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REVIEW ARTICLE

Application of polyaniline-based adsorbents for dye removal from water and wastewater—a review

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Abstract

Several industries release varying concentration of dye-laden effluent with substantial negative consequences for any receiving environmental compartment. The control of water pollution and tighter restriction on wastewater discharge directly into the environment to reduce the potential ecotoxicological effect of dyes is forcing processors to retreat and reuse process water and chemicals. Among the different available technologies, the adsorption process has been recognized to be one of the finest and cost-effective wastewater treatment technologies. Various adsorbents have been utilized to remove toxic dyes from water and wastewater. Here, we review the application of polyaniline-based polymeric adsorbent for the adsorption of dyes which have been received considerable attention. To date, various modifications of polyaniline have been explored to improve the adsorption properties. Review on the application of polyaniline for adsorption of dyes has not been present till date. This article provides relevant literature on the application of various polyaniline composites for removing dyes, and their adsorption capacities with their experimental conditions have been compiled. It is evident from the literature survey that polyaniline provides a better opportunity for scientists for the effective removal of various dye.

Keywords Dyes · Dye pollution · Polyaniline · Adsorbents · Wastewater treatment · Dye removal

Introduction

The intensification of industrial activities, rapid growth of mankind, society, science, and technology since the latter half of the nineteen century and throughout the twenty century, our world is reaching new high horizon and alternatively causes severe environmental pollution with dramatic consequences in atmosphere, water, and soil and leads to the major global concern (Cherniwchan 2012; Ahuti 2015). Besides other prerequisites, the demand for water has increased enormously in the agricultural, domestic, and industrial sectors. Thus, the high volume of wastewater containing a number of dangerous and virulent contaminants (like heavy metals, dyes, radioactive elements, and pesticides) are produced. This causes environmental pollution and their toxicity leads to the major problem around the globe (Jarup 2003; Kar et al. 2008; Jadhav et al. 2010; Schwarzenbach et al. 2010; Qamruzzaman and Nasar 2014a, b, c, 2015; Chang et al. 2014, 2018). One of the common class of pollutants is a dye, which has high color intensity, toxicity, synthetic origin, and complex molecular structure making it stable and difficult to be biodegraded (Forgacs et al. 2004; Revankar and Lele 2007; Mittal et al. 2010). Presence of dyes in water bodies increases the BOD level and reduces the light penetration; this consequently causes dramatic changes in the aquatic life as well as on human and terrestrial animals (Deshannavar et al. 2016; Nasar and Shakoor 2017). Dye molecules consist of two key components: chromophore, responsible for imparting color and auxochrome helps in improving the color attraction. Chromophore consists of the conjugated double bond and shows characteristic absorption of electromagnetic radiation in the visible region. An auxochrome is a functional group of atoms attached to the chromophore which modifies the ability of the chromophore to absorb light by altering the wavelength or intensity of the absorption (Gürses et al. 2016). Dyes have substantial structural diversity and can be classified in many ways such as on the basis of their sources (natural and synthetic dyes), nature of chromophore group (acridine, anthraquinone, arylmethane, azo, nitroso, xanthene, indophenol

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dyes), and their application to substrates (acidic, basic, disperse, azoic, direct, nitro, anthraquinone, vat, mordant, sulfur, solvent, reactive dyes, etc.) (Adegoke and Bello 2015; Nasar and Shakoor 2017). The dyes are used to color large varieties of substrate materials such as cotton, wool, silk, nylon, polyester, acrylic fiber, paper, paint, leather products, inks, printer cartridge, food products, cosmetics, plastics, gasoline, lubricants, oils, and waxes, wood, soaps and detergents, fibers, oils, paints, and plastics. Because of huge applications in diversified fields, large quantities of dyes are used throughout the world. There is a long list of dyes available in the market with approximately 7×10^5 tonnes (with more than 10,000 types) of annual consumption, and this value is likely to drive due to increased high-performance colorants, increased consumer preference is expected to propel coloring needs (Shanker et al. 2017). The large consumption of dyes by several industries such as textile, dyeing, paper, tannery, and paint results in the release of effluents containing dyes in sufficient quantities. A large volume of dye-loaded wastewater is generated, and in most cases, it is directly discharged to the freshwater system without proper treatment. Dyes are considered a disagreeable class of pollutant because they are toxic. Dyes can cause problems such as skin irritation, respiratory diseases, mental disorder, vomiting, and in many cases they may be carcinogenic and mutagenic (Prüss-Ustün et al. 2011). Further dyes impart color to water which is observable to the naked eye and therefore highly disagreeable on aesthetical aspects. Besides this, dyes also interfere with the transmission of light and disturb the biological metabolism processes which cause a serious threat to the aquatic life of the ecosystem. Thus, sequestration of dyes from the wastewater is of great worry from the human and ecological point of views as well. During recent years, several physical, chemical, and biological technologies have been developed and used for the treatment of wastewater containing dyes and other contaminants.

Wastewater treatment technologies

Wastewater treatment methods were first developed in response to the adverse conditions caused by the release of untreated effluent directly to the environment and the concern for human health. People started showing responsiveness toward the environment when it started causing a lot of distress not only to humans but also to the animals, driving many species to endangerment and even extinction. The water treatment method consists of preliminary, primary, secondary, and tertiary or advanced wastewater treatment (Amit Sonune 2004). Preliminary treatment methods involve the removal of rags, grits, papers, clarification, coarse screening, and comminution of large solids along with the removal of oil and grease which impede efficient wastewater treatment and also alleviate the biological oxygen demand of the wastewater. The purpose of primary treatment is the elimination of settleable organic and inorganic materials by sedimentation and the exclusion of solid that will froth by skimming. The ambition of secondary treatment is the further handling of the discharge from primary treatment to eradicate the residual organics and suspended solids (Stasinakis et al. 2013). Secondary treatment method involves the elimination of biodegradable dissolved and colloidal organic matter using aerobic treatment (such as activated sludge, aerated lagoons, constructed wetland, membrane bioreactor, biofilters, aerobic bioreactor, anaerobic bioreactor, microalgae bioreactor, vermifilter, trickling filter, rotating biological contactors, facultative lagoons, and biooxidation process). In the advanced wastewater treatment methods, physical (such as sedimentation, coagulation-flocculation, reverse osmosis, ultrafiltration, microfiltration, nanofiltration, adsorption), chemical (such as ion exchange, chemical precipitation, Fenton/photo-Fenton/electro-Fenton oxidation, ozonation, photolysis, photocatalysis, solar driven, ultrasound process), and biological (microbial degradation) technologies are employed for the treatment of wastewater containing contaminants such as dyes and other contaminants such as heavy metals, radioactive materials, additional suspended solids, refractory organics, and dissolved materials which cannot be aloof from secondary treatment (Kurniawan et al. 2006). Each of the above techniques has some merits and demerits (Gogate and Pandit 2004; Singh and Arora 2011; Ahmed et al. 2017; Cai et al. 2017). The advantages and disadvantages of some commonly used treatment methods, primarily for the removal of dyes, are briefly summarized in Table 1. Amongst the different available techniques, adsorption has received considerable attention due to its several advantages regarding cost, ease of operation, flexibility, and simplicity of design and insensitivity to toxic pollutants.

Adsorption methods and choice of adsorbent

Adsorption method has been widely accepted as one of the most effective wastewater treatment techniques to reduce hazardous inorganic and organic pollutants present in the effluent because it is rapid, convenient, cheap, effective, efficient, producing nontoxic by-product, and simple in operation design (Lee et al. 2006; Raval et al. 2016). Further, in many cases, the adsorption is a reversible process, and therefore, the adsorbents can be regenerated for repeated use, and therefore, the method becomes more economical. An ideal adsorbent for dye removal should have a number of desirable properties such as large surface area, porosity, high adsorption capacity, easy availability, mechanical stability, economically feasible, compatibility, ease of regeneration, eco-friendly, and high selectivity, to remove a wide range of dyes (Yagub et al. 2014). Further, the adsorbents should be nontoxic, effortlessly

Table 1 Treatment technologies for the wastewater laden dyes and associated advantages and disadvantages (Gogate and Pandit 2004; Singh and Arora 2011; Ahmed et al. 2017)

Treatment methods	Advantages	Disadvantages
Fenton's reagent (H_2O_2 + Fe(II)salt)	Effective and proficient in treating soluble and insoluble dye, suitable for the contaminants which are resistant to biological treatment, or poisonous to live biomass, less expensive	Sludge generation through the flocculation of the reagent and the dye molecules, sludge disposal problem, and the requirement of strict pH control
Ozonation	Applied in a gaseous state, no chance of sludge formation	Shorter lifetime, high cost, formation of oxidative by-products, ozone decomposes in the alkaline atmosphere, and so careful monitoring of the effluent pH is needed
Ion exchange	Regeneration of adsorbent, no sludge generation, and less time consuming	Highly pH sensitive, adsorbent requires regeneration or disposal, high capital cost, and not effective for all dyes
Chemical precipitation	Simple, ease of handling	Require a large amount of chemicals, excessive generation of sludge
Irradiation	Effective at laboratory scale	The necessity of dissolved oxygen
Photocatalysis	Rapid and efficient destruction of pollutants	Production of by-products, long-durational time, and limited application
Electroflotation	High separating efficiency, simple to operate, and few accessories required	Power consumption, difficulty in pH control
Magnetic separation and purification technique	Induced separation and purification of magnetically influenced contaminants	The collection of particles depends strongly on the creation of large magnetic field gradients, as well as on the particle size and magnetic properties
Electrochemical method	No chemical consumption, rapid and selective process	Long-term operational and maintenance costs, continuous energy supply
Electrokinetics	Cost-effective	Large sludge production
Coagulation and flocculation	Cost-effective, efficient, simple to operate, and complete decolorization of the waste stream	Bulk of toxic sludge production, not environmentally sustainable technique
Electrodialysis	Highly efficient	The high cost of maintenance, energy consumption
Ultrafiltration	Low energy input, best pollutant removal technique	Additional chemical agents are required for aggregation of pollutants
Nanofiltration	Highly efficient, separation of low molecular weight compound	Fouling of membrane during operation, production of concentrated sludge
Reverse osmosis	Maximum salt rejection	Require high pressure, high operation cost, and susceptible to membrane fouling
Aerobic	High organic pollutant removal efficiency	High sludge production, high nutrition requirement
Anaerobic	High organic removal efficiency, bioenergy, or nutrient recovery	Moderate effluent quality, high odor problem
Adsorption	Simple, effective, easy and widely used technique, suitable for toxic species, inexpensive, adsorbents can be obtained from waste materials, regeneration of adsorbent is possible, flexibility, and simplicity of design,	Efficiency depends upon the nature of adsorbents. Some adsorbents are very costly

available, and can easily be regenerated. Because of the benefits of the large surface area, microporous structure, uniform pore size distribution, high porosity, high surface reactivity, superior mechanical strength, and high adsorption capacity, activated carbon is the most attractive and has been considered as a perfect adsorbent for the subtraction of dyes, heavy metals, and other pollutants from wastewater. However, activated carbon has many disadvantages like high cost, regeneration problem, and ineffectiveness against disperse and vat dyes (Yagub et al. 2014). The purification of the large volume of wastewater by using expensive starting material is not justified. Thus, the attention has been shifted towards the development and utilization of cost-effective alternative adsorbents for such purpose. However, many alternative low-cost adsorbents have the drawback of low surface area and porosity. The drawback of low porosity can be overcome by the activation process (Chang et al. 2015). A variety of adsorbents based on wastes, natural and synthetic materials have commonly been used for the removal of dyes from water and wastewater. The adsorption capacity of dyes on these adsorbents along with their experimental conditions are given in Table 2 with some of them are briefly discussed below.

Agricultural, industrial, and domestic waste materials

The most convenient choice was to utilize the agricultural, industrial, and domestic residues or wastes as adsorbents for the effective decontamination of water. This is because of the facts that these materials have no or very little economic value and often associated with the disposal problem. These waste materials have been very commonly preferred to be exploited as adsorbents even without chemical modification or thermal activation. The waste materials have unlocked the door for researchers into the production of alternative adsorbents to replace the expensive activated carbon. Researchers effectively utilized many waste materials for the effective confiscation of dyes from aqueous solution. These include almond shell (Doulati Ardejani et al. 2008; Ben Arfi et al. 2017), bagasse ash (Gupta et al. 2000), banana peel (Amela et al. 2012; Munagapati et al. 2018), blast furnace slag (Gao et al. 2017a), bleached oil mill waste (Rizzi et al. 2017), bottle gourd peel (Palamthodi and Lele 2016), chestnut husk (Georgin et al. 2018), citrus limetta peel (Shakoor and Nasar 2016), coffee waste (Franca et al. 2009; Kyzas et al. 2012; Lafi et al. 2014; Anastopoulos et al. 2017b), coir pith (Kavitha and Namasivayam 2007), corn stalks (Fathi et al. 2015), cucumis sativus peel (Lee et al. 2016; Smitha et al. 2017; Shakoor and Nasar 2017), egg shell (Mittal et al. 2016), elephant grass (Menkiti et al. 2018; Aniagor and Menkiti 2018), fly ash (Mohan et al. 2002; Sun et al. 2010; Gao et al. 2017b), garlic peel (Hameed and Ahmad 2009), garlic root (Ren et al. 2016), glossogyne tenuifolia leaves (Yang and Hong 2018), gram seed husk (Somasekhara Reddy et al. 2017), limonia acidissima (Sartape et al. 2017), melon peel (Djelloul and Hamdaoui 2014), mussel shell (Papadimitriou et al. 2017), olive pomace boiler ash (Marrakchi et al. 2017), orange peel (do Nascimento et al. 2014; Hai 2017), peanut hull (Allen et al. 2005; Tanyildizi 2011; do Nascimento et al. 2014; Wang et al. 2017), pomelo peel (Argun et al. 2014), punica granatum peel (Shakoor and Nasar 2018a), red mud (Namasivayam and Arasi 1997; Gadigayya Mavinkattimath et al. 2017), rice husk (Vadivelan and Kumar 2005; Mane et al. 2007; Han et al. 2008; Chieng et al. 2013; Chowdhury et al. 2013; de Azevedo et al. 2017), sawdust (Shaaban et al. 2013; Aljeboree 2016; Deshannavar et al. 2016; Djilali et al. 2016; Shakoor and Nasar 2018b; Mashkoor et al. 2018), steel and fertilizer industry waste (Bhatnagar and Jain 2005), sugarcane bagasse (Chakraborty et al. 2012; Fideles et al. 2018), sugar industry wastes (Anastopoulos et al. 2017a), sumac leaves (Gülen et al. 2016), tea waste (Foroughi-Dahr et al. 2015), timber industry waste (Garg 2004), walnut shell (Gallo-Cordova et al. 2017), lotus seed (Nethaji et al. 2013), and corncob (Hou et al. 2013) that have been exploited as a low cost, eco-friendly, and easily available adsorbents.

Inorganic materials

Many researchers have used the inorganic adsorbents to achieve the higher adsorption capacity. Natural and modified clay minerals are well known, familiar, and potential adsorbent for the confiscation of dyes from contaminated water. The clay adsorbent has advantages over the other commercially available adsorbents in terms of economic, abundant in nature, high effective surface area, high adsorption capacity, nontoxic nature, and exhibit strong attraction for both heteroatomic cationic and anionic dye (Ngulube et al. 2017). Clays also comprise interchangeable cations and anions present on the surface and for these reasons, the attention of researchers has been focused on natural and modified clay for wastewater purification. In recent years, interest has been growing extensively towards clay minerals such as bentonite (Tahir and Rauf 2006), kaolinite (Ghosh and Bhattacharyya 2002; Abidi et al. 2017), diatomite (Al-Ghouti et al. 2005), and Fuller's earth (Shah et al. 2017), because of their ability to interact with dye molecules and purify contaminated water. Natural zeolite is the hydrated aluminosilicates porous mineral, found abundantly in nature, low-cost resource, and significantly used as an adsorbent for decontamination of wastewater (Meshko et al. 2001; Armağan et al. 2004; Alver and Metin 2012; Humelnicu et al. 2017). From the earlier decade, explosive interest has also been shown in ordered mesoporous silica-based materials, high-specific surface area, uniform pore distribution, and high adsorption capacity; these

Table 2 Dye adsorption capacities for different adsorbents based on agricultural, industrial, and domestic waste sand inorganic materials

Adsorbent	Dye	Experimental conditions			Adsorption capacity (mg/g)	Maximum adsorption capacity*	Reference
		pH	Concentration (mg/L)	Temperature (°C)			
Almond shell	Eriochrome Black T	4.8	100	22	15.26	123.92	(Ben Arfi et al. 2017)
Almond shell	Malachite green	4.8	100	22	48.71	126.90	(Ben Arfi et al. 2017)
Banana peel	Reactive Black 5	4	100	25	13.4	21.2	(Munagapati et al. 2018)
Banana peel	Congo red	4	100	25	76.2	111.8	(Munagapati et al. 2018)
Citrus limetta peel	Methylene blue	9	50	25	23.26	227.3	(Shakoor and Nasar 2016)
Spent coffee ground	Methylene blue	5	50	25	4.45	18.73	(Franca et al. 2009)
Coffee waste	Toluidine blue	6	80	20	14.29	142.5	(Lafi et al. 2014)
Coffee waste	Crystal violet	6	80	20	13.016	125	(Lafi et al. 2014)
Coir pith carbon	Methylene blue	6.9	40	35	1.85	5.87	(Kavitha and Namasivayam 2007)
Corn stalks	Direct Red 23	3	10	45	2.64	Freundlich	(Fathi et al. 2015)
Cucumis sativus peel	Methylene blue	8	100	25	21.46	Freundlich	(Shakoor and Nasar 2017)
Cucumis sativus	Crystal violet	7	50	27	11.83	33.22	(Smitha et al. 2017)
Cucumis sativus	Rhodamine B	7	50	27	10.86	40.82	(Smitha et al. 2017)
Fly ash	Acid Black 1	–	100	20	10.42	18.94	(Sun et al. 2010)
Fly ash	Acid Blue193	–	100	20	11.01	22.20	(Sun et al. 2010)
Fly ash	Reactive red 23	–	100	20	2.11	5.04	(Sun et al. 2010)
Fly ash	Reactive Blue 171	–	100	20	1.87	3.75	(Sun et al. 2010)
Garlic peel	Methylene blue	–	100	30	63.69	Freundlich	(Hameed and Ahmad 2009)
Garlic root	Malachite green	–	50	25	38.46	172.41	(Ren et al. 2016)
Bengal Gram Seed Husk	Congo red	7.3	50	30	7.90	41.66	(Somasekhara Reddy et al. 2017)
Melon peel	Methylene blue	5.3	100	25	45.45	333	(Djelloul and Hamdaoui 2014)
Luffa aegyptica peel	Malachite green	7	50	30	70.21	166.67	(Mashkoor and Nasar 2019)
NaOH-Luffa aegyptica peel	Malachite green	7	50	30	78.79	161.29	(Mashkoor and Nasar 2019)
K_2CO_3-activated olive pomace boiler ash	Acid blue 29	–	100	30	31.09	38.48	(Marrakchi et al. 2017)
K_2CO_3-activated olive pomace boiler ash	Methylene blue	–	100	30	37.15	149.11	(Marrakchi et al. 2017)
Peanut hull	Remazol Golden Yellow RNL-150%	2	–	25	10.4	15.4	(do Nascimento et al. 2014)
Peanut hull	Gray Reactive BF-2R	2	–	25	10.2	12.7	(do Nascimento et al. 2014)
Peanut hull	Reactive Turquoise Q-G125	2	–	25	15.4	18.3	(do Nascimento et al. 2014)

Table 2 (continued)

Adsorbent	Dye	Experimental conditions			Adsorption capacity (mg/g)	Maximum adsorption capacity*	Reference
		pH	Concentration (mg/L)	Temperature (°C)			
Orange peel	Remazol Golden Yellow RNL-150%	2	–	25	5.49	5.63	(do Nascimento et al. 2014)
Orange peel	Gray Reactive BF-2R	2	–	25	12.9	11.4	(do Nascimento et al. 2014)
Orange peel	Reactive Turquoise Q-G125	2	–	25	16.8	–	(do Nascimento et al. 2014)
Pomelo peel	Reactive Blue 114	2	–	30	9.9	16	(Argun et al. 2014)
Starch/rice husk ash	Methylene blue	5	2000	33	1906.3	2225	(de Azevedo et al. 2017)
Rice husk ash	Brilliant Green	3	50	30	8.24	25.13	(Mane et al. 2007)
Terminalia arjuna sawdust	Crystal violet	7	50	25	7.80	Freundlich	(Shakoor and Nasar 2018b)
Tectona grandis Sawdust	Crystal violet	7.5	50	25	23.74	131.58	(Mashkoor et al. 2018)
Coir pith carbon	Congo Red	7.7	20	35	3.096	6.72	(Namasivayam and Kavitha 2002)
Orange peel	Direct Red 23	2	50	25	10.72	–	(Arami et al. 2005)
Orange peel	Direct Red 80	2	50	25	21.05	–	(Arami et al. 2005)
Polyacrylamide hydrogel	Direct red 31	3	50	25	47.058	155.28	(Didehban et al. 2017)
Polyacrylamide hydrogel	Reactive orange 20	3	50	25	49.14	Freundlich	(Didehban et al. 2017)
Polyacrylic acid hydrogel	Direct red 31	1.5	50	25	39.32	143.88	(Didehban et al. 2017)
Polyacrylic acid hydrogel	Reactive orange 20	2	50	25	13.10	Freundlich	(Didehban et al. 2017)
Polyacrylamide	Methyl violet	7	50	25	549	1136	(Rahchamani et al. 2011)
Polyvinyl alcohol	Bromothymol blue	6	30	25	92.5	276.2	(Agarwal et al. 2016a)
Polyvinyl alcohol	Methylene blue	6	30	25	80	123.3	(Agarwal et al. 2016a)
Chitosan/montmorillonite	Congo red	7	400	30	50.63	54.52	(Wang and Wang 2007)
Cyclodextrin/Carboxymethylcellulose	Malachite Green	8	40	25	8.2	91.9	(Crini et al. 2007)
Magnetic chitosan/poly(vinyl alcohol) hydrogel beads	Congo Red	–	–	25	12.8	467.3	(Zhu et al. 2012)
Carbon slurry-based carbonaceous material	Chrysoidine G	–	–	25	–	80.6	(Jain et al. 2003)
Carbon slurry-based carbonaceous material	Crystal violet	–	–	25	–	163.0	(Jain et al. 2003)
Carbon slurry-based carbonaceous material	Meldola blue	–	–	25	–	171.2	(Jain et al. 2003)
Rubber tire-activated carbon	Acid Blue 113	2	–	25	9.72	9.2	(Gupta et al. 2011)
Commercial-activated carbon	Acid Blue 113	5	–	25	7.84	7.19	(Gupta et al. 2011)
Fe (III)/Cr (III) hydroxide	Direct red 12B	–	10	–	0.873	5	(Namasivayam and Sumithra 2005)
Fe (III)/Cr (III) hydroxide	Methylene blue	–	10	–	2.24	22.8	(Namasivayam and Sumithra 2005)

Table 2 (continued)

Adsorbent	Dye	Experimental conditions			Adsorption capacity (mg/g)	Maximum adsorption capacity*	Reference
		pH	Concentration (mg/L)	Temperature (°C)			
Calcium alginate-MWCNT	Methylene blue	7	100	25	190.5	606.1	(Sui et al. 2012)
Calcium alginate-MWCNT	Methyl orange	7	100	25	11.4	12.5	(Sui et al. 2012)
$CoFe_2O_4$-MWCNT	Methylene blue	–	5	25	9.8	11.1	(Farghali et al. 2012)
Porous carbon nanosphere	Methylene blue	–	250	–	624.7	3152	(Chang et al. 2013)
Porous carbon nanosphere	Malachite green	–	250	–	623.6	1455	(Chang et al. 2013)
Porous carbon nanosphere	Rhodamine B	–	250	–	617.8	1409	(Chang et al. 2013)

*Maximum theoretical adsorption capacity based on Langmuir isotherm

attractive features make silica an ideal adsorbent for adsorptive removal of pollutants from water (Salahshoor and Shahbazi 2014). Because of the low cost, abundance, and good adsorption characteristics, the siliceous materials like silica beads, dolomite, and perlite have also been exploited for the decontamination of polluted water. Some such materials (Ahmed and Ram 1992; Phan et al. 2000; Krysztafkiewicz et al. 2002; Walker et al. 2003; Sulistiyo et al. 2017) have successfully been employed for the adsorptive treatment of dyes from aqueous solutions. The utilization of alumina-based materials as effective adsorbents have also been reported (Renuka et al. 2012a, b; Banerjee et al. 2017).

Polymer-based adsorbents

Polymeric adsorbent constitutes a promising category of adsorbents because of the wide range of porous structures that one can develop within the framework of a particular chemical system. Hence, interest has been increased on the development of polymer-based adsorbents to be served as an alternative to the natural and waste material-based adsorbents with the improved adsorption capacity without compromising the low cost. Wide varieties of adsorbents from waste materials have been used as low-cost alternatives to commercial-activated carbon. However, the major shortcomings of these adsorbents are their relatively weak interactions, poor mechanical stability, and difficulties of separation and regeneration of some of them from the water. Polymer-based materials constitute a new and unique class of adsorbent because of the wide range of pore structure, strong binding affinities, high adsorption capacity, and good mechanical, chemical, and thermal stability. Pure and modified polymeric materials are presently intensely studied as an adsorbent for their proficient adsorption efficiency. Functionalized hybrid polymeric materials are regarded as one of the most effective adsorbents for adsorption of the dye molecule from decontaminated water (Pan et al. 2009). Hence, researchers have recently focused on material based on polymers as an adsorbent for pollutant removal from wastewater. Different types of polymeric materials such as polyaniline (Laabd et al. 2016; Nasar 2018), chitosan (Wan Ngah et al. 2011; Debrassi et al. 2012; Vilela et al. 2018), polyvinyl alcohol (Agarwal et al. 2016a), polyacrylamide (Rahchamani et al. 2011), cyclodextrin (Hao et al. 2017), polystyrene (Pan et al. 2009), polyurethane (Sultan 2017) starch (de Azevedo et al. 2017), alginate (Pettignano et al. 2017), cellulose (Malik et al. 2017), and acrylamide (Didehban et al. 2017) in their pure or

modified form are currently being explored for their usage in purification of water.

Polyaniline-based adsorbents

Polyaniline is one of the best conductive polymers due to the presence of –NH– groups (Saravanan et al. 2016). It is broadly used in batteries, electronic devices, solar cells, sensors, electromagnetic shielding devices, and anti-corrosion coatings. This polymer is one of the most studied polymers because of easy synthesis, the feasibility of doping, good physicochemical characteristics, mechanical flexibility, environmental stability, and easy availability of its monomer. Further, polyaniline has also been most widely studied for the development of adsorbents by chemical modification, doping, and making composites. The potential use of polyaniline, as an adsorbent, in wastewater treatment, is due to the presence of active groups, viz., amine and imine, which have interactions with molecules of various contaminants present in polluted water (Li et al. 2015).

