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The removal of heavy metal ions from wastewater/aqueous solution using polypyrrole-based adsorbents: a review

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Water pollution caused by heavy metal ions is becoming a serious threat to human and aquatic lives day by day. Therefore, the treatment of heavy metal ions is of special concern for environmental scientists and engineers. Historically, various methods, such as physical and chemical precipitation, ion-exchange, reverse osmosis, membrane filtration, electrochemical treatment, solvent extraction, and adsorption, have been widely studied for the removal of these metal ions from aqueous/wastewater. However, over the past few decades, conducting polymer-based adsorbents have received considerable attention owing to their potential applications for different heavy metal ions especially Cr(VI), Zn(II), and Pb(II). Among the various conducting polymers, polypyrrole (PPy) based adsorbents play a major role for the removal of various heavy metal ions due to their ease of synthesis, biocompatibility and redox properties. The current review has mainly focused on the physico-chemical properties, adsorption characteristics and mechanism of different polypyrrole-based adsorbents, including PPy/biosorbents, PPy/Fe_3O_4 nanocomposites, PPy–polyaniline nanofibers, PPy–graphene nanocomposites, exfoliated PPy-organically modified clay nanocomposites, and hierarchical porous PPy-nanoclusters, as well as their applications towards the removal of heavy metal ions.

1. Introduction

Nowadays, hazardous heavy metal pollution of wastewater is the utmost significant environmental problem and endangers human beings throughout the world. Due to rapid urbanization and industrialization, such as metal plating, mining, tanneries,

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painting, batteries, paper industries, printing and photographic industries, pesticides and fertilizer industries, and car radiator manufacturing, heavy metal ions, such as As(III)/AS(V), Pb(II), Cd(II), Ni(I), Cr(III)/Cr(VI), Zn(II), Cu(II), Hg(I)/Hg(II), and Co(II) contained in wastewater are increasingly directly or indirectly discharged into streams, lakes, rivers or oceans, especially in developing countries.[1–9] Moreover, the soils surrounding military bases offer a potential risk of certain heavy metals, which can be a threat to groundwater and surface water.[9,10] Characteristically, these heavy metal ions are not biodegradable and tend to easily accumulate in living organisms.[10–13] Although taking in a trace amounts of different heavy metals is extremely necessary for human beings due to their presence of some vitamins or co-factors, excessive exposure or intake can have dangerous consequences. In addition, a lot of physical and mental retardation, such as nausea, vomiting, diarrhea, asthma, pneumonia, skin degeneration, kidney and liver malfunction, congenital abnormalities, weight loss and various cancers, can be the result of heavy metals found in industrial wastewater.[8–16] The toxicity and the consequences of these heavy metals are highlighted here using the findings of the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA).

1.1. Arsenic (As)

Although arsenic (As) is a naturally occurring metalloid and common constituent of the earth's crust, its ground and surface water contamination is very critical.[13–16] It has led to a massive epidemic of arsenic poisoning such as skin or lung cancer and even bladder cancer in Asia and America, and especially in India, Bangladesh, Vietnam, Cambodia, Thailand, Chile, Southwest USA and Canada.[13,14,17] Therefore, it is categorized as the first priority toxic element by the WHO and US EPA.[18,19] The inorganic species, arsenate [As(V)] and arsenite [As(III)] are the predominant forms of As in groundwater and surface water.[20] The main problem of As is that even at low concentrations, chronic exposure may cause As poisoning.[13–17,20–22] Thus, the WHO and various environmental protection agencies set the permissible limits of As at 0.01 mg L^{-1} in drinking water.[18,19]

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1.2. Lead (Pb)

Inorganic lead (Pb) arises from a number of industrial fuel, leaded gasoline and mining sources, much of which eventually enters natural water systems.[23,24] Acute Pb poisoning in humans causes severe dysfunction in the kidneys, liver and reproductive system.[23–28] Pb poisoning from environmental exposure is also known to cause mental retardation, especially in children.[27,28] Its toxic symptoms are anaemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damage.[23–28] Therefore, Pb has been classified as a priority pollutant by the US EPA. The maximum contaminant level (MCL) of Pb ions in drinking water has been set at a very low level of 0.015 mg L^{-1}, whereas the WHO limits it at 0.05 mg L^{-1}.[18,19]

1.3. Chromium (Cr)

Chromium (Cr) is extensively used in electroplating, leather tanning, metal finishing, nuclear power plant, dying, photography industries and textile industries.[29–33] In an aqueous solution, it exists in both the Cr(III) and Cr(VI) forms. Hexavalent chromium, which is more toxic, alters human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung cancer.[31–38] The permissible limit of Cr(VI) for industrial effluents to be discharged into surface water is 0.1 mg L^{-1} and for drinking water is 0.05 mg L^{-1}.[18,37]

1.4. Mercury (Hg)

Mercury (Hg) is released into the environment through the discharge from agricultural fungicide, chemicals, waste incineration, electronic materials, scientific instruments (thermometers, barometers), batteries, dental amalgams, textile, photographic and pharmaceutical industries, and fossil fuel combustion.[39–42] It is a neurotoxin that can cause damage to the central nervous system.[43] High concentrations of Hg causes the impairment of pulmonary and kidney function, chest pain and dyspnea.[39–49] The classic example of mercury poisoning is Minamata Bay.[44,45] In consideration of its risk, the US EPA has listed mercury as a priority pollutant and has mandated an upper limit of 2 ppb for Hg(II) in drinking water.[19]

1.5. Cadmium (Cd)

Cadmium (Cd) is spread in some surface and subsurface waters *via* welding, electroplating, Cd and Ni batteries, nuclear fission plants, paints and plastics, and fertilizers.[50–52] It is well known that chronic cadmium toxicity is the cause of Japan Itai–Itai disease.[51] Acute or chronic exposure of Cd also causes high blood pressure, kidney damage, the destruction of testicular tissue, osteoporosis and the destruction of red blood cells.[50–58] Cd may replace zinc in some enzymes, thereby altering the stereostructure of the enzyme and impairing its catalytic activity.[57] It has been classified by US EPA as a probable human carcinogen and the safe drinking water limit set up to 0.005 mg L^{-1}.[18,19]

1.6. Zinc (Zn)

Trace amounts of some metal ions, such as zinc (Zn), copper (Cu) and cobalt (Co), are required by organisms as cofactors for enzymatic processes.[59,60] However, an excess of these metal ions will cause serious problems in living organisms due to their higher toxicity, carcinogenic and bioaccumulation.[59–62]

Zn is one of the most common pollutants for surface and groundwater as it has versatile uses.[62] Again, due to its non-biodegradability and acute toxicity, Zn-containing liquid and solid wastes are considered as hazardous wastes. An excessive amount of Zn exposure can cause well-known health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia.[59–62] The WHO recommends the maximum acceptable concentration of Zn ions in drinking water at 5.0 mg L^{-1}.[18]

1.7. Copper (Cu)

Like Zn, copper (Cu) is an essential element for living organisms, including humans and is necessary in small amounts in our diet to ensure good health. However, the excessive ingestion of Cu brings about serious toxicological concerns, such as vomiting, diarrhea, stomach cramps and nausea, or even death.[56,63–66] The WHO recommends the maximum acceptable concentration of Cu ions in drinking water at 1.5 mg L^{-1}, whereas the US EPA defines it at 1.3 mg L^{-1}.[18,19]

1.8. Cobalt (Co)

Cobalt (Co) is one of the most important transition metals, which plays double-dealing in both harmful and beneficial impact on human beings. The increased use of Co(II) in nuclear power plants and in many industries, such as petrochemical, metallurgical, electroplating, battery, dye, mining and electronic industries, generates large quantities of effluent and thus contaminates surface and groundwater.[9,61,67–68] Although, a minute amount of Co is needed for the formation of vitamin B_{12}, excessive exposