scanning electron microscopy (SEM) device in conjunction with energy dispersive X-ray spectrometry (EDS) analysis. Furthermore, the experiment involved the utilization of transmission electron microscopy (TEM) at an acceleration voltage of 100 kV, employing a JEOL-2010 TEM apparatus. The Fourier transform infrared (FT-IR) spectra were acquired with the KBr methodology employing a Jasco FTIR-310 spectrophotometer. The spectrophotometric measurements, specifically within the ultraviolet-visible (UV-Vis) region, were conducted utilizing a PerkinElmer Lambda 25 spectrophotometer manufactured in the United States. The measurements were conducted utilizing a quartz cell possessing 10 mm width.

2.5. Adsorption Studies. The work focused on examining the adsorption behavior of MgF-CS-Ze and NiF-CS-Ze nano-

composites when AR dye is taken out of water solutions. A 20 mg/L solution of AR dye that was kept at a pH2 (the pH at which optimal dye adsorption occurs using MgF-CS-Ze and NiF-CS-Ze NCs) was employed. The experimental procedure utilized a quantity of 75 mg for each adsorbent component. The assessment also included an examination of the impact of operational factors like the amount of the absorbent, the contact time, the pH, and the temperature. Using a UV-Vis spectrophotometer, the amount of dye left in the solution after binding was determined. A wavelength of 530 nm was chosen for the analysis [43]. The formulae below were utilized to compute the relative adsorption capacity (q_e in mg/g) and adsorption efficiency (*E*%) [44].

$$\%E = \frac{C_{\rm o} - C_{\rm t}}{C_{\rm o}} \times 100,\tag{1}$$

$$q_{\rm t} = \frac{\left(C_{\rm o} - C_{\rm t}\right) V}{m}.$$
 (2)

Here, V is the dye solution volume in liters, m is the mass of the adsorbent in grams, C_t is the dye solution concentration at equilibrium, and q_t is the adsorption capacity at equilibrium in milligram/gram.

2.6. Kinetic Models. To evaluate the AR dye adsorption, the pseudo-first- and pseudo-second-order kinetic models were used. Pseudo-first-order equation is given as [45]

$$\log (q_{\rm e} - q_{\rm t}) = \log (q_{\rm e}) - \frac{K_1}{2.303}t,$$
(3)

where q_e and q_t in mg g⁻¹ are the amount of dye that was adsorbed by at equilibrium and time *t*, respectively.

Pseudo-second-order equation is given as follows [46]:

$$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \left(\frac{1}{q_{\rm e}}\right)t,\tag{4}$$

where k_2 (mg/g/min) uptake capacities are represented by the variable q_t (mg g) and q_e (mg/g) at equilibrium is used.



FIGURE 1: The XRD patterns (a), FT-IR spectra (b), and BET (c) of MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze NCs.

2.7. Sample Collection and Environmental Applications. This study included three separate environmental samples derived from wastewater obtained from a water treatment facility, Red Sea water, and tap water. The samples underwent filtering using 0.45 m filter membrane and afterwards kept in Teflon bottles under dark conditions at 5°C. To ease AR dye adsorption, each sample was prepared with a volume of 100 mL and contained 20 mg of each nanocomposite. The pH of the samples was set to 2. Following this, the concoction underwent agitation for a period of 90 minutes at a temperature of 295 kelvins. The ultimate stage entailed the

TABLE 1: The S_{BET} , total pore volumes, and pore size of samples.

Sample	$S_{\rm BET}$	$V_{\rm total}$	Pore size
MgF-Cs-Ze	112.021 m ² /g	0.155748 cc/g	2.91337 nm
NiF-Cs-Ze	$102.032 \text{ m}^2/\text{g}$	0.109105 cc/g	2.27019 nm
MgF@NiF-Cs-Ze	$100.736 \text{ m}^2/\text{g}$	0.25273 cc/g	5.37426 nm



FIGURE 2: The SEM image of MgF-Cs-Ze (a), NiF-Cs-Ze (b), and MgF@NiF-Cs-Ze (c) and TEM of MgF-Cs-Ze (d), NiF-Cs-Ze (e), and MgF@NiF-Cs-Ze (f).

determination of the concentration of the adsorbed dye using spectrophotometric analysis.

