

## Review Article

# Recent Literature Review of Significance of Polypyrrole and Its Biocomposites in Adsorption of Dyes from Aqueous Solution

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The usage of dyes has been tremendously augmented due to industrialization and human's intrinsic fascination with colors. Owing to their excessive usage in industries like textiles, food, cosmetics, paints, printing etc., it is indisputably a contributing factor in aquatic pollution. Dyes effluents have emerged as a burgeoning challenge. Owing to issues such as toxicity, mutagenicity, and disturbed photosynthesis associated with dye contamination, it is crucial to look for an explication to deal with this challenge. Polypyrrole-based biocomposites have been reported as good adsorbents for textile wastewater treatment. In the last decade, numerous studies have stated the effective removal of dyes via Polypyrrole-based biocomposites. This review concentrates on the implication of different Polypyrrole-based biocomposites for decontamination of dyes and synthesis methods, characteristics, and mechanism of dyes degradation by these biocomposites from wastewater.

## 1. Introduction

Aquatic pollution is presently the most critical worldwide concern for our environment that requires some significant solution on priority basis. The provision of unadulterated water for masses has become a task difficult to accomplish. There is a general decline of freshwater resources and the leading cause of this problem is release of unprocessed or poorly processed wastewater from industrial plants which majorly consists of pollutants such as dyes, insecticides, heavy metals, drugs by-products, and wasted chemicals from respective industries [1, 2]. Dyes are chromophores carrying substances which impart them the ability to absorb light from visible spectrum and unabsorbed light is reflected as complementary color. Dyes are mostly composed of aromatic hydrocarbons. Some examples are in Abbreviations. Chromophores in their chemical structure possess conju-

gated double bonds which favor absorption of light [2, 3]. Dyes are largely divided into two groups, i.e., inorganic and organic dyes as shown in Figure 1. Organic dyes are most popular among textile and food industries [4].

Reactive red 120 is a polyaromatic compound vastly used in textile dyeing. It blends well with cotton fabrics via covalent bonding and leaves a vibrant color. Its ease of application and low cost makes it a feasible dye to work with however it has been reported to cause nuclear and cell aberrations in aquatic animals like Catla fish [5]. In humans, its exposure can cause chronic inflammation of the skin and bronchial asthma [6].

Sulfur black dye makes up almost 80% of cellulosic fibers dyes. It has been documented to be one of major contributing factors of aquatic pollution [7, 8]. Its utilization on industrial scale produces wastewater with high COD, high salt concentrations, and dark color. The salts and by-

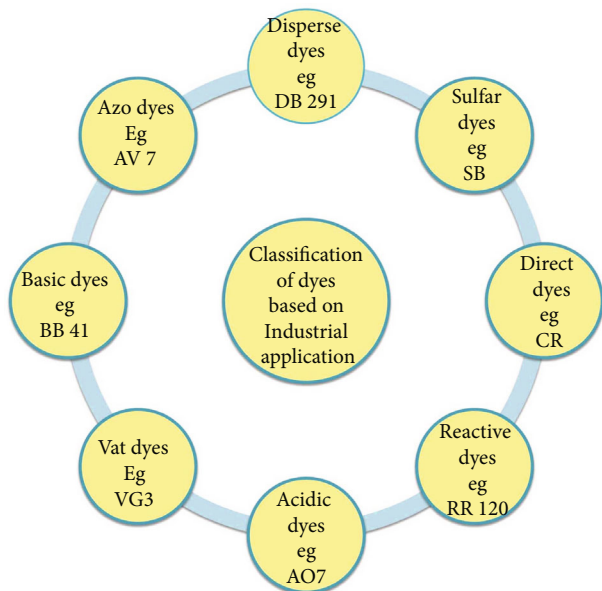


FIGURE 1: Classification of dyes based on their industrial applications.

products that are generated during synthesis of sulfur black contain  $\text{Na}_2\text{S}_2\text{O}_3$  which result in high COD and higher the COD value, the more severe the pollution of organic matter in water which causes issues for aquatic life and human being in general [9]. It can also cause skin and eye irritation in humans [10].

Vat green 3 is an anthraquinone dye which is mostly used for coloring and printing of cotton fiber, cotton blend dyeing, and synthetic polymers like PVA. It is highly toxic to sea life, for instance, it leads to developmental stage toxicity in zebrafish and also poses health threats to *Daphnia similis* and *Raphidocelis subcapitata* which has decreased their viability [11]. Oral contact with vat dyes can lead to poisoning and toxic infection of human tissues [12].

Acid violet 7 is an azo dye used as a colorant in wool and silk fibers, beauty products, and blending of yarn. It is reported to inflict mutagenicity, clastogenicity, aneuploidies, and apoptosis in myeloid tissue of rats [13–15]. It has been reported to be a strong carcinogen for human body [16].

Acid orange 7 is also known as 2-naphthol orange. It is an azo dye. It is commonly used as hair dye employed via either direct application or added to other hair dye formulations. It is also used for coloring wool. The dye is reported to cause detrimental effects in climbing perch fish and damages its organs such as liver and kidneys. Especially, it was reported to cause irreversible damage to morphology of organic tissue [17, 18]. Its by-products can induce urothelial carcinoma in human [19].

Basic blue 41 is an azo dye which is very popular in textile industries especially in Algeria. It is an intractable mono azo basic dye, employed as a colorant in leather industries or for dyeing natural or synthetic polymers. It is also used in microbial staining techniques. However, use of its higher color index (C.I = 11105) can be hazardous. As per ECHA's reports, it can cause inflammation of respiratory system in

human and acute long term toxicity in aquatic life with long lasting effects [20]. It is reported to cause irreversible damage of the skin and eyes in human [21].

Congo red is a direct dye basically composed of sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid). Its color is pH dependent, i.e., blue at pH 3 and red at pH 5. It can be used as an indicator or histological stain [22, 23]. It is also used to color cotton [24], paper [25], textile fabrics [26] etc. However it has been reported to cause impotence in various organisms even at minimum concentration [27, 28]. It is not only carcinogenic for human but also poses pregnancy risks and can be harmful to a developing fetus [29, 30].

Disperse blue 291 is an azo dye often applied as colorant in polyester fibers. It is chemically composed of aminoazobenzene 2-[(2-bromo-4,6-dinitrophenyl)azo]-5(diethylamino)-4-methoxyacetanilide. The dye is found to be hazardous for microorganisms and mammals as well. For instance, mutagenic aberrations in the salmonella and human hepatic cells leading to less viability were observed [31]. It was also reported to induce irregularities in DNA structure, chromosomal arrangement, and infection (TNFA) in rats inhaling the dye orally [32]. In humans, it is reported to induce hepatotoxicity [33].

Basic characteristics of these dyes have been given in Figure 2.

**1.1. Methods Used for Removal of Dyes from Wastewater.** Dyes effluents can be removed from wastewater via different biological, chemical, and physical methods [34, 35]. Physical method can be categorized as (i) adsorption, (ii) ion-exchange, (iii) membrane diffusion, (iv) coagulation (v) flocculation, and (vi) precipitation. Chemical methods comprise of (i) irradiation and (ii) fenton process. Biological methods are (i) microbial decomposition and (ii) degradation by agricultural biomass. Adsorption is most preferred out of all these for remediating wastewater as it is easily affordable, simple in operation, less untidy with no damaging side products [36, 37]. Moreover, it is quiet ecofriendly. Table 1 shows advantages of adsorption over other techniques.

**1.2. Adsorption and Its Mechanism.** Adsorption is mainly aggregation of any substance or its particles at the intersection of two phases which can either be liquid/solid or gas/solid. These aggregated particles are termed as adsorbate, and the surface on which they are disposed is adsorbent [39]. Adsorption can be both chemical and physical. Chemisorption occurs when there is a possibility of strong chemical bonding between adsorbate and adsorbent's surface via exchanging of electrons which is mostly irreversible. Physisorption, on other hand, is a result of weak van der Waals attractions between adsorbate and adsorbent so it can be reversed sometimes [40]. Agro-waste adsorbents observe physisorption with some exceptions. The directive forces behind this physisorption are van der Waals forces, hydrogen bonding, and dipole-dipole interactions, etc. [41]. Conducting polymers mostly exhibit chemisorption which involves origin of a distinct chemical species by formation of electronic bond between adsorbent and the adsorbate.

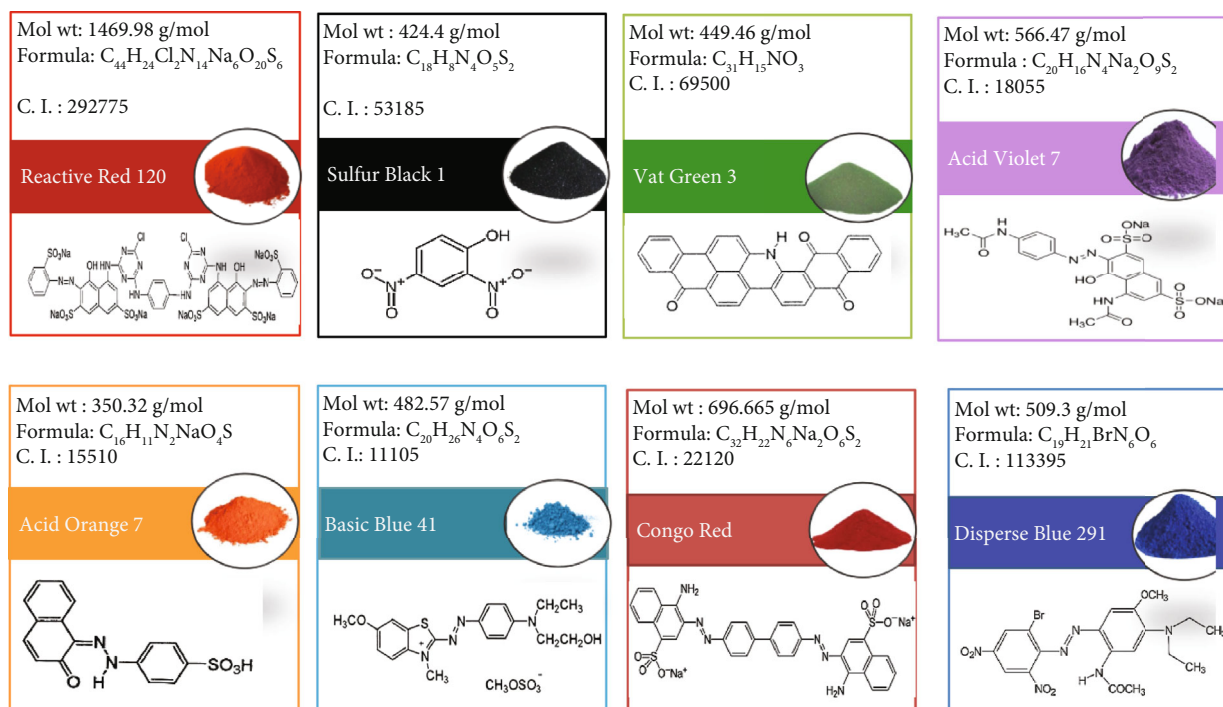


FIGURE 2: Basic characteristics of some dyes mentioned in literature.

TABLE 1: Advantages and disadvantages associated with different dye removal techniques [38].

Methods	Advantage	Disadvantage
Biological treatments	Cheap	Not suitable for all dyes
Coagulation	Low cost	High sludge production
Membrane diffusion	Low pressure	Poor quality of water post treatment
Fenton process	Effective oxidation of contaminants	High sludge production
Adsorption	Cost friendly, nonhazardous, and reusable	Require disposal

This procedure offers a valuable substitute for wastewater treatment which can be made really affordable with selection of an inexpensive adsorbent without needing any further treatment. Adsorption techniques are exclusively utilized to eliminate some specific chemical contaminants from waters which remain unfazed by classic biological methods of wastewater treatment [42]. Adsorption has an edge of having unique features such as adaptability and effortlessness, modest cost, imperviousness to noxious contaminants, and an over simplified setup. Moreover, it is least likely to generate detrimental side products. Adsorption potential of any adsorbate is mostly governed by following factors [43]:

- (i) surface area of adsorbent
- (ii) adsorbate/adsorbent interaction
- (iii) adsorbate/adsorbent ratio
- (iv) particle size of adsorbent
- (v) physical factors such as temperature, pH, etc.

## 2. Role of Biomaterials in Wastewater Treatment

Lately, biomaterials-based adsorbents have garnered massive attention owing to their proficiency and environmentally benign nature for wastewater treatment [44]. There is a grave interest in development for more efficient but cost effective adsorbents like natural materials. Agricultural waste products like rice husks [45], wheat husks [46], peanut hulls [47], sugarcane bagasse [48], and cellulosic biomass [49] have been successfully used as effective adsorbents. However, biosorbents have to be modified by different methods as their performance is not up to mark in their natural form. The adsorption potential of these substances can be improved by designing their composites with other natural or synthetic materials. Composite adsorbents have been reported to exhibit much higher adsorption activity compared to a single adsorbent [50]. These days, efforts have been shifted into designing biocomposites. Biocomposites are mainly obtained by hybridizing a naturally occurring material of biological origin with any other material. These

TABLE 2: List of common agro waste-based biosorbents used for removal of dyes.

Biosorbent	Characterization	Dye	Adsorption conditions				Adsorption potential (mg g <sup>-1</sup> )	Source
			Adsorbent (g/L)	Temp (°C)	pH	Time (h)		
Coconut shell	FTIR, SEM, EDS	MB	1	30	9	24	200.01	[55]
Corn stalks	XPS, FT-IR	MB	2	34.8	9	1	129	[56]
Tea waste	SEM, XRD	MB	0.04	25	10	0.5	119.05	[57]
Wheat straw	TGA, SEM, FTIR	MB	1	19.8	5	1	396.9	[58]
Rice husk	TGA, XPS, BET	MG	0.5	30	6	2	67.60	[59]
Saw dust	SEM, FTIR	MG	0.01	30	8	2	52.61	[60]
Sugarcane bagasse	Pore size	RhB	0.1	20	5.7	4	263.85	[61]
Coffee ground powder	XRD, SEM, FTIR	RhB	0.05	18	7	3	5.25	[62]
Cotton stalk and hull	TAPPI 93 & ASTM E 1755-01 analysis	RB15	0.025	25	1	6	35.70	[63]
Chitosan/polyvinyl	FESEM, XRD, FTIR	MO	0.05	25	7	6	153.00	[64]

biological substances generally comprise of lignocellulosic residues like natural fibers, which are considered as sustainable sources for the synthesis of biocomposites [51, 52]. This review concentrates on polypyrrole-based biocomposites for wastewater treatment.

**2.1. Agricultural Wastes as Low-Cost Adsorbents.** Cellulose containing biomaterials display great adsorption potential for water contaminants. Agro waste is basically composed of cellulose, lignin, starch, proteins, hydrocarbons, and water. These biomaterials are easily accessible, sustainable, profitable, and renewable. Agro waste is enriched with carbon content due to its solidity and low ash content [53, 54]. These features make agro waste a suitable source for designing inexpensive biosorbents for wastewater treatment in an environmentally benign way (Table 2).

At present, agro waste-based polymeric biocomposites are being extensively explored as potential adsorbents for degradation of dyes and removal of metal ions from industrial wastewater (Table 3). They have an edge over conventional biosorbents due to their massive surface area, mutable surface chemistry, great mechanical strength, enhanced porosity, and easy recovery. Polymeric materials both in raw and modified form are being studied for remediation of wastewater and incorporation of agricultural waste makes them more sustainable and safe for our environment [65].

### 3. Polypyrrole

Polypyrrole (PPy), a conducting polymer, has become a subject of great interest due to its exceptionally remarkable characteristics like synthetic accessibility, sustainability, high conductance, and redox potential [74–77]. Polypyrrole is synthesized via polymerization of pyrrole. P-doping of pyrrole is carried out through oxidation. This p-doping generates holes via loss of electrons which leads to formation of a conductive substance. Polypyrrole can further be molded into complex conductive forms like polythiophene, polyaniline, and polyacetylene polymers (Figure 3) [78]. The electric

properties of PPy majorly depend on the method of synthesis. If doping agents like Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc. are added to the synthesis reaction then it behaves as an anion exchanger as the ions constantly move in the polymer matrix, but if we introduce doping agents like PVs and PS into reaction mechanism, it act as cation exchanger since these doping agents are highly immobile [79].

**3.1. Applications and Advantages of Polypyrrole and Polypyrrole-Based Biocomposites.** PPy is used in biosensors and immune-sensors, drug delivery, Li-S batteries, CO<sub>2</sub> gas sensor, pH sensors, TE devices, etc. [80–85] (Table 4). Polypyrrole possesses inherent antibacterial properties and is utilized in antimicrobial textiles (e.g. bandages, wet wipes, hospital wear, and bedspreads). Polypyrrole Nps are effectively used as photothermal agents in cancer therapy, regenerative therapy of neural tissues, and cardiomyocyte proliferation [86]. PPy biocomposites with cellulose and Ag nps are reported to be excellent material for wound dressing and act as drug delivery agents [87]. Its biocomposites with yeast is used as MFCs [88]. It can be combined with flowering plants and implemented in applications [89]. PPy is widely used in adsorption applications owing to presence of nitrogen atoms in its polymer chains. Therefore, it is significantly used for wastewater treatment including removal of heavy metal ions and dyes effluents. These positively charged nitrogen atoms on polymeric matrix of Ppy easily chelate with heavy metals and dye effluents. Some oppositely charged ions are integrated in polymeric chains to retain overall neutral charge on it. These unique properties of PPy establish it as a good adsorbent [90].

Currently, development of hybrid PPy composites with different materials has become a topic of great interest owing to their wide-ranging applications in various fields of science. PPy has been combined with different materials of both chemical and biological nature to expand its area of applications. Composites with other polymers [102], graphene [103], silica [104], activated carbon [105], metal oxides [106], and carbon nanotubes [107] are extensively

TABLE 3: List of polymer/agro waste-based biocomposites used for dyes adsorption.

Polymer biocomposites	Characterization	Dye	Adsorption conditions				Adsorption potential (mg g <sup>-1</sup> )	Source
			Adsorbent (g/L)	Temp (°C)	pH	Time (h)		
SMA/SD	FTIR, SEM	CR		25	7	2	1.3020	[66]
PANI/Rh	FTIR, SEM	AR 18	0.12	25	3	2	100.00	[67]
PDDACD/Pd	FTIR, SEM	MB	0.03	25	9	1	150	[68]
PANI/as	FTIR, SEM, EDS	OG	0.225	25	2	3	9.01	[69]
PANI/Ws	FTIR, SEM, EDS	OG	0.01	25	6	3	17.79	[69]
PPY/starch	FTIR, SEM	AB 234	0.05	30	3	1	66.6	[70]
PANI/as	FTIR, SEM, EDS	CV	0.8	30	7	2	263.2	[71]
PPy/CGW	FTIR, SEM, XRD	RhB	0.125	25	9	2	19.0	[72]
PANI/PJs	FTIR, SEM, BET	DR 23	0.1	45	3	2	109.89	[73]

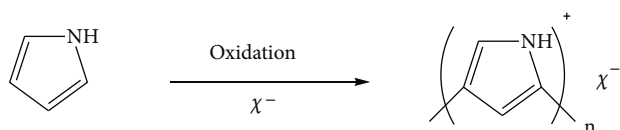


FIGURE 3: General polymerization reaction of PPy.

TABLE 4: Sensory applications of PPy-based composites.

PPy-based composites	Sensory properties	Sources
Pd/PPy Ncps	NH <sub>3</sub> gas sensors	[91]
PPy films	VOCs sensors	[92]
PPy/PVA composites	Room temperature sensors	[93]
PPy/NiO Ncps	NO <sub>2</sub> sensors	[94]
PPy/cu nanowires	H <sub>2</sub> O <sub>2</sub> sensors	[95]
PPy/carbowax Ncps	2, 4-DNT vapor sensors	[96]
PPy/hydrogel membranes	Cholesterol sensor	[97]
PPy electrodes	DNA	[98]
PPy thin films	Glucose sensor	[99]
PPY ZnO Nps	Xanthine	[100]
PPy/BSA films	Urea	[101]

used for adsorption of heavy metals and dyes from water. These hybrid composites display excellent adsorption properties due to synergistic effect between PPy and the hybridized material (Table 5).

**3.2. PPy-Based Biocomposites as Adsorbents.** PPy-based biosorbents provide a cost effective, replenishable, and biodegradable means of wastewater treatment [51]. The main attraction of these biosorbents is their outstanding performance in removal of dyes effluents but at an affordable rate. Most anticipated biomaterials in this regard are saw dust, rice husks, chitosan, sugarcane bagasse, cellulosic biomass, etc., which are combined with PPy and have been investigated as potential adsorbents for dyes.

**3.3. PPy-/SD-Based Biocomposites for Dyes Adsorption.** Sawdust is a side product of wood industry, highly economical, and an active biosorbent for removal of contaminants from wastewater. It is easily accessible. Its chief composition is cel-

lulose, hemicellulose, lignin etc. Fusion of sawdust and polymers has become a popular practice to procure products with desired properties to be used in various fields of science. Various different methods can be used for preparing PPy/SD biosorbents such as shown in (Figure 4).

First of all SD is purified from impurities by washing with dd H<sub>2</sub>O and oven dried at 60°C for 120 minutes. For preparation of polypyrrole, 0.2 M monomeric pyrrole is used. SD is immersed in it for 12 hrs at 25°C. Later 0.5 M FeCl<sub>3</sub> is added to it as an oxidizing agent at same temperature and agitated for 4 hrs. This addition of oxidizing agent leads to polymerization of PPy on top of SD. The final product is separated by filtration, washed with dd H<sub>2</sub>O, and dried.

This composite has been successfully employed as adsorbent for various dyes for instance PPy/SD composite was used for adsorption of AO 10 dye in a batch experiment. SD was obtained from Indian tree spurge. The adsorbent successfully removed 243.9 mgg<sup>-1</sup> of dye following pseudo 2<sup>nd</sup> order kinetics. Rate of removal increased with increasing temperature and agitation speed while 4 was optimum pH of reaction. Pseudo 2<sup>nd</sup> order kinetics suggests ion exchange mechanism between positive active sites on PPy and anionic dyes. The anions on its surface were exchanged with anionic molecules of AO10 from solution since they have greater affinity for PPy. Moreover, strong electrostatic forces are operative between positive charge bearing PPy and anionic AO 10 particles. The value of  $\Delta H_{ads}$  measured by (C-C) equation confirmed the ion exchange adsorption. However, these attractive forces were weak enough to recover and reuse the biosorbent [118].

Another such composite was used for adsorption of EY dye where source of SD was balsam tree. The novelty of this composite was electropolymerization of PPy to synthesize a conducting electroactive polymer via following route. A negatively charged ion X<sup>-</sup> was introduced into reaction system which was used by charged polymer to trade with anionic EY molecules and the development of polymeric film through diffusion of anion and electrons across the film. This electroactivity of PPy enables it to be employed in sensors, rechargeable batteries, and controlled drug release. It also allows PPy to adsorb dyes from water system under simple open circuit conditions [15–18]. The sorption

TABLE 5: PPy and its composites used for degradation of dyes.

PPy composites	Characterization	Dye	Adsorption conditions				$Q_{\max}$ (mg g <sup>-1</sup> )	Source
			Adsorbent (g/L)	Temp (°C)	pH	Tim (min)		
PPy/Ze	Tem,SEM,XRD	RB	1.8	50	9	60	122.32	[108]
PPy/TiO <sub>2</sub>	XPS, BET	MB	0.3	25	13	120	273.22	[109]
PPy NF/Zn-Fe LDH	XRD, FT-IR, HSEM, HRTEM, BET	Sf	0.05	25	8	120	63.4	[110]
PPy/ZnO	XRD, FTIR, TEM	BG	0.075	45	7	20	140.8	[111]
PPy/SBA-15	XRD, TGA, FTIR	MO	0.025	20	6.5	15	41.66	[112]
PPy/Atp/Fe	TEM, XRD XPS	NGB	1.0	25	6	25	253.9	[113]
PPY/Chl	SEM, FTIR	CR	0.05	30	5	20	772.7	[114]
PPy/Fe <sub>3</sub> O <sub>4</sub> mnps	SEM, FTIR, XRD	RB19	0.02	25	3	10	112.36	[115]
PPy/SiO <sub>2</sub>	FTIR,XRD,TGA,TEM,SEM	AO7	1.0	55	3	90	181.4	[116]
PPy/TiO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	SEM, FT-IR, XRD,TGA	AR G	2.0	25	7	120	161.8	[117]

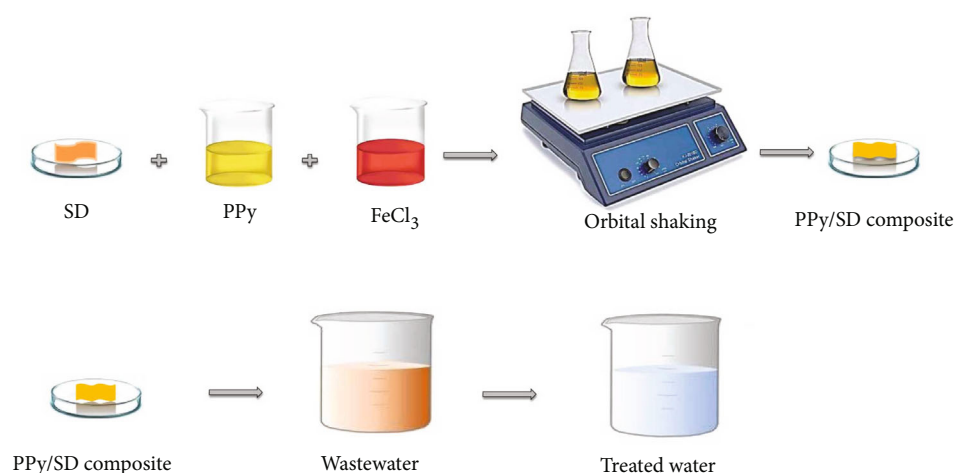


FIGURE 4: Diagrammatic description of synthesis of PPy/SD composite.

procedure was carried out via both batch and continuous process. The experimental data showed agreement with pseudo 2<sup>nd</sup> order mechanism. Since the batch process is not considered reliable for commercial scale projects, column adsorption studies were carried out using 0.05 M NaOH and HCl solutions. Alkali treatment was able to successfully recover the polymer. The excessive OH<sup>-</sup> were able to expel the adsorbed EY ions from PPy due to electrostatic or coulombic repulsions and 99% dye was desorbed [119].

In another study, PPy/SD composite was prepared by using SD obtained from walnut wood source. This adsorbent was utilized for degradation of MB dye under various conditions like pH, contact time, dose etc., and the results were compared with untreated walnut SD. Adsorption of MB varied directly with pH while at lower pH there were a higher number of H<sup>+</sup> ions in solution that repulsed the incoming positively charged dye particles. At higher pH, this electrostatic repulsion was dropped and adsorption activity increased. Adsorption data also varied directly with adsorbent dosage due to addition to surface area and availability of more active sites. PPy/SD composite ( $Q_{\max}$  34.36 mg/g) was better adsorbent for the adsorption of MB than untreated SD ( $Q_{\max}$  19.41 mg/g). However the drawback of

this study was unsatisfactory recovery rate of PPy/SD which was possibly due to strong binding forces between highly polar functional groups on PPy and MB dye. Conversely, lower cost and ease of accessibility of raw materials alleviated the concern [120].

**3.4. PPy/Rice Milling Waste-Based Biocomposites for Dyes Adsorption.** Rice bran is another organically abundant agro waste which is a side product of rice milling and hence it is low cost and easily accessible. A PPy/Rb biocomposite was synthesized for adsorption studies of MG dye [121]. The composite was prepared by mixing Rb and PPy in a simple process in which refined Rb was treated with a mixture of 5% soln of surfactant, salts, and metallic ions, and subjected to shaking for 2 hrs at room temperature. PPy/Rb composite was prepared by mixing FeCl<sub>3</sub> soln to pyrrole solution and 1 g of Rb was added to this mixture, it was agitated for 180 minutes. The final product was removed from solution via filtration, cleansed with H<sub>2</sub>O and C<sub>2</sub>H<sub>5</sub>OH. It was further dried at 50°C for 2 days in oven. This composite was employed in MG dye adsorption. The optimum conditions were reached at 50°C temperature, 1 hr contact time, 0.05 g/L adsorbent dose at acidic pH following a pseudo

2<sup>nd</sup> order mechanism. It was easily separable post adsorption and was reused. The presence of natural component in this composite helped capturing the dissolved contaminants [122, 123]. It was reported that calcination of rice milling waste in a polymeric composite forms a network of SiO<sub>2</sub> on surface of respective polymer and modifies and strengthens its mechanical properties.

These agro waste composites are further modifiable by morphological changes or incorporation of other additives. For instance, a PPy/PMMA/Rh composite membrane was prepared and utilized for E 102 and IC dyes removal [124]. Membranes provide a highly porous surface for more effective adhesion of the contaminant molecules and are ideal to be used in the remediation of wastewater [125, 126]. Especially, there is a growing interest in polymeric composite membranes composed of PPy, PMMA, and PANi owing to their ease of synthesis, impressive biocompatibility, and sustainability. PPy/PMMA/Rh composite was prepared following an electrospinning technique followed by in situ polymerization. The incorporation of Rh on the PMMA results in a reinforced membrane but PPy behaves as conducting polymer and controls the interaction between composite and dye molecules. For synthesis of this composite, Rh was passed through a series of pretreatment steps including washing, drying, charring, maceration, etc. Rh dissolved in DMF was ultrasonicated for 1/2 hr and PMMA was added to this dispersion and reacted for 24 hrs at 40°C. 2 mL of this PMMA/Rh mixture was injected to a stainless steel needle of an electrospinning system and electro-spun at a voltage of 17 kV. These membranes were alternatively sandwiched between Al sheets and left in oven 2 days at 100°C for heat treatment. The membranes were then sliced up to thickness of 0.02 m<sup>2</sup>sq, treated in air plasma system for few minutes and PPy was added in the end in situ (Figure 5). The composite membrane was able to remove 165.7 mg/g of E 102 and 142.9 mg/g of IC within an hour in acidic media and the membranes were reusable up to 5 consecutive cycles without any considerable loss in their activity. The combined privilege of an easy recovery of the adsorbed dye along with the opportunity of reusing the adsorbents makes these membranes attractive substitute for remediation of wastewater polluted with contaminations of different nature.

**3.5. PPy/Agrarian Peeling-Based Biocomposites for Dyes Adsorption.** Agrarian waste is considered as a potential substitute for the remediation of dyes effluents from wastewater compared to high end commercial adsorbents which are not only expensive but also produce by-products that may be hazardous to human health. Hence, scientists are in quest of finding cost-friendly, productive, and green sources to accomplish their mission [127–129]. The residual waste recovered from agricultural industry are low-priced, biodegradable, accessible without much effort, and do the job almost as good as synthetic adsorbents so they are an ideal choice, e.g., peanut hulls, garlic peels, sugarcane bagasse, pineapple peels, orange peels, pitahaya peels, pumelo peels, bamboo shells, coconut shells, ground nut shells, etc. [130–138]. Figure 6 shows a general procedure of synthesizing PPy/Agro waste-based bio-composites.

Biocomposites of these agro waste materials even enhance their adsorption potential such as peanut waste's composite with PPy which was utilized for adsorption of CV dye. It was synthesized following a reported method and adsorption was carried out in batch mode. 150.16 mg/g dye was removed in an hour. The optimized conditions were found to be 50°C temperature, 50 mg dose, and >8 pH. The adsorption potential of PPy/pH was much higher than simple agro waste (i.e. 33.23 mg/g) [139].

Agrarian peelings such as Chinese yam peelings which (CY) are obtained from Chinese Yam, one of popular cuisine in China can be used as potential adsorbents for water purification. It is composite with PPy was successfully used for adsorption of CR dye from waste water. Simplistic synthesis, affordable price, and outstanding adsorptive potential are the prominent aspect of this PPy/CPy composite. Post in situ synthesis and characterization of adsorbent, it was utilized for adsorption of CR under different factors like pH, temperature, etc. 86% of 100 ppm CR dye was adsorbed in 2 hrs using 10 g/L adsorbent at 45°C which reached up to 98.9% in 20 hrs. The adsorbent was recyclable and could be utilized thrice post recovery [140].

Another agrarian waste is sugarcane bagasse, a dried fibrous residue collected after crushing sugarcane stalks for their utilization in milling. It was combined with PPy as a biocomposite and employed in removing AB 234. The optimum conditions for adsorption of 100 mg/g dye were found to be pH 3, adsorbent dose 50 mg for contact time of 1 hr in a pseudo 2<sup>nd</sup> order reaction. Its remarkable performance makes it an ideal adsorbent for wastewater purification [70].

**3.6. PPy-/Chs-Based Biocomposites for Dyes Adsorption.** Chitosan (Chs) is an organic, biodecomposable, innocuous polysaccharide-based macromolecule. It is easily accessible and can be decomposed by microbial enzyme catalysis. –NH<sub>2</sub> and –OH groups on its surface make it a good adsorbent for heavy metals and dyes [141].

Chs has the ability to be adsorbed on PPy surface and used as a size stabilizer during the polymerization. This modification inhibits the clumping of PPy particles and makes adsorption process more coherent, productive, less time consuming, and economical through an effortless recovery of adsorbent. One such PPy/Chs composite was utilized for adsorptive removal of AR 18 dye. Composites of different mass ratios were prepared by a simple method in which PPy monomer was thoroughly mixed with glacial CH<sub>3</sub>COOH by constant shaking till formation of a pale yellow soln. Powdered Chs was then mixed in it and it was subjected to shaking once again till it got dispersed. NH<sub>4</sub>S<sub>2</sub>O<sub>8</sub> dissolved in CH<sub>3</sub>COOH was added to this mixture and reacted for 12 hrs. The final product was separated from solution via filtration and oven dried at 60°C. The adsorbent was structurally characterized and employed for adsorption of AR 18. 98.71% of dye was removed in half hour in a pseudo 2<sup>nd</sup> order reaction and adsorbent was reusable for 4 cycles. Actually there seemed to be strong electrostatic forces and H-bonding operating and binding the dye particles to adsorbent's surface which made adsorption feasible [142].

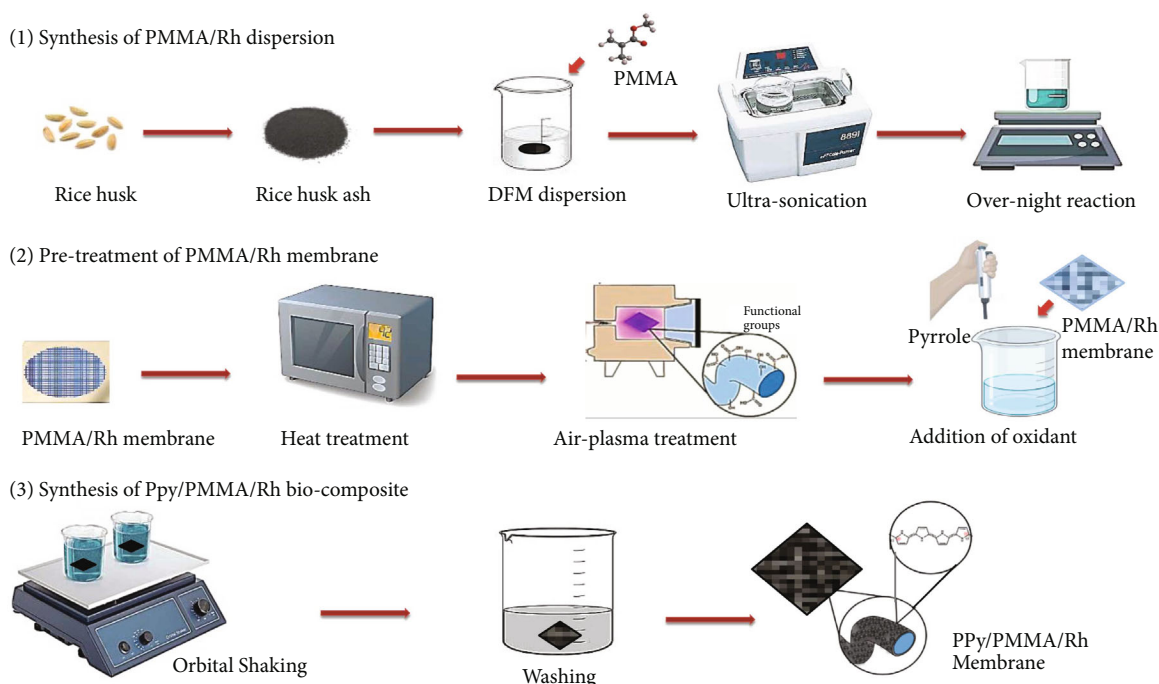


FIGURE 5: Synthesis of PPY/PMA/Rh membrane biocomposite.

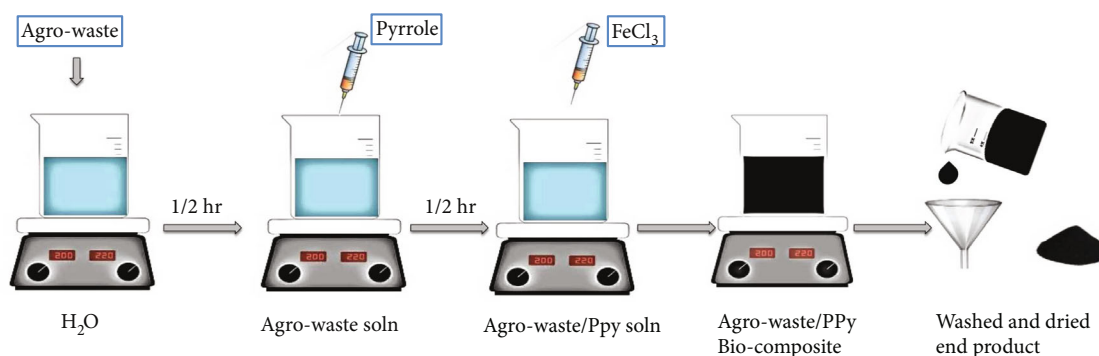


FIGURE 6: General schematic representation of synthesis of PPY/agrarian waste-based biocomposites.

Various modifications are introduced to enhance adsorption potential of PPY/Chs composites. One such modification is magnetization by  $\text{Fe}_2\text{O}_3$  nps. Properties of  $\text{Fe}_2\text{O}_3$  such as magnetic susceptibility, prolificacy, and bioadaptability make it ideal water disinfectant. Thus, hybridization of these magnetic nps with other adsorbent can expand its surface area, multiplicities its porosity, elevate its adsorption activity, and eases its recovery after adsorption is accomplished [39, 40]. It also expands an adsorbent's adsorption range by improving its affinity for cationic and anionic dyes. One such PPY/Chs/Fe composite was employed for successful adsorption of CV and MO dye and various factors such as dyes concentrations, pH of the soln, adsorbent dose, contact time, and temperature, etc., were optimized in a batch process. 88.11% of CV and 92.89% of MO were successfully removed following pseudo 2<sup>nd</sup> and pseudo 1<sup>st</sup> order, respectively. Recovery of adsorbent was simple and effectual and it was reusable up to 3 cycles. This unique coupling of PPY/

TABLE 6: List of common PPY-/Chs-based biosorbents used for removal of dyes.

PPy/chitosan Biocomposites	Dye	Adsorption potential ( $\text{mg g}^{-1}$ )	Sources
PPy/Chs	AO-RL	76.9	[144]
PPy/Chs	CR	73.2	[145]
PPy/Chs/LS	CR	90.7	[145]
PPy/Chs/GO	P4R	6.799	[146]

Chs/Fe developed an innocuous, highly effective, eco-friendly adsorbent for wastewater treatment at a very low cost [143]. Table 6 shows some other PPY/Ch based biocomposites used for dyes adsorption.

3.7. PPY/Cellulosic Fiber-Based Biocomposites for Dyes Adsorption. Adding a natural polymer like cellulose in a



minute quantity to PPy during the polymerization reaction shrinks the size of final product and helps it to stabilize with their several functional groups in its structure. These functional groups also boost the chance of contact between adsorbent and active sites of incoming dye particles. Hence adsorption activity is amplified [147, 148]. Furthermore, reduction of cellulose to nanosize can remarkably tune up composite's performance as an adsorbent by expanding its specific surface area and cutting down the distance for intraparticle diffusion. PPy in this equation is a source of provision of high mechanical strength and stability [149, 150].

A PPy/nCl composite was reported to be able to remove CR dye and Cr metal in a binary mixture [151]. Cellulose was first converted to nanocrystalline form by reacting an emulsion of cellulose with 65%  $H_2SO_4$  at 40°C while stirring for 180 minutes. After centrifugation for 10 mins, dialysis was carried out via a dialysis membrane for removing extra acid and it was subjected to ultrasonication in an ice bath [31]. PPy was obtained by the addition of oxidant  $(NH_4)_2S_2O_8$  while stirring constantly. Then nanocrystalline cellulose added to PPy and left at 3°C for 1/2 hr, after that the upper layer was removed and final product was obtained by cryodesiccation. It was employed for batch adsorption of CR from a binary mixture containing Cr(VI) and CR dye under different parameters such as pH, temperature, adsorbent dose, etc. Results showed that even in the presence of secondary contaminants, i.e., Cr ions, 85% was removed under optimum conditions of pH 2, initial concentration of 30 ppm, adsorbent dose of 0.02 g at 30°C temperature. The binary action of this composite makes it a cost-effective and resourceful water purifier.

Even though combination of cellulose and PPy improves their individual performance as adsorbents, another important aspect of adsorption is recycling of adsorbent and reuse which makes it feasible to be employed on commercial scale. One solution to this problem is synthesizing adsorbent with magnetic properties that enables it to be easily recovered under external magnetic field. Fe-based magnetic nps have extraordinary physiochemical properties owing to their mesoscopic effect, paramagnetic property, and benign nature [152]. A magnetic PPy/Cl/Fe<sub>3</sub>O<sub>4</sub> composite was prepared and utilized in adsorptive removal of RB 5 dye from wastewater. Magnetite nps were synthesized by mixing FeCl<sub>2</sub>·4H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O in 1:2 ratio in a mechanical stirrer and magnetite nps were recovered using magnetic force, washed and dried at 60°C overnight. These sonicated magnetite nps were mixed with H<sub>2</sub>O dispersion of  $\alpha$ -cellulose, agitated for 5 min, mixed with pyrrole monomer, and again agitated for 1/2 hr.  $(NH_4)_2S_2O_8$  was added to initiate polymerization and magnetic composite was ready after 120 minutes. It was separated using a magnet, washed, dried, and utilized for adsorption of RB 5 in a batch experiment. 62.31 mg/g RB 5 was absorbed in highly acidic media, i.e., pH 3 as the adsorbent surface acquires an extremely high positive charge at this pH and electrostatic interactions between the dye and adsorbent's surface become more favorable but prominent feature of this study was ease of regeneration and reusing of adsorbent without much loss in its performance, i.e., dye adsorption stayed consistent

(74%, 56%, and 72% for 50 ppm, 100 ppm, and 150 ppm, respectively) for over 2 cycles [153].

#### 4. Effect of Reaction Parameters on Adsorption Potential of PPy-Based Biocomposites

Various reaction parameters control adsorption of dyes via PPy based adsorbent with different intensity as explained below.

*4.1. Effect of pH.* The adsorption of dyes from waste water is pH dependent. Thus, this parameter is thoroughly studied to accomplish maximum adsorption by finding out optimum value for respective adsorption process. Mostly, dyes exhibit high adsorption in acidic media. Tanzifi et al. [154] have reported best pH for removal of RR 56 and RB 160 dyes via PPy/CMC nps at pH values ranging from 1-5. 98% of both dyes were removed under this pH range and the adsorption rate started to drop at higher pH. This adsorption behavior can be ascribed to the change in surface charge of the adsorbent and dye molecules. At pH < 5, the adsorbent was positively charged and sulfonate groups of the dyes were protonated, i.e., SO<sub>3</sub>H and nitrogen atoms of nonaromatic nature. A huge decline of dye adsorption in basic media can be caused by electrostatic repulsion between the negatively charged adsorbent and the deprotonated dye particles. Other than electrostatic interaction, mechanisms like hydrogen bonding and hydrophobic-hydrophobic reactions could also be dominating and controlling the reaction.

However it is not always true. For instance, Ovando-Medina et al. [155] reported better adsorption of MB dye on PPy/Cl composite in alkaline media pH. 143.5 mg/g of dye was absorbed at pH > 6 owing to the positively charged surface of MB dye. At lower pH, H<sup>+</sup> ions on the surface of adsorbent repel the incoming positively charged dye contaminants and this electrostatic repulsion leads to decreased adsorption in this case.

*4.2. Effect of Temperature.* Tasrin et al. [156] reported effect of temperature on adsorption of BB and DB 6 dyes using PPy/nC composite. The results showed that adsorption of BB raised from 7.24 to 20.98 mg/g with increasing temperature from 298 to 323 K. Likewise, adsorption of DB 6 raised from 4.57 to 20.11 mg/g which can be credited to the expansion in size of PPy/nC adsorbent at higher temperature which intensifies hydrophobic interactions between alkyl groups of nanocellulose and dye molecules. At higher temperature, the solution becomes more dilute and motion of the dye molecules increases. Thermodynamic studies signified that adsorption reaction was indeed chemisorption and valence bonds are supposed to be formed via electron sharing between PPy/nC and dyes.

*4.3. Effect of Dosage.* Heybet et al. [157] investigated the effect of adsorbent dose on the adsorption of MB dye using PPy/SA biocomposite for which 50 mL of 10 ppm dye was reacted with different quantities of adsorbent varying from 1 to 5 g. The optimum conditions set for the reaction were 150 rpm agitation speed, 25°C temperature, and 7 pH.

TABLE 7: Optimum conditions for desorption studies of few PPy/Sd adsorbents.

Adsorbent	Dye	Eluent	Adsorbent (g)	Optimum conditions			Desorption %	Source
				Dye (ppm)	Temp (°C)	Time (min)		
PPy/walnut SD	MB	HCl + NaCl (1 M)	1.0	20	25	45	15	[120]
PPY/mixed SD	EY	NaOH (0.05 M)	1.0	50	25	20	96	[119]
PPy/SD films	CM	NaCl (0.05 M)	1.0	50	25	40	98.7	[159]

The effect of dosage on adsorption activity was not very prominent, i.e., only 91.5% to 93.0% increased with increasing it. Hence, adsorption process is not much dependent on this factor. This can be attributed to unavailability of active sites on adsorbent surface after most vacant active sites getting occupied by constant adsorption of dye molecules at each adsorbent dose. Thus, minimum quantity of adsorbent is selected for further studies to minimize the cost to accomplish maximum adsorption.

**4.4. Effect of Contact Time.** Huang et al. [158] studied effect of contact time on adsorption of EY dye using PPy/WS composite as adsorbent. The adsorption study was carried out over time span of 24 hrs. As per results, adsorption was comparatively higher during the first 1.5 hrs, and 90% of dye was removed during first 4 hrs and became constant after 6 hrs. It seemed as if equilibrium was reached by that time. With time, number of active sites on adsorbent decrease due to attachment of adsorbate molecules, and hence further possibility of adsorption decreases. It mostly occurs in cases where number of adsorbent active sites and adsorbate molecules are equivalent. In another procedure, Ansari et al. [159] reported effect of contact time on adsorption of carmoisine dye via a PPy/SD biocomposite where 1 g adsorbent was added to 25 mL of 100 ppm dye for 1 hr duration and adsorption was noted every 10 minutes. The results were pretty much the same showing a very rapid adsorption during initial 40 minutes which became consistent after that.

## 5. Desorption Studies

The main purpose of regenerating adsorbents is to recover their potency to adsorb so that they can be reprocessed and their life cycle can be prolonged. Researchers have come up with 3 different ways to revive these adsorbents depending on the chemical treatment they utilize. These may include treatment of PPy/SD composites using (i) simple H<sub>2</sub>O, (ii) 1 M NaOH solution, or (iii) 1 M HCl/H<sub>2</sub>SO<sub>4</sub> solution. After recycling via these methods, recovered composites are employed for wastewater treatment and regeneration efficacy is measured. It has been reported that NaOH treatment is comparatively better in recycling the adsorbent as clear from Table 7. Desorption studies aid in interpreting the nature of adsorption process and helps in deciding whether the adsorbent is worth implementing on commercial level or not. A successful adsorbent is not only high productive after regeneration but to be also cost-friendly. Ansari and Mosayebzadeh [119] used NaCl and HCl for desorption studies of PPy/Sd composite after its utilization in EY adsorption. The selection of these chemicals was done due

to inclusion of Cl<sup>-</sup> ions based dopant in desorbing the EY anions. The process was carried out by reacting, 1 g of PPy/Sd adsorbent with 50 mL of 50 ppm of EY dye at pH 4. During desorption of H<sub>2</sub>O, 1 M NaCl, 0.1 M HCl, and 0.05 M NaOH were used. The results indicate that 0.05 M NaOH was most successful desorbing agent and more than 99% of adsorbed EY was removed from the PPy/SD column. Using more concentrated, NaOH is likely to elevate the chances of desorption. However, mild concentrations of desorbing agents are used as SD and PPy are not very chemically stable in strong alkaline or acidic media. These results suggest that operative adsorption mechanism is physisorption via ion-exchange process onto adsorbent.

In another study where PPy/Rb composite was used for adsorption of MG dye [121], various concentration of HCl (0.2-1 M) were used as desorbing agent. Dried and used adsorbent was added to different concentrations of HCl and agitated overnight. The adsorbents were then recovered via filtration and reused in a new adsorption cycle. 0.3 M HCl showed highest regeneration efficacy of 50.4% thus HCl can be ideally used to recycle and reemploy such adsorbents.

## 6. Chemical Characterization Techniques

Chemical characterization of PPy and its composites are mostly carried out via following techniques. They are summarized in Table 8.

**6.1. Fourier Transform Infrared (FTIR) Spectroscopy.** It is for vibrational properties of such functional groups that respond immediately even if there is a minor change in structure, e.g., amino acids and cofactors. The technique can be employed for examining a wide range of functional groups, amino acid side chains, and H<sub>2</sub>O molecules. Moreover reaction-induced FTIR can be utilized for recognition of a specific function groups by controlled selection of vibrations specified to that group in a given reaction by using several strategies such as isotope labeling, fixed site mutations, exchange between H isotopes, etc. A growing emphasis on compound modeling and theoretical chemistry has made it obligatory to characterize compound of interest using FTIR spectroscopy and provide specific vital structural and functional information from its data analysis [160]. FTIR spectra are the easiest way to confirm the success of a chemical reaction and formation of a new composite such as FTIR spectra of PPy/SBA-15 Ncps observed a slight shift of absorption bands compared to the reactants (SBA-15 and PPy) endorsing the formation of PPy/SBA-15 Ncps by distribution of PPy on SBA-15. Bands intensity also varied with increasing percentage of PPy in composite. Bands shifting towards

TABLE 8: Summary of characterization techniques used for PPy/agro waste composites reported in this review.

Techniques	Reported studies	Sources
FTIR	PPy/Chs/LS, PPy/Chs, PPy/Cyp	[140, 142, 165]
SEM	PPy/ $\alpha$ -cl, PPy/Lig, PPy/Rha/PMMA,	[124, 166, 167]
TEM	PPy/Ws, PPy/MChs	[143, 158]
XRD	PPY/SBA-15, PPy/nCl, PPy/cl	[112, 151, 156]
TGA	PPy/cl/Fe <sub>3</sub> O <sub>4</sub> , PPy/Chs/Fe <sub>3</sub> O <sub>4</sub> , PPY/CGW	[72, 143, 153]

higher wave number propose that the PPy particles deposited within pores of SBA-15 were smaller than pure PPy [112].

**6.2. Scanning Electron Microscope (SEM).** It is a highly functional technique for the study and characterization of the microstructure morphology and chemical composition of given compound. It has the ability to magnify an image up to resolution of  $\sim 2,000$  Å by amplifying the visual angle with optical lens which is impossible for naked eye which has a resolution of only  $\sim 0.1$  mm at a distance of 25 cm [161]. A PPy/Ze composite's morphological analysis was carried out by SEM and the SEM micrographs suggested spherical shapes of these NCPs piled up as clusters having an average size of 40–80 nm [108].

**6.3. Transmission Electron Microscopy (TEM).** It is another technique for analyzing detailed features of micro sized specimens. This technique also uses an accelerated beam of electrons, which upon passing through a very small piece of sample, generates an image and enables characterization of structure and morphology of sample. The difference between SEM and TEM is that SEM analyzes reflected electron beams while TEM is a study of transmitted electrons [162]. TEM images of PPy/APT-nZVI were compared with its reactants. APT appeared as neat rod-like structures enclosed in PPy microspheres while nZVI nps were finely distributed on its surface. The micrographs confirmed the formation of PPy/APT-nZVI Ncps which was also settled by improved activity of these Ncps compared to single nZVI [113].

**6.4. X-Ray Powder Diffraction (XRD).** It is a quick analysis based on phase identification of a crystalline substance and mostly specifies unit cell dimensions of given substance. The sample should be finely powdered and uniformly distributed. Long range ordered X-rays are passed through sample, X-rays get deflected by crystal since their wavelength is analogous to interatomic spacing in given crystal and thus average bulk composition is determined [163]. The XRD analysis was carried out for PPy/SiO<sub>2</sub> composites. A broad peak at  $2\theta = 21^\circ$  indicated the presence of SiO<sub>2</sub> nps in non-crystalline form [116].

**6.5. Thermogravimetric Analysis (TGA).** Thermal stability of a compound is determined via this technique. The sample is subjected to temperature variations and change in composition/weight is measured as a function of temperature and time. The sample may undergo various physical and chemical reactions such as decomposition, oxidation, vaporization, and sublimation. The fraction of volatile components in sam-

ple of interest is determined by observing change in its weight as it is heated at a constant rate [164]. The ratio of PPy and SiO<sub>2</sub> in the PPy/SiO<sub>2</sub> was determined by TGA. 99.9% decomposition of PPy was observed at 800°C. At 100°C about 9% of weight was lost by evaporation of H<sub>2</sub>O molecules, 40% of remaining weight was lost by 800°C due to the decomposition of Polypyrrole. 52% of remaining weight at 800°C is indicative that PPy:SiO<sub>2</sub> is 0.784 to 1 [116].

## 7. Conclusion

This review compiles detailed information on adsorption potential and consequent decontamination of dyes by PPy based biocomposites. The results reported in the literature depict that PPy biocomposites can easily remove 90% of the dyes from wastewater. The effects of different factors operating throughout the adsorption process and their outcome are also briefly discussed. The utilization of PPy based biocomposite have both its pros and cons. Pros include biocompatibility, fast reaction kinetics, high productivity, renewability, and reusability. However, there are certain limitations such as mechanisms of adsorption and decontamination of dyes not being clearly outlined and mostly assumed on the basis of the kinetics and isotherm models. More comprehensive and elaborative analysis is required to figure out exact nature of interaction between PPy based biocomposites and adsorbates. Hence, the implementation of these biocomposites on industrial scales for the diminution of dyes demands more experimentation and time. Extensive research is critical for commercializing PPy based biocomposite adsorbents, which will offer a new direction in wastewater remediation and alleviate the environmental pollution.

## Abbreviations

AB 234:	Acid black 234
AO7:	Acid orange 7
AO 10:	Acid orange 10
AO-RL:	Acid orange-RL
AR 18:	Acid red 18
ARG:	Acid red G
Atp:	Attapulgit
BB:	Basic blue
BG:	Brilliant green
BSA:	Bovine serum albumin
Chs:	Chitosan
Cl:	Cellulose
CMC:	Carboxymethyl cellulose
Cr:	Chromium

CR:	Congo red
CV:	Crystal violet
CY:	Chinese yam
DB 6:	Disperse blue 6
DB 291:	Disperse blue 291
DMF:	Dimethyl foramide
DR 23:	Disperse red 23
E 102:	Tartrazine dye
EY:	Eosin yellow
GO:	Graphene oxide
IC:	Indigo carmine
LS:	Lignosulfonate
MB:	Methyl blue
MG:	Malachite green
MO:	Methyl Orange
NGB:	Naphthol green B
Nps:	Nanoparticles
OG:	Orange G
PANi:	Poly alanine
P4R:	Ponceau 4R
PH:	Peanut hulls
PMMA:	Polymethyl methacrylate
PPy:	Polypyrrole
Rb:	Rice bran
RB:	Reactive blue
RB 5:	Reactive blue 5
RB 15:	Reactive blue 15
RB 19:	Reactive blue 19
RR 56:	Reactive red 56
Rh:	Rice husk
RhB:	Rhodamine B
RO 16:	Reactive orange 16
SA:	Sodium Alginate
Sb:	Sugarcane bagasse
SD:	Saw dust
Sf:	Safranin
WS:	Wheat shells
Ze:	Zeolite

## Data Availability

All data presented here is along with references.

## Conflicts of Interest

Authors have no conflict of interest regarding publication of this paper.

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