Polyaniline in its pure and modified forms was reported as an effective adsorbent for adsorption of dyes and heavy metals (Boeva and Sergeyev 2014; Jiang et al. 2018; Mohammadi Nodeh et al. 2018; Mahmoud et al. 2018). The conducting polyaniline polymer has a highly ordered structure comprising of benzoid and quinoid functional groups. Polyaniline exists in three redox form, i.e., leucoemeraldine, emeraldine, and pernigraniline and these are fully reduced, half oxidized, and fully oxidized, respectively. Emerldine is the most stable and useful form of polyaniline due to its high stability at room temperature, inexpensive, environmentally friendly, ease of synthesis, simple doping/de-doping chemistry. Figure 1 shows the three different forms of polyaniline where y is the degree of oxidation whose values lies in between 0 and 1. $y = 1$, corresponds to the leucoemeraldine form of polyaniline, $y = 0.5$, polyaniline in the form of emeraldine, and $y = 0$, represents the pernigraniline form of polyaniline. Two form of polyaniline that is pernigraniline and emeraldine may exist as either salts or bases. Emeraldine is regarded as the most stable and most useful form of polyaniline. It consists of an equal number of the oxidized and reduced units. Imine group of emeraldine base doped or protonated when treated with acid, as a result, polycation appears. The conductivity of emeraldine form increased by tenfold as the degree of protonation increased from 0 to 20%. Leucoemeraldine is a colorless form of polyaniline, nonconducting in nature, and consist of the amine nitrogen atom. In acidic medium, leucoemeraldine oxidizes to emeraldine form. Pernigraniline consists of imine linkage, aminobenzene, and quinonediimine alternatively present in the pernigraniline form of polyaniline. Pernigraniline and its salts decompose in the air because of quinonediimine fragment which is unstable in the presence of a nucleophile, specifically water (Song and Choi 2013; Shinde and Kher 2014). During recent years polyaniline has been used as a starting material, modifying agent, or a component of composite for making a variety of adsorbents for the effective treatment of dye-laded water. Different polyaniline-based adsorbents with their adsorption capacity of dye are listed in Table 3.

Polyaniline

The polyaniline nano-adsorbent having a particle size of 70 nm was used for the adsorption of methyl orange (Tanzifi et al. 2017). The efficiency of the adsorbent for the adsorption of methyl orange was measured by analyzing the effect of different batch parameters, and they were optimized by an artificial neural network model. The investigators observed that with the increase of initial dye concentration from 10 to 100 mg/L, the adsorption capacity of dye increased from 3.34 to 32.04 mg/g at 65 °C and from 3.28 to 30.28 mg/g at 25 °C. The kinetics and isothermal results of the adsorption data was

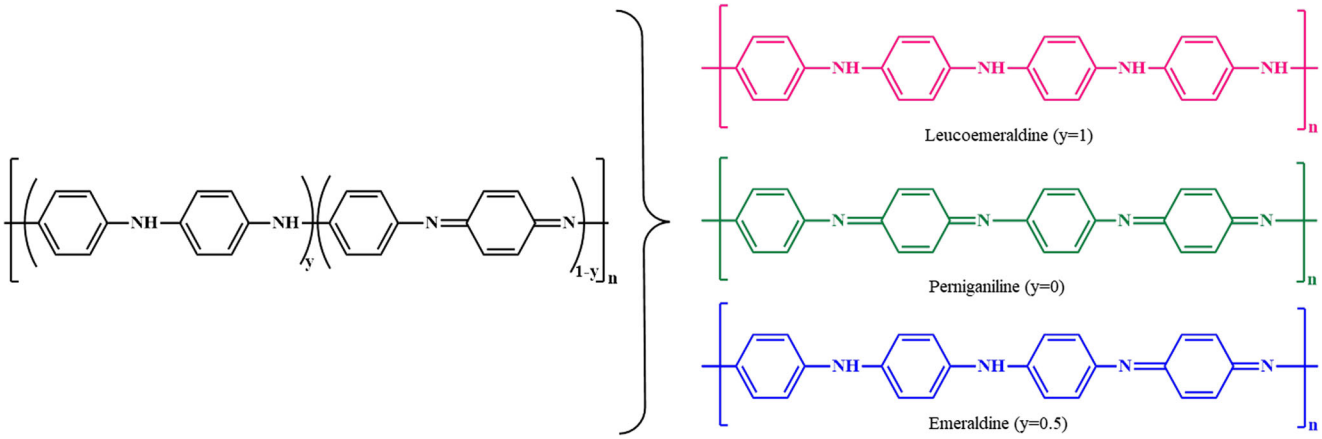

Fig. 1 Chemical structures of different forms of polyaniline

Table 3 Dye adsorption capacities for the different polyaniline-based adsorbents

Modifying/doping agent	Dye	Experimental conditions			Adsorption capacity (mg/g)	Monolayer adsorption capacity** (mg/g)	Reference
		pH	Concentration (mg/L)	Temperature (°C)			
Polyaniline	Methyl orange	10	50	65	16.09	75.9	(Tanzifi et al. 2017)
Polyaniline nanotubes	Methylene blue	–	3.1	25	5.02	9.21	(Ayad and El-Nasr 2010)
Hyper-crosslinked polyaniline	Methyl orange	–	100	–	200	188	(Sharma et al. 2016)
Hyper-crosslinked polyaniline	Crystal violet	–	100	–	196	227	(Sharma et al. 2016)
Polyaniline nanofibers	Reactive black 5	6.03	50	25	51.02	312.5	(Bhaumik et al. 2016)
Polyaniline/HCl-rice husk	Acid red 18	3	100	25	75	100	(Shabandokht et al. 2016)
Polyaniline	Diamond green dye	–	–	–	0.911	0.911	(Kanwal et al. 2018)
Polyaniline/*Alstonia scholaris* leaves	Diamond green dye	–	–	–	8.130	8.130	(Kanwal et al. 2018)
Polyaniline/$FeCl_3$/Sawdust	Acid Red G	2	100	35	50.87	212.97	(Lyu et al. 2018)
Polyaniline/activated carbon (*Prosopis juliflora* seeds)	Direct red 23	3	50	30	44.84	90.91	(Gopal et al. 2014)
Polyaniline/Starch	Reactive violet	3	–	25	0.8311*	811.3	(Janaki et al. 2012b)
Polyaniline/Starch	Reactive blue dye	3	-	25	0.5731*	811.3	(Janaki et al. 2012b)
Polyaniline/Starch/Montmorillonite	Reactive dye					91.74	(Olad et al. 2014)
Polyaniline/Chitosan	Congo red	3	100	–	104.16	322.58	(Janaki et al. 2012a)
Polyaniline/Chitosan	Coomassie brilliant blue	3	100	–	108.69	357.14	(Janaki et al. 2012a)
Polyaniline/Chitosan	Remazol brilliant blue R	3	100	–	109.89	303.03	(Janaki et al. 2012a)
Polyaniline/Chitosan/zinc oxide	Reactive orange 16	7	50	30	299.7	476.2	(Kannusamy and Sivalingam 2013)
Alginate/montmorillonite/polyaniline	Reactive orange 13	2.59	64.4	–	45.9	111.111	(Ayazi et al. 2017)
Polyaniline/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)	Rose bengal	7	100	25		440.0	(Shen et al. 2018b)
Polyaniline/poly(2-acrylamido-2-methyl-1-propanesulfonic acid)	Methylene blue	7	100	25		466.5	(Shen et al. 2018b)
Polyaniline nanotube/silica	Methylene blue dye	–	3.1	25	5.7	10.31	(Ayad et al. 2012)
Polyaniline nanotube/silica	Acid green 25	–	18.6	25	2.7	6.896	(Ayad and El-Nasr 2012)
Polyaniline/zirconium oxide	Methylene blue	–	0.5	26		77.5	(Agarwal et al. 2016b)
Polyaniline/zirconium/silicophosphate	Methylene blue	–	9.6	25	2.85	12	(Gupta et al. 2014)
Polyaniline/gamma alumina	Acid blue 62	2	50	25	25.51	222.2	(Javadian et al. 2014)
Polyaniline/gamma alumina	Direct blue 199	2	50	25	25.57	1000	(Javadian et al. 2014)
Polyaniline/iron oxide	Malachite green	7	10	30	4.92	240	(Mahto et al. 2014)
Clay/polyaniline/Fe_3O_4	Methylene blue	6.3	100	25	99.3	184.50	(Mu et al. 2016)
Polyaniline /zinc ferrite	Rhodamine B	–	–	–	500	1000	(Rachna et al. 2018)
Polyaniline microsphere	Methyl orange	–	–	–	48.05	154.56	(Ai et al. 2010)
Polyaniline/kapok fiber	Congo Red	–	200	30	30.95	40.82	(Zheng et al. 2012)
Polyaniline/kapok fiber	Orange II	–	200	30	154.8	188.7	(Zheng et al. 2012)
Polyaniline/kapok fiber	Orange G	–	200	30	161.5	192.3	(Zheng et al. 2012)
Polyaniline hollow sphere	Methyl orange	–	60	–	287	384.62	(Guo et al. 2011)

Table 3 (continued)

Modifying/doping agent	Dye	Experimental conditions			Adsorption capacity (mg/g)	Monolayer adsorption capacity** (mg/g)	Reference
		pH	Concentration (mg/L)	Temperature (°C)			
Polyaniline fiber/sheets	Methyl orange	–	60	–	263	316.46	(Guo et al. 2011)
Polyaniline hydrogel	Methyl blue	6.5	50	25	38.5	71.2	(Yan et al. 2015)
Polyaniline/carbon nanotube	Malachite green	7	16	-	15.23	13.95	(Zeng et al. 2013)
Crosslinked polyaniline	Methylene blue	–	3.9	25	7.33	13.854	(Ayad and Zaghlol 2012)

*mmol/g

**Maximum theoretical adsorption capacity based on Langmuir isotherm

followed pseudo-second-order model and Langmuir adsorption isotherm with the maximum monolayer adsorption capacity of 75.9 mg/g. Polyaniline nanoparticle was utilized for the ultrasonicated adsorption of crystal violet dye (Saad et al. 2017). The effect of sonication time, temperature, adsorbent dosage, and dye concentrations was studied to measure the efficacy of the ultrasonicated adsorption process. The optimum operating parameters were estimated by response surface methodology based on the central composite design for the removal of crystal violet. Adsorption experimental data were fitted well with Freundlich and Dubinin-Radeshkevich isotherms at all reported temperatures. Kinetic results indicated that the adsorption of crystal violet followed pseudo-second-order kinetics. In another research study, nanotubes of polyaniline were used for the adsorption of methylene blue (Ayad and El-Nasr 2010). In this study, batch experiments at a different concentration of methylene blue and kinetic analysis of the sorption process were performed. The complete adsorption of methylene blue onto the polyaniline nanotube occurred within 20 min. The adsorption process was analyzed with the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. The pseudo-second-order was found to be a best-fitted model. The adsorption process was found to follow the Langmuir isotherm with 9.21 mg/g was the maximum adsorption capacity. Sharma et al. 2016 prepared nanoporous hyper crosslinked polyaniline having 1083 m^2/g specific surface area and used as a proficient adsorbent for the removal of both cationic crystal violet and anionic methyl orange dyes from the aqueous system. Equilibrium for both the dyes was achieved within 60 min of contact time. Maximum adsorption capacity for crystal violet and methyl orange reaches up to 245 and 220 mg/g respectively. Both the dyes perfectly follow pseudo-second-order kinetics model and Langmuir adsorption isotherm. Polyaniline nanofibers with diameter 50–80 nm were prepared by using ferric chloride as an oxidant through a simple polymerization method (Bhaumik et al. 2016). Polyaniline nanofibers were used for the adsorption of reactive black 5 from aqueous solutions. The kinetics data obeys the pseudo-second-order model while the equilibrium isotherm data were well agreeable with the Langmuir isotherm model. The maximum monolayer adsorption capacity of reactive black 5 at pH 6.0 was found to be increased with increase in temperature (312.5, 389.1 and 434.7 mg/g at 25 °C, 35 °C and 45 °C, respectively). The adsorption process was feasible, spontaneous, and endothermic. Moreover, adsorption-desorption experiments revealed that the polyaniline nanofibers effectively reused for five consecutive cycles.

Polyaniline salts

Three salts of polyaniline, i.e., polyaniline-H_2SO_4, polyaniline-H_3PO_4, and polyaniline-HNO_3, were synthesized and exploited to study their adsorption capacity for direct blue 78 dye (Salem 2010). The investigator reported that the

removal rate of direct blue 78 was followed by the following order: polyaniline-H_3PO_4, polyaniline-H_2SO_4, and polyaniline-HNO_3, with values of 89.3%, 80.2%, and 76.5% respectively. The rate of adsorption of direct blue 78 decreased with increase in the concentration of solution and pH. In a strongly acidic medium, the polyaniline exists as emeraldine salt form, which is positively charged and undergoes interaction with anionic dye. With the increase in pH of the solution, the doped emeraldine salt convert into the undoped emeraldine base which leads to the depletion of active sites, consequently, the adsorption of dye onto the polyaniline salts was retarded. It was suggested that the electrostatic interaction between direct blue 78 and polyaniline was the dominating factor for the efficient removal (Salem 2010). The adsorption of direct blue 78 onto the polyaniline salts obeys the pseudo-second-order kinetics model.

Polyaniline/natural materials composites

Polyaniline/agricultural waste

Rice husk is the low-cost agricultural waste material usually burnt in the environment, which causes generation of pollutant. Application of rice husk as an adsorbent reduces the chance of agricultural effluent discharge into the environment (Mane et al. 2007). Rice husk rich in floristic fiber, protein, and some functional groups such as carboxyl, hydroxy, and amidogen, which make the adsorption processes promising (Han et al. 2008). Shabandokht et al. (2016) synthesized HCl-modified rice husk functionalized with polyaniline to increase the removal efficiency of acid red 18. The adsorbent was characterized by FTIR and SEM techniques. Adsorption of acid red 18 was best followed by pseudo-second-order kinetics and Langmuir isotherm model. It has also been reported that increase in initial dye concentration results in an increase in adsorption capacity. Further, the increase in pH value leads to a decrease in removal efficiency, which was explained by the ionic effect.

Polyaniline and its composite with *Alstonia scholaris* leave were utilized for the adsorption of diamond green dye (Kanwal et al. 2018). The experimental adsorption data was well fitted with both Langmuir and Freundlich adsorption isotherm with maximum monolayer adsorption capacity of 0.911 and 8.130 mg/g onto the polyaniline and polyaniline *Alstonia scholaris* composite, respectively. Hydrogen bonding, electrostatic and π-π interaction were reported to be responsible for the interaction of diamond green dye with the adsorbents.

Polyaniline nanofibers synthesized via a simple polymerization method using ferric chloride as an oxidant were coated on the alkali pretreated sawdust (Lyu et al. 2018). The composite was characterized via FTIR, SEM, TGA, XRD, and zeta potential measurements. The adsorption of anionic azo dye acid red G was carried out at different pH of the solution, initial concentration dye, adsorbent dose, and temperature. Thermodynamic suggested that the adsorption process was feasible, spontaneous, and endothermic nature. The kinetics and isothermal data showed that the adsorption process followed the pseudo-second-order kinetics model and Freundlich isotherm model. The maximum experimental adsorption capacity was found to be 212.97 mg/g at pH 2.0 and temperature 308 K. Moreover, the adsorption-desorption experiment revealed that polyaniline-coated sawdust was an effective and reusable adsorbent for 29 sequential adsorption-desorption cycles. The mechanism for the adsorption of dye showed that excellent adsorption efficiency of the adsorbent was associated with the highly doping chemistry of polyaniline and ferric chloride with high crystallinity.

A polyaniline-coated activated carbon with a very high BET surface area of 1028 m^2/g was prepared from *Prosopis juliflora* seeds (Gopal et al. 2014). The prepared adsorbent was used to remove direct red 23. The adsorption process follows pseudo-second-order kinetics. The intraparticle model confirms that pore diffusion plays a significant role in the adsorption of direct red 23. The Langmuir monolayer adsorption capacity increases from 90.91 to 109.89 mg/g with an increase in temperature from 30 to 45 °C.

Polyaniline/biopolymer

Starch is a cheap renewable and naturally occurring polysaccharide and has extensive application in many fields because of its characteristic properties (Sajilata et al. 2006). Due to the weak adsorbing nature of the starch, numerous tactics have been applied to transform starch as a potential adsorbent. Janaki et al. 2012b examined the adsorption of reactive dye from aqueous solution using starch polyaniline nanocomposite. The high crystalline nature of the nanocomposite was confirmed by XRD. The irregular shape of the particles and the rough surface of the nanocomposite provide the better possibility for the dye molecule to adsorb. Due to the protonation of nitrogen atom present at the surface of adsorbent at pH 3, the anionic dye molecule gets attracted to the surface which results in the higher adsorption of reactive dye. Increase in pH above 3 leads to the deprotonation of nitrogen, and hence, the adsorption process gets hindered. The maximum adsorption capacity obtained for reactive violet and reactive blue dye was 578.39 and 811.3 respectively. The nanocomposite was removed 99% reactive blue and 98% reactive violet and equilibrium for both the dye was achieved in 40 min. The result was found to obey the pseudo-second-order kinetics. The researchers also experimented with dye bath containing reactive blue, reactive violet, and other chemicals at pH 5 and found that due to reducing dissociation rate of the dye molecule, the starch polyaniline nanocomposite was adsorbed only 87% of dyes in the dye bath. Toth model was found to describe the adsorption isotherm for both the dyes. Starch-montmorillonite

polyaniline nanocomposite was used for the removal of reactive dye (Olad et al. 2014). The ternary nanocomposite was characterized via FTIR, XRD, and SEM techniques. Langmuir isotherm well fitted the experimental equilibrium data and maximum adsorption capacity was found to be 91.74 mg/g. Pseudo-second-order kinetics model was successfully described the adsorption of reactive dye onto the nanocomposite.

Chitosan is a natural polymer and has widespread adsorption application due to biocompatibility, biodegradability, antibacterial properties, nontoxicity, low-cost, and renewable nature (Wan Ngah et al. 2011). The amino and hydroxyl groups present in the chitosan can serve as coordination and reaction site for the adsorption of several groups of pollutants (C. C. Ryan and Bardosova 2017). However, inadequate mechanical properties (Chatterjee et al. 2009), low surface area, pH sensitivity, and low porosity (Crini and Badot 2008) have reduced the applications of chitosan in industrial scale (Vakili et al. 2014). These limitations have been rectified by blending the chitosan by different materials such as *Typha latifolia*-activated carbon (Jayasantha Kumari et al. 2017), polyvinyl alcohol/zeolite (Habiba et al. 2017), clay beads (Bée et al. 2017), and magnesium oxide (Haldorai and Shim 2014). An eco-friendly polyaniline/chitosan composite was prepared and studied for enhanced removal of sulfonated anionic dye (congo red, coomassie brilliant blue, and remazol brilliant blue R) and nonsulfonated cationic dye (methylene blue) (Janaki et al. 2012a). It was reported that the negatively charged anionic dyes, viz. congo red, coomassie brilliant blue, and remazol brilliant blue R, were effectively removed with the respective efficiency of 95.4, 98.2, and 99.8% by positively charged polyaniline/chitosan composite while only 10.6% removal efficiency of anionic methylene blue was observed. The adsorption of sulfonated anionic dye onto the polyaniline chitosan composite was analyzed at different initial concentration varied from 100 to 500 mg/L and found that at low concentration movement of dye molecule into the active site of adsorbent was very high. However removal efficiency was decreased with increase in initial dye concentration, this was observed due to the steric hindrance between the dye molecule and the diffusion of the solute particle to the adsorbent sites via intraparticle diffusion. In acidic condition, the composite gets protonated, and finally, the adsorption of anionic dye occur due to the chemical attraction between two oppositely charged ions. The experimental data was found to obey the pseudo-second-order kinetics and Langmuir adsorption isotherm. Morphological and surface characterization of polyaniline chitosan composite was obtained from SEM, XRD, and FTIR. SEM images revealed the porous and pleated surface of polyaniline chitosan composite with a particle size varied from 150 to 350 nm, and FTIR analysis indicated the involvement of amino and hydroxyl group in adsorption. In another notable work, chitosan/polyaniline/zinc oxide hybrid composite was synthesized by the polymerization of aniline in the presence of chitosan and zinc chloride (Kannusamy and Sivalingam 2013). The synthesized composite was used for the adsorptive removal of reactive orange 16. The experimental data were analyzed through Langmuir and Freundlich isotherm, and it was observed that adsorption of reactive orange 16 perfectly obeys Langmuir isotherm with the maximum monolayer adsorption capacity of 476.2 mg/g. The investigators also studied the effect of the mass ratio of ZnO in the composite to enhance the dye removal efficiency. Very recently, a polyaniline/chitosan composite was prepared and studied for the effective removal of tartrazine (Sahnoun and Boutahala 2018). Based on the thorough kinetic and equilibrium studies, it was reported that polyaniline played an important role in modifying the morphology and decreasing the crystallinity of chitosan which resulted in favorable adsorption due to the presence of amine and imine group in the composites. Sahnoun and Boutahala (2018) studied the adsorption of tartrazine onto the polyaniline chitosan composite. The kinetics and isotherm of tartrazine adsorption onto the composite obey the pseudo-second-order and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity of tartrazine was 584 mg/g. Abbasian et al. (2017) carried out the comparative studied of chitosan-grafted polyaniline, chitosan-grafted poly(N-methylaniline), and chitosan-grafted poly(N-ethylaniline) for the removal of acid red 4 and direct red 23. The adsorption kinetics data were well described by the pseudo-second-order kinetic model for all the adsorbents. The methanol-KOH (10% *w*/*v*) was the best desorbing agent for acid red 4 and direct red 23 dyes from the synthesized adsorbents. Regeneration experiments showed that the synthesized chitosan-grafted polyaniline adsorbents could be reused up to five cycles.

Alginate is a natural, low-cost polymer extracted from brown seaweeds. It is a linear homopolymeric block of (1-4)-linked β-D-mannuronate (M) and α-L-glucuronate (G) residues. It has many attractive applications in food, pharmaceutical, and textile. Due to its weak mechanical and high-swelling properties in water, its usage is limited. This problem was overcome by preparing alginate-based composite, which was used widely in the different field. Alginate is rich in hydroxyl and carboxyl functional groups spread along the backbone chain of the polymer. These two functional groups can be modified to change the properties in comparison to the parent compounds (Yang et al. 2011; Pawar and Edgar 2012). Ayazi et al. (2017) synthesized alginate montmorillonite polyaniline nanocomposite for the adsorption of reactive orange 13 azo dye. The central composite design was used to optimize and modeling of the adsorption process. The experimental adsorption data were fitted well with the pseudo-second-order kinetics model. The equilibrium adsorption data followed Langmuir adsorption isotherm with maximum adsorption capacity of 111.1 mg/g.

Polyaniline/synthetic polymers

Polyaniline/polypyrrole

An interconnected polypyrrole polyaniline nanofibril was synthesized via in situ chemical polymerization technique in the presence of a $FeCl_3$ oxidant and exploited for the adsorption of congo red from aqueous solutions (Bhaumik et al. 2013). The presence of both polypyrrole and polyaniline polymeric moieties were confirmed by attenuated total reflectance Fourier transform infrared spectroscopy. Interconnected and nanostructured fibers were observed by SEM and TEM. The effects of different parameters including solution pH, contact time, initial concentration, and temperature on the removal of congo red using polypyrrole polyaniline nanofibril were investigated. Adsorption experiments confirmed that the removal of congo red increased with a decrease in solution pH. Adsorption data were fitted well with pseudo-second-order kinetic equation whereas the Langmuir model was the best-followed adsorption isotherm. The obtained maximum adsorption capacities of congo red onto the polypyrrole polyaniline nanofibril were 222.2 mg/g and 270.3 mg/g at 25 °C and 35 °C, respectively.

Polyaniline/polyvinyl alcohol

Polyvinyl alcohol is biocompatible, environmentally friendly, water soluble, and chemical resistant synthetic polymer (Li et al. 2007). Due to its high water solubility, poly(vinyl alcohol) needs to be blended with other materials (such as chitosan/polyvinyl alcohol (Salehi and Farahani 2017), Fe_3O_4/cellulose/polyvinyl alcohol (Shen et al. 2018a), graphene/polyvinyl alcohol (Xiao et al. 2017), and chitosan/polyvinyl alcohol/zeolite (Habiba et al. 2017)) for use in several applications. In another notable work, the polyaniline/polyvinyl alcohol/clinoptilolite nanocomposite was used for the adsorption of methylene blue (Rashidzadeh and Olad 2013). FTIR spectra showed the characteristic band of polyaniline, polyvinyl alcohol, and clinoptilolite which confirmed the successful synthesis of polyaniline/polyvinyl alcohol/clinoptilolite nanocomposite. XRD analysis shows the crystalline nature of the nanocomposite as the pure polyaniline exhibits amorphous nature and has a noncrystalline pattern, while the nanocomposite possesses typical crystallite associated with the zeolite component. It has been established that the adsorption of methylene blue dye onto polyaniline/polyvinyl alcohol/clinoptilolite composite occurs through chelating interaction between nanocomposite components and methylene blue dye. It was reported that the adsorption capacity of methylene blue onto the nanocomposite was found to be 44.44 mg/g. The experimental data were best explained by intraparticle diffusion model, and adsorption isotherm was well described by the Langmuir isotherm model.

Polyaniline/polyacid

(Shen et al. 2018b) synthesized new and high surface area adsorbent by polymerizing aniline with a polyacid namely poly(2-acrylamido-2-methyl-1-propanesulfonic acid). Adsorption properties were estimated by using methylene blue and rose bengal as the adsorbate. The composite was reported to possess porous structure having a specific surface area much higher than emeraldine base polyaniline by tenfold. The maximum adsorption capacities for methylene blue and rose bengal were 466.5 and 440 mg/g respectively. The mechanism for successful adsorption of dyes involves electrostatic and π-π interaction as confirmed by FTIR and zeta potential measurement.

Polyaniline/inorganic materials

Polyaniline/silica

In the two research reports, polyaniline nanotube-based silica composite was used as an adsorbent for the adsorption of cationic methylene blue dye (Ayad et al. 2012) and acid green 25 (Ayad and El-Nasr 2012). The composite thus formed was characterized by SEM. The researchers carried out the adsorption of dyes onto the polyaniline nanotube-based silica composite in a batch system concerning the initial concentration of dyes and contact time. In both the studies, the pseudo-second-order kinetics model was best described the adsorption process. The adsorptions of methylene blue (Ayad et al. 2012) and acid green 25 (Ayad and El-Nasr 2012) onto the polyaniline nanotube-based silica composite found to followed Langmuir adsorption isotherm with maximum monolayer adsorption capacity were 10.31 and 6.896 mg/g respectively. In both the research article, it was observed that amount of methylene blue and acid green 25 onto the convention polyaniline and polyaniline nanotubes was found to follow the order polyaniline nanotubes base/silica composite > polyaniline nanotubes base > conventional polyaniline base/silica composite > conventional polyaniline base.

Polyaniline/zirconium

Zirconium oxide has been expansively explored for a variety of applications related to its valuable optical, dielectric, and physical properties and excellent thermal and chemical properties including high wear resistance and biocompatibility (Patel et al. 2016). Zirconium was used in forming the polyaniline zirconium oxide nanocomposite for the removal of methylene blue dye (Agarwal et al. 2016b). It was observed that polyaniline retain higher conductivity by adding

zirconium oxide. The synthesized nanocomposite was found to be an efficient adsorbent for the adsorption of toxic methylene blue dye. The isothermal adsorption study revealed that monolayer adsorption capacity was 77.51 mg/g with 25 min as the observed equilibrium time. Polyaniline nanocomposite functionalized with zirconium (IV) and silicophosphate was synthesized for the adsorption of methylene blue (Gupta et al. 2014). The nanocomposite was synthesized through sol-gel method. SEM and XRD analysis of polyaniline zirconium (IV) silicophosphate nanocomposite showed rough and fibrous morphology and semicrystalline nature of the nanocomposite respectively, and TEM analysis revealed the spherical shape of nanoparticles with around 20-nm diameter (Pathania et al. 2014). The adsorption capacity of methylene blue onto polyaniline zirconium (IV) silcophosphate nanocomposite was found to be 12 mg/g, and the data were best fitted to Freundlich adsorption isotherm. Based on the kinetic study, the pseudo-second-order was found to be the rate-determining step (Gupta et al. 2014).

In another study, the hybrid material of polyaniline α-zirconium phosphate via in situ oxidative polymerization reaction was synthesized for the adsorption of methyl orange dye (Wang et al. 2012). The XRD analysis confirmed the crystalline structure of the hybrid and 30.40 m^2/g was the BET surface area with rough and pleated surface confirmed from SEM analysis. The polyaniline α-zirconium phosphate nanocomposites displayed outstanding adsorption capacity of 377.46 mg/g toward methyl orange which was much greater than that of many other adsorbents. The adsorption isotherm of methyl orange was best fitted with the Langmuir model, and the adsorption kinetics follows the pseudo-second-order model. Adsorption of methyl orange decreased with increasing solution pH. At pH > 4.0, adsorption of methyl orange may occur via electrostatic interactions between amine and imine groups on the surface of polyaniline α-zirconium phosphate and methyl orange molecules.

Polyaniline/silver

Silver nanoparticles have fascinated increasing importance due to their unique properties and a wider range of application in medical, environmental, cosmetic, optical, and so on (Morones et al. 2005). Silver nanocomposite had been used for the synthesis of polyaniline composite via chemical oxidation polymerization for the adsorption of brilliant green dye (Salem et al. 2016). Adsorption of brilliant green dye onto polyaniline silver nanocomposite perfectly obeys Langmuir isotherm, and the maximum monolayer adsorption capacity was found to be 49 mg/g. Pseudo-second-order kinetics was found to follow the adsorption of brilliant green dye onto polyaniline silver nanocomposite. The polyaniline silver nanocomposite was characterized via SEM, TEM, EDX, FTIR, XRD, and thermal analysis (Neelgund et al. 2008; B. Wankhede et al. 2013; Salem et al. 2016). It was observed from the SEM analysis that silver particle have a strong affinity for nitrogen which leads to the strong adhesion of silver nanoparticle to the polyaniline substrate. Silver nanoparticles have been much attached at the periphery than that of the center of the polyaniline which resulted in the uniform capping of silver nanoparticle in the polyaniline. TEM images revealed the dark spot of the silver nanoparticles of size ranging from 6.92–12.4 nm located at the periphery of the polyaniline nanotubes. From the EDX analysis, the degree of crystallinity increases as the concentration of silver nanoparticles increased, signifying the homogeneous distribution of silver nanoparticles in the polymer medium. It was observed from the thermal analysis that the nanocomposite possessed greater thermal stability than the pure polymer and decomposed at a higher temperature after doping with a silver particle of concentration even less than 1.0%.

Polyaniline/alumina

The gamma alumina is extensively appreciated for catalytic and adsorption application due to its high thermal stability and large surface area (Renuka et al. 2012a). Polyaniline gamma alumina nanocomposite synthesized by chemical oxidation method used for the adsorption of three different anionic dyes that were reactive red, acid blue 62, and direct blue 199 (Javadian et al. 2014). From the SEM and TEM analysis, it was observed that light and black spots of spherical shape gamma alumina having particle size 20 nm were surrounded by polyaniline. The specific surface area of the nanocomposite was found to be 60 m^2/g. The composite exhibited good adsorption capacity as it could adsorb up to 99.79% reactive red dye, 99.85% acid blue 62, and 99.91% direct blue 199 within 20, 20, and 10 min of time interval respectively. The maximum adsorption for all dyes occurred at pH 2. Electrostatic attraction and ionic attraction between the amino group of adsorbent and a sulfonated group of dye molecules are the two mechanisms involve in the process of adsorption. The adsorption process followed Langmuir isotherm, and the kinetic data revealed that the adsorption process for all dyes was controlled by pseudo-second-order.

Polyaniline/iron oxide

Magnetic nanoparticles are emerging as an attractive adsorbent because of the availability of greater surface area, a large number of active sites, and possess firm reaction under applied external magnetic field which provides better applicability in wastewater treatment (Usmani et al. 2017). Adsorption of malachite green was carried out on Fe_3O_4 nanoparticle functionalized with polyaniline (Mahto et al. 2014). Detailed research studies include the effect of initial dye concentration,

pH, contact time, particle size, and adsorbent dosage on the adsorption of malachite green dye over Fe_3O_4 nanoparticle functionalized with polyaniline. Paper also includes characterization of the composite by using FTIR, TEM, XRD, and VSM. The nanocrystalline structure of the composite was confirmed by XRD and TEM analysis. It was also concluded that electrostatic interaction between cationic malachite green dye and amine and imine nitrogen group on polyaniline was the key force for adsorption. The percentage removal of dye increased with increase in pH from 1 to 7 after that percentage removal of dye decreased with increase in pH. Maximum adsorption occurs at pH 7 with 98% removal of dye. Equilibrium time for adsorption of malachite green onto Fe_3O_4 nanoparticle functionalized with polyaniline was found to be 4 h. The adsorption was reported to be exothermic. The kinetic study revealed that pseudo-second-order is the rate-determining step. Experimental data was found to be best fitted by Langmuir adsorption isotherm. Desorption was best carried out with methanol. In another research, it was established that the adsorption of methyl orange and rhodamine B onto the polyaniline iron oxide composite followed Langmuir isotherm and Freundlich isotherm respectively (Xie et al. 2017). The maximum monolayer adsorption capacity of methyl orange onto the polyaniline iron oxide composite was found to be 63.9 mg/g.

Montmorillonite- and vermiculite-based polyaniline/Fe_3O_4 nanocomposites were successfully prepared through one-pot method combining in situ intercalation polymerization and coprecipitation technique and utilized for the adsorption of dye (Mu et al. 2016). The XRD results showed that montmorillonite and vermiculite were well interpolated and entirely exfoliated by polyaniline and Fe_3O_4. The produced Fe_3O_4 nanoparticles with 10-nm diameter and polyaniline well adhered to the clay surface without the free aggregates. The nanocomposites could be recycled and reused for the adsorption of dyes by magnetic separation. The adsorption efficiency for 100 mg/L of brilliant green, methylene blue, and congo red reached up to 96.2%, 99.6%, and 98.1%, respectively. The adsorption process followed the pseudo-second-order kinetic model and Langmuir adsorption isotherm model. The synthesized two-dimensional superparamagnetic nanocomposites offer outstanding adsorption properties to the cationic dyes as well as anionic dyes.

Polyaniline/nickel ferrite

Nickel ferrite has an inverse spinel structure and extensively used as one of the most attractive magnetic nanomaterials. However, due to the superparamagnetic behavior of nickel ferrite, it has wide application in electrical, optical, and biomedical field, etc. (Mahmoodi 2013). In literature, polyaniline nickel ferrite nanocomposite has been used in the adsorption of malachite green (Patil and Shrivastava 2015) and methylene blue (Patil and Shrivastava 2016). Polyaniline nickel ferrite nanocomposite was synthesized via in situ self-polymerization of aniline monomer. SEM micrograph images revealed that the surface of black green-colored polyaniline nickel ferrite nanocomposite was homogeneous with micro and mesopores over their surface. XRD analysis showed that polyaniline-functionalized nickel ferrite was highly crystalline. EDS and VSM techniques were used for the analysis of composite chemical composition and magnetic behavior respectively. Detailed research study includes the effect of initial dye concentration, pH, contact time, particle size, and adsorbent dose. In both the research articles, it was observed that the adsorption rate increased significantly by increasing the amount of adsorption dose, while reverse trend was obtained with an enhancement in dye concentration. At pH 7, adsorption efficiency for methylene blue was 95.2% and for malachite green, 87.8%. The rate of adsorption for both malachite green and methylene blue was found to follow the pseudo-second-order kinetics model, and Langmuir isotherm model was found to be best fitted with experimental data. From the desorption experiment, it was observed that polyaniline nickel ferrite nanocomposite could be recycled and reused.

Nickel ferrite/polyaniline magnetic composite was synthesized through in situ oxidative chemical polymerization of aniline monomer in the presence of nickel ferrite particles, where the nickel ferrite particles were produced by a facile hydrothermal method (Liang et al. 2018). The composite was characterized by XRD, FTIR, BET, and VSM techniques. The adsorption properties of the composite were evaluated by using alizarin red S as an adsorbate. The experimental adsorption data was well fitted to the pseudo-second-order kinetics model and Langmuir isotherm model and the maximum monolayer adsorption capacity was 186 mg/g at 303 K. The amazing adsorption capacity of alizarin red S was ascribed to the stronger π-π interaction and weak electrostatic attraction. Thermodynamic parameters revealed that the adsorption of alizarin red S on the nickel ferrite/polyaniline composite was spontaneous and endothermic.

Polyaniline/zinc ferrite

Zinc ferrite polyaniline nanocomposite was synthesized by in situ polymerization method, and this composite was used for the adsorptive removal of rhodamine B (Rachna et al. 2018). The synthesized composite was characterized by XRD. Electrical conductivity and the dielectric constant were analyzed at different temperatures and frequencies. Effective removal of dye was observed at pH 2. Percent removal of dye decreases by adding sodium chloride into the aqueous solution. Adsorption of rhodamine B was spontaneous and exothermic. In another research, rhodamine B was successfully adsorbed and photocatalytic degraded onto the reduced graphene oxide zinc ferrite polyaniline composite

(Feng et al. 2016). The composite was well prepared by in situ polymerization of aniline on the reduced graphene oxide zinc ferrite surface. The SEM, TEM, and STEM images confirmed the successful synthesis of the composite. The XRD, TGA-DTG, and FTIR analysis confirmed the interaction between reduced graphene zinc ferrite composite with polyaniline. The adsorption followed pseudo-second-order kinetics and Langmuir adsorption isotherm.

Adsorption mechanism

In order to understand the adsorption process of dye onto the polyaniline- and polyaniline-based adsorbents, an accurate knowledge on the mechanism of adsorption is essential. In fact, the process of adsorption is controlled by many factors including the nature of functional groups present in adsorbate and adsorbent, the textural and surface properties of the adsorbent, diffusion behavior of adsorbate towards adsorbent, and the mode of their interaction (Zare et al. 2018). In fact, the adsorption of dye is occurred through physisorption, chemisorption, or by both depending on the nature of mutual interaction between adsorbate and adsorbent. In many cases, the adsorption of dyes on polaniline-based materials is executed by the involvement of π-π interaction, electrostatic attraction, and hydrogen bonding. In Fig. 2, the involvement of these interactions on PANI adsorbent has been represented by taking a typically chosen cationic methylene blue dye as an adsorbate. Further, usually, more than one iterations are simultaneously involved. Thus, pH of the medium also plays a critical role to decide the overall adsorption process. In addition, film diffusion and particle diffusion models have been frequently used for examining their diffusion mechanism.

According to Javadian et al. (2014), adsorption of anionic dyes onto the polyaniline gamma Al_2O_3 occurred through ionic attraction between the cationic amino group of protonated polyaniline gamma Al_2O_3 and sulphonated group of anionic dyes, viz., reactive red 194, acid blue 62, and direct blue 199. A convincible mechanism for the adsorption of rhodamine B and congo red onto the polyaniline-modified MoO_3 composite was proposed (Dhanavel et al. 2016). According to their report, benzoid and quinoid rings of polyaniline form π-π interaction with aromatic rings of dye molecules and also electrostatic interaction and hydrogen bonding might also play a crucial role in adsorption mechanism of rhodamine B and congo red. Interestingly, the adsorption capacity for the removal of cationic methylene blue and anionic rose bengal by polyacid-doped polyaniline was found to be respectively increased (by 48%) and decreased (by 36%) with the increase of pH from 3 to 12 (Shen et al. 2018b). The adsorption was explained on the basis of π-π and electrostatic interactions.

Employing the thorough analyses of FTIR spectra while studying the adsorption of reactive orange 16 onto the chitosan polyaniline zinc hybrid, sole chemisorption was suggested (Kannusamy and Sivalingam 2013). The disappearance of hydroxyl, amine, imine, carboxylic, alkene, and aromatic functional groups peak in FTIR spectrum after adsorption of reactive orange 16 onto the chitosan polyaniline zinc hybrid indicated that the adsorbate form chemical bond with the adsorbent.

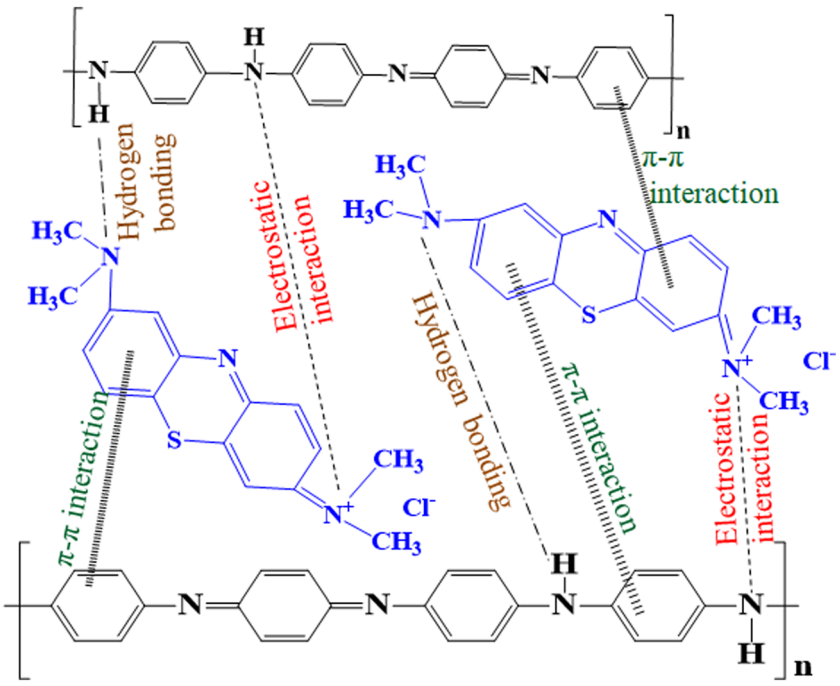

Fig. 2 Mechanism of adsorption of methylene blue onto polyaniline showing different interactions

The combined role of electrostatic interaction, π-π interaction and hydrogen bonding for the adsorption of diamond green dye by polyaniline and polyaniline-*Alstonia scholaris* leaves composite was suggested (Kanwal et al. 2018). The functional group of emeraldine form of polyaniline, i.e., imine and amine groups, form hydrogen bonding. Conjugated backbone of the polyaniline was behind the π-π interaction with aromatic rings of diamond green dye and counter ion in the salt was responsible for electrostatic interactions. It has also been illustrated that in acidic pH, the sulfonated group of orange G gets ionized and the dye exists in anionic form which attracted electrostatically towards the positively charged backbone of polyaniline emeraldine salts while in basic media, no chemical interaction of dye occurred due to blocking in the dissociation of functional groups present in dye (Mahanta et al. 2008). It was also reported that when emeraldine base was used in place of emeraldine salts, no adsorption occurred. This shows that the positively charge backbone and chloride ion that are present in the emeraldine salt were the main sites for the successful adsorption of sulfonated dye. In another study, the interaction mechanism of cationic and anionic dyes with various functional groups present in the hyper-crosslinked polyaniline was investigated by FTIR analysis (Sharma et al. 2016). They stated that the adsorption of crystal violet onto the hyper-crosslinked polyaniline was due to the π-π interaction between localized aromatic π-electron of hyper-crosslinked polyaniline and aromatic ring of dye molecules and the adsorption mechanism of methyl orange was governed by the combined effect of π-π interaction, Lewis acid-base interaction, and hydrogen bonding between oxygen atom of S=O of methyl orange and hydrogen atom of amine groups of hyper-crosslinked polyaniline. The adsorption mechanism of methylene blue, brilliant green, and congo red onto the montmorillonite/polyaniline/Fe_3O_4 nanocomposites before and after de-doping was well demonstrated (Mu et al. 2016). They observed that the de-doped montmorillonite/polyaniline/Fe_3O_4 nanocomposites had admirable adsorption characteristic towards cationic methylene blue and brilliant green due to electrostatic interaction, π-π interaction, and hydrogen bonding between adsorbate and adsorbent and these interactions are ensued due to the presence of opposite surface charge, π electronic configuration structure, and occurrence of functional groups onto the de-doped nanocomposite while congo red showed good adsorption behavior onto the montmorillonite/polyaniline/Fe_3O_4 nanocomposites after being protonated. It was also suggested that the difference in adsorption behavior of cationic and anionic dye onto the montmorillonite/polyaniline/Fe_3O_4 nanocomposites and de-doped montmorillonite /polyaniline/Fe_3O_4 nanocomposites was due to the different electrical characteristics. At pH 6.3, the de-doped montmorillonite/polyaniline/Fe_3O_4 nanocomposites were negatively charged while the montmorillonite/polyaniline/Fe_3O_4 was positively charged. Also, the difference in removal efficiency of these dyes onto the montmorillonite/polyaniline/Fe_3O_4 nanocomposites before and after de-doping was due to the difference in specific surface areas and the number of surface active adsorbing sites. It was also observed that pristine montmorillonite exhibited adsorption behavior towards cationic methylene blue and brilliant green while no adsorption was observed toward anionic congo red due to electrostatic repulsion.

Conclusion and future perspective

This review paper specifies that adsorption using polyaniline composite is becoming a promising alternative in eliminating dyes from aqueous solution. The adsorption phenomenon of adsorbate onto the polyaniline is indeed a unique process as it is reliant on its cationic nature. The amino group of polyaniline undergoes protonation which can adsorb dye molecules through various type of interactions mechanism and shows higher adsorption of an anionic dye. Modification of polyaniline can change the surface charge, making them relevant for adsorption of cationic dye also. Modified polyaniline shows improved ability to adsorb dyes from wastewater, greater adsorption efficiency probably due to increased porosity or higher number of active binding site, improved interaction due to the formation of the new functional group, and enhanced ion exchange properties that favor the uptake of dye molecules. In most of the reported research literature, adsorption experiments were carried out by the batch method to report the maximum adsorption capacities towards targeted dye, approving their applicability and selectivity. Adsorption is one the most effective process for elimination of dyes. Various batch parameters such as pH of the solution, the contact time between adsorbate and adsorbent, concentration, temperature, and the dosage of adsorbent have been examined and adsorption isotherm, kinetics, and thermodynamic study have been demonstrated in order to evaluate the adsorption rate, adsorption mechanism, and efficiency of polyaniline composite in removing dyes from wastewater. Characterization techniques for polyaniline composite such as FTIR, XRD, SEM, TEM, and TGA were used in almost all the reported research. Desorption and regeneration had been carried out by various scientists in the reported research studies to determine the recovery, and reuse of polyaniline composite. Many composites of polyaniline have shown outstanding potential for the removal of dye. Polyaniline, an inexpensive and effective adsorbent materials, will undoubtedly offer numerous promising profits in the future. The enormous large effective surface area, high adsorption efficiency, high selectivity, appropriate pore size and volume, economical, easy accessibility, compatibility, environmentally friendly, reusability, and high mechanical, chemical, and thermal stability imparts tremendous importance to the polyaniline composite and can be demonstrated in future research.

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