3. Result and Discussion

3.1. Characterization of NCs. The introduction of MgF and NiF, along with Cs, into Ze has resulted in the improvement of the characteristics of the NCs, namely, the augmentation of the adsorption surface area. The incorporation of Cs enhances the adsorption characteristics by introducing a multitude of efficient adsorption sites inside NCs. The schematic representation of the synthesis procedure for MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze NCs is depicted in Scheme 1.

3.1.1. XRD and FT-IR Data Analysis. Figure 1(a) illustrates XRD patterns corresponding to MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze. The incorporation of Cs as a polymer component exhibits distinct peaks at 20.28° (273), which are consistent with previous studies [47], therefore supporting the present research findings. The inclusion of Ze in the composite material leads to lessening of the force of specific characteristic Ze-correlated peaks. The peaks that were seen exhibit alterations in their intensities, resulting in reduced intensities. These alterations are evident at specific angles, namely, 7.99°, 8.90°, 23.17°, and 23.97°. The aforementioned observation indicates a significant interplay between the

polymer and the Ze substrate [48]. The observed phenomena can be ascribed to the incorporation of an amorphous constituent inside the composite material. Furthermore, the confirmation of the presence of NiF and MgF can be observed through peak diffraction intensity which occurs at 2θ for 30.29°, 35.8°, 37.32°, 43.31°, 53.6°, and 57.38°. These peaks are associated with (220), (311), (400), (422), and (511) diffraction planes of the NiF and MgF spinel structures [49]. The ferrites exhibit a notable and heightened peak at an angle of 35.8°, which experiences a minor displacement towards longer wavelengths while concurrently diminishing in intensity. The observed change can be ascribed to the incorporation of an amorphous constituent inside the composite material [50].

The FT-IR data depicted in Figure 1(b) offers additional support for the effective amalgamation of Ze, Cs, and MgF-NiF. The spectra detected for all the generated NCs display intricate bands that correspond to the presence of Ze, MgF, and NiF as the inorganic constituents, in conjunction with Cs serving as the organic constituent. This observation provides evidence for the interplay and incorporation of these constituents within the nanocomposites. The bending vibrations of the inner AlO_4^{5-} or SiO_4^{4-} units are represented by the peaks at 447 cm^{-1} and 543 cm^{-1} . Also, the peaks at 1089 cm^{-1} and 1224 cm^{-1} may be explained by the symmetrical and asymmetrical stretching vibrations of the Si-O-Si bonds inside the Ze [51]. In addition, the bands seen in the



FIGURE 3: EDX spectrum of MgF-Cs-Ze (a), NiF-Cs-Ze (b), and MgF@NiF-Cs-Ze (c).

region of $3362-3282 \text{ cm}^{-1}$ may be explained by the stretching vibration modes shown by the NH and OH functional groups. Aliphatic C-H stretching is indicated by a peak at 2922 cm^{-1} , whereas the existence of N-H is indicated by a peak at 1582 cm⁻¹ [52, 53]. The spectral measurements

described here are compatible with those found in previous research.

3.1.2. BET Analysis. In the NC adsorbent, mesoporosity is essential for increasing the specific surface area and



FIGURE 4: (a) Comparison of the efficiency of the three nanocomposites in removing the AR dye from an aqueous phase. (b) The electronic spectra of (A) acid red dye's 20 ppm concentration in aqueous phase (B) and poststirring with 7.5 mg of the NiF-Cs-Ze nanocomposite solid phase and (C) poststirring with 7.5 mg of the MgF-Cs-Ze nanocomposite solid phase.

facilitating the efficient adsorption of contaminants. It also makes mass transfer to reactive areas easier, which eventually improves the adsorption process as a whole. The ternary MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze NCs' N2 adsorption-desorption isotherms were investigated, and the associated pore size distribution curves were looked at (see Figure 1(c)). According to the IUPAC classification, the research shows that the isotherms exhibit an H3 type hysteresis loop and adhere to a pattern of type IV. The nature of mesoporous displayed by the NCs is confirmed by the observed characteristic pattern. Table 1 displays the outcomes of the BET analysis. Comparative analysis shows that MgF-Cs-Ze NCs have the largest surface area and average volume of pores among the three NCs, despite their identical composite compositions that differ primarily in the kind of ferrite utilized. The filler's instability, which causes the filler particles to aggregate inside the adsorbent's pores, may be the cause of the other ternary NCs' lower average pore volume and S_{BET} values.

3.1.3. Surface Textural and EDX Spectroscopy. The analysis of the NCs using SEM indicates that the Ze crystals are enveloped by elongated Cs particles, resulting in the formation of irregular and bulky aggregates. Furthermore, the presence of MgF particles can be observed on the MgF-Cs-Ze sample, as depicted in Figure 2(a). Similarly, the NiF-Cs-Ze sample exhibits the visibility of NiF particles, as illustrated in Figure 2(b). The instance of the MgF@NiF-Cs-Ze specimen in Figure 2(c) is shown that both NiF and MgF particles coexist. TEM pictures in Figures 2(d) and 2(e) demonstrate that the MgF and NiF nanoparticles are observed mostly as agglomerates consisting mainly of spherical particles. TEM pictures of the MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze composites are presented in Figure 2(f). The provided photos serve as convincing evidence of the effective integration and distribution of MgF and NiF nano-particles within the Cs and Ze matrices.

Distinct peaks corresponding to the elements C and O were seen in EDS investigation of the existence of Cs. The typical constituents of Ze, namely, O, Si, and Al, were observed in all three nanocomposites. Furthermore, the detection of Fe and Mg is noted in Figure 3(a), providing confirmation of the inclusion of magnesium ferrite MgF. The integration of NiF is evidenced by the presence of Fe and Ni in Figure 3(b). The validation of the incorporation of both NiF and MgF into the composite material was confirmed by the simultaneous presence of Fe, Ni, and Mg, as depicted in Figure 3(c).

3.2. Adsorption Study. Figure 4(a) provides a comparative evaluation of the efficacy of three NCs in extraction of AR dye from a water-based solution. The purpose of this study was to evaluate the efficacy of three distinct nanocomposites, namely, MgF-Cs-Ze, NiF-Cs-Ze, and MgF@NiF-Cs-Ze, in terms of their efficacy for removing AR dye from aqueous solutions. The experimental procedure was utilized in a similar manner to exclude AR dye from the aquatic phase, as depicted in Figure 4(a). The results of the study suggest that MgF-Cs-Ze shows a higher level of effectiveness in removing dyes when compared to the other materials tested. In contrast, the experimental outcomes of NiF-Cs-Ze and MgF@NiF-Cs-Ze exhibited similar trends, albeit exhibiting lower values in comparison to MgF-Cs-Ze. As a result, MgF-Cs-Ze and NiF-Cs-Ze were chosen as the most suitable nanocomposites for all further experimental studies. At 530 nm, the electronic spectra showed an absorption peak of AR dye in the aqueous phase. Nevertheless, after extensive blending of MgF-Cs-Ze and NiF-Cs-Ze with the aqueous



FIGURE 5: Adsorbent dosage effect on adsorption of AR dye ($C_0 = 20 \text{ mg/L}, t = 90 \text{ min}, T = 22^{\circ}\text{C}, \text{ and } \text{pH} = 2$).

phase containing AR dye, a discernible decrease in the absorption peak was detected in Figure 4(b). The observed result provides evidence supporting the efficacy of solid-phase nanocomposites in the process of filtering AR dye out of water.

3.2.1. Adsorbent Dosage Effect. The dosage of adsorbents has a crucial role in determining the adsorbent's capacity under specific operational conditions, making it a significant chemical parameter. The current investigation is aimed at examining the adsorbent dose effected on AR dye adsorption. This was achieved by employing different quantities of MgF-CS-Ze and NiF-CS-Ze NCs, ranging from 5 to 20 mg. According to the data presented in Figure 5, there was an observed rise in the adsorbed amount of AR dye from 69.5% to 99.7% as the dosage of MgF-Cs-Ze increased from 5 to 20 mg. In a similar manner, the quantity of AR dye that was adsorbed exhibited an increase from 54.5% to 99.2% as the dosage of NiF-Cs-Ze increased from 5 to 20 mg.

In this investigation, a mass of 7.5 mg of the solid-phase material was employed for the purpose of removing 25 ml of AR dye. The removal efficiencies observed were 76.9% for MgF-Cs-Ze and 61.4% for NiF-Cs-Ze. The selected dosage facilitated the examination of the influence of various parameters on the process of adsorption, while ensuring a substantial degree of dye removal. Since the increase in the amount of current solid phase results in an increase in the precentage, more active sites are available for adsorption.

3.2.2. Effect of pH. The role of pH in adsorption is well known to be crucial, as it has a substantial impact on the ionization state of both adsorbent molecules and adsorbate species, as well as the appropriateness of the adsorbent surface [54]. Within the scope of the present investigation, different pH levels from 2 to 10 were examined to evaluate its effect on AR dye's removal. The 20°C temperature and 20 mg/l concentration of the solutions were held constant throughout the experiments, while manipulating the pH. As illustrated in Figure 6, the adsorption effectiveness of

MgF-Cs-Ze and NiF-Cs-Ze decreased as the pH values increased. According to the data, the pH range of 2 to 3 exhibited the maximum percentage of adsorption for AR dye. This examine shows that in acidic settings, AR dye disappears much more quickly, indicating that the adsorption mechanism exhibits optimal efficacy within this specific pH range.

3.2.3. Contact Time Effect. Figure 7 shows how the contact time affects the adsorption of the AR dye onto MgF-Cs-Ze and NiF-Cs-Ze NCs. By varying the duration of contact time between 0 min and 100 min, it was observed during the first 15 min that increasing the contact time gradually increased the adsorption percentage. A slow increasing in AR dye adsorption by MgF-Cs-Ze and NiF-Cs-Ze was seen at contact times greater than 15 minutes, and equilibrium was reached in 90 min. This suggests that AR dye was adsorbed by MgF-Cs-Ze and NiF-Cs-Ze NCs in two stages. The first step was the fastest and could be explained by the transfer of AR dye from the aqueous phase to the external surface of MgF-Cs-Ze and NiF-Cs-Ze NCs. The second step was slower and could be explained by the diffusion of AR dye between the MgF-Cs-Ze and NiF-Cs-Ze matrices.

3.2.4. Temperature Effect. Figure 8 depicts the influence of various temperatures, specifically 285, 295, 308, and 318 kelvins, on the efficiency of AR dye removal using MgF-Cs-Ze and NiF-Cs-Ze NCs. The data shows that the efficiency with which AR dye is removed by NCs decreases as the solution temperature rises. According to the behavior, adsorption is an exothermic process. It appears that higher temperatures have a detrimental influence on the effectiveness of dye removal when utilizing the specific nanocomposites.

3.2.5. Adsorption Kinetics. Used of pseudo-first-order and pseudo-second-order models to examine the kinetics of the adsorption process. Figures 9(a) and 9(b) show the linear representations of the kinetic models, respectively. Table 2 presents a more complete summary of the information



FIGURE 6: Effect of pH on the removal of AR dye by MgF-Cs-Ze and NiF-Cs-Ze NCs ($m = 7.5 \text{ mg}/25 \text{ ml}, t = 90 \text{ min}, \text{ and } T = 22^{\circ}\text{C}$).



FIGURE 7: Effects of contact time on the removal of AR dye by MgF-Cs-Ze and NiF-Cs-Ze NCs (m = 7.5 mg/25 ml, pH = 20, and $T = 22^{\circ}$ C).

gathered. Figures 9(a) and 9(b) and Table 2 indicate that the pseudo-second-order model has higher R^2 values than the pseudo-first-order model. The R^2 values for the pseudo-second-order model for the adsorption of AR dye onto MgF-Cs-Ze and NiF-Cs-Ze are both 0.999. However, for MgF-CS-Ze and Ni-CS-Ze, the pseudo-first-order model has an R^2 of 0.961 or less. In addition, coefficient values were significantly higher than that of the pseudo-first-order model, indicating that the pseudo-second-order model is appropriate for the adsorption process and that the adsorption rate depends on the amount of dye adsorbed at equilib

rium and on the surface of the MgF-Cs-Ze and NiF-Cs-Ze NC sat a given time [55].

3.2.6. Thermodynamic Analyses. The comprehension of the energy alterations associated with the adsorption process is significantly enhanced by the consideration of thermodynamic parameters, which provide useful elucidation into the characteristics of the interaction. Hence, it is imperative to conduct a meticulous assessment of these variables. To provide a complete picture of the adsorption process, the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS)



FIGURE 8: Effects of temperature on the removal of AR dye by MgF-Cs-Ze and NiF-Cs-Ze NCs (m = 7.5 mg/25 ml, pH = 20, and t = 90 min).



FIGURE 9: (a) Pseudo-first-order and (b) pseudo-second-order linear designs for AR dye removal onto MgF-Cs-Ze and NiF-Cs-Ze Nsc (m = 7.5 mg/25 ml, $C_0 = 20 \text{ mg/L}$, $T = 20^{\circ}$ C, and pH = 2).

TABLE 2: The parameters for pseudo-first-order and pseudo-second-order kinetic models for removal AR dye onto MgF-CS-Ze and NiF-CS-Ze at 22°C.

	The pseudo	-first-order kinetic (Lagergren) me	odel	
	$q_{\rm e,exp} \ ({\rm mg/g})$	$q_{\rm e,calc} \ ({\rm mg/g})$	k_1	R^2
MgF-Cs-Ze	52.47	19.27	0.05	0.961
NiF-Cs-Ze	41.26	15.13	0.022	0.981
	The pse	eudo-second-order kinetic model		
	$q_{\rm e,exp} \ ({\rm mg/g})$	$q_{\rm e,calc} \ ({\rm mg/g})$	k_2	R^2
MgF-Cs-Ze	52.47	55.55	7×10^{-3}	0.999
NiF-Cs-Ze	41.26	41.66	9.4×10^{-3}	0.999



FIGURE 10: Regressions of van't Hoff plots.

TABLE 3: Thermodynamic parameters of AR dye onto MgF-Cs-Ze and NiF-Cs-Ze Nsc.

	Т	$K_{\rm L}$	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
MgF-Cs-Ze	295	3.648	-3.241	-15.24	-40.67
NiF-Cs-Ze	295	1.634	-1.172	-15.11	-47.26

were calculated. To calculate the thermodynamic constants, the following equations were used [56, 57]:

$$k_{\rm L} = \frac{C_{\rm a}}{C_{\rm e}},\tag{5}$$

$$\Delta G = -RT \ln (K_{\rm L}), \tag{6}$$

$$\ln K_{\rm L} = \frac{\Delta S}{R} - \frac{\Delta H}{RT},\tag{7}$$

where the Langmuir equilibrium constant is $K_{\rm L}$ (L/mol), $C_{\rm e}$ is the concentration at equilibrium for AR-1 dye in aqueous solution (mg/L), and $C_{\rm a}$ is the concentration of AR-1 dye uptake onto the solid phases per liter at equilibrium (mg/L). The gas constant R (8.314 x 10⁻³ kJ/mol K), and the temperature T (K). van't Hoff plots of ln ($K_{\rm L}$) vs. 1/T were used to find the intercept and slope, which were then used to calculate ΔH and ΔS . Figure 10 displays van't Hoff plot regressions.

The thermodynamic parameters ΔG , ΔH , and ΔS are shown in Table 3. Several estimated ΔG values, including 22°C, were seen to be negative. This proves that the spontaneous and thermodynamically advantageous process of direct dye adsorption onto NCs occurred. Adsorption of direct dyes onto NCs is thought to be an exothermic process due to the existence of negative ΔH values. This observation provides evidence in favor of the hypothesis that lower temperatures lead to a larger adsorption capacity [58, 59]. Furthermore, the presence of a negative ΔS value indicates that the manipulation of entropy is accomplished during the reorientation phase in the activation process. This procedure facilitates the establishment of nonelectrostatic adsorption-saturated solid-phase interactions. In addition, the observation of negative ΔG values at 295 kelvins for the anionic dye provides more evidence supporting the spontaneous and physical sorption mechanism involved in the retention of anionic dye species on MgF-Cs-Ze and NiF-Cs-Ze nanocomposites. This observation suggests a positive interaction between the anionic dye species and adsorbent materials under the specified temperature conditions.

3.2.7. The Adsorption Mechanism. It is commonly known that the structure and functional groups of the adsorbent and adsorbate determine the dye adsorption mechanism. The literature has suggested a number of possible interactions for dye adsorption, including ion exchange, pore filling, hydrogen bonding formation, electrostatic attraction, $n - \pi$ interaction, and $\pi - \pi$ interaction [60]. The surface of MgF-Cs-Ze and NiF-Cs-Ze NCs becomes strongly protonated, which accelerates the rate at which the molecules of the anionic dye are adsorbed [61]. Therefore, it is assumed that the interactions in the ferrite-Cs-Ze NC-AR system result from the (i) Yoshida H-bonding interaction between the aromatic rings in AR and the -OH groups of NCs (Scheme 1) [62], (ii) dipole-dipole H-bonding between the electronegative residue (N lone pair) of the dye molecule and the hydroxyl groups (H-donor) of Cs [63], (iii) the positively charged active sites of the dye molecule and the adsorbent's -NH group interact electrostatically [62], and (iv)



FIGURE 11: The efficiency of AR dye removed by MgF-Cs-Ze and NiF-Cs-Ze from various real three samples (experimental conditions: 25 ml solution, contact time = 90 min, pH solution = 2, temperature = 295 K, 20 mg of NCs, and 20 mg L^{-1} concentration for AR dye).

 $n - \pi$ interaction (also referred to as $n - \pi$ electron donoracceptor interactions), in which the aromatic rings of AR function as electron acceptors and the oxygen groups of NCs as electron donors [63]. However, due to the high concentration of OH- ions in the very alkaline dye solution (pH = 10), the surface of the MgF-Cs-Ze and NiF-Cs-Ze NCs draws hydroxyl ions, neutralizing the charges on the surface and preventing dye molecules from attaching. Due to this, the rate of dye removal was incredibly low [61].

3.2.8. Environmental Applications and Reusability. This work highlights the significance of evaluating the efficacy of solid phases composed of MgF-Cs-Ze and NiF-Cs-Ze NCs in authentic environmental samples for the purpose of eliminating osteogenic chemicals. In order to achieve the objective, three distinct water samples were procured, namely, Red Sea water, wastewater obtained from a water treatment facility, and tap water. After conducting measurements on the concentration of AR dve in the three samples. it was found that the concentration fell below the detection limit of UV-vis calculations. As shown in Figure 11, in the context of actual samples, the efficacy of MgF-Cs-Ze and NiF-Cs-Ze NCs in the removal of AR dye was determined to be 92.8%, 94.7%, and 96.5% for Red Sea water, wastewater, and tap water. The elements Mg, F, Cs, and Ze correspondingly pertain to the compound MgF-Cs-Ze. In a similar vein, the removal efficiencies for NiF-Cs-Ze were found to be 92.6%, 93.9%, and 95.8% for the corresponding water sources. Following the adsorption process, the MgF-Cs-Ze and NiF-Cs-Ze NCs were gathered, dried, and rinsed with acetone to get rid of the adsorbed colors. The adsorbent's capacity for recycling was investigated using four adsorption-harvesting cycles. The outcomes showed the MgF-Cs-Ze and NiF-Cs-Ze NCs' capacity for adsorption.



FIGURE 12: Removal performance of MgF-Cs-Ze and NiF-Cs-Ze NCs towards AR dye over four cycles.

Following four cycles, there was little change in the AR-1 and BG dyes. This indicates that MgF-Cs-Ze and NiF-Cs-Ze NCs can be recycled and treated more than once without losing their ability to adsorb substances (as shown in Figure 12).

The results of this investigation demonstrate the potential of cross PANI/Chito-GO-OXS NCs as a workable adsorbent to remove dye from actual water samples, an important task for environmental preservation and pollution management. The adsorbent is a desirable option for real-world uses in water treatment processes because of its stable adsorption capabilities and recyclability.

4. Conclusion

Adsorption is the removing method of AR dye from aqueous solutions, and in this work, we compared the efficiency of MgF-CS-Ze and NiF-CS-Ze NCs for this purpose. The research results provide light on the underpinnings of adsorption's essential processes. The study revealed that electrostatic interactions are a prominent factor in the adhesion of AR dye to the NCs. A thorough examination was undertaken, considering multiple factors such as the quantity of adsorbent used, the pH level of the experimental solution, the duration of contact, and the adsorption temperature. The equilibrium results were accurately characterized by the pseudo-second-order model, highlighting the significance of employing this kinetic technique to elucidate the adsorption behavior. The comprehensive dataset highlights the considerable potential of MgF-CS-Ze and NiF-CS-Ze NCs as highly effective, environmentally sustainable, and reusable adsorbents for the elimination of AR dye from wastewater generated in industrial settings. This study establishes a foundation for the practical use of these findings in mitigating water pollution issues within industrial environments.

Data Availability

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

Conflicts of Interest

The authors declare that they have no known financial or interpersonal conflicts that would have seemed to have an impact on the research presented in this study.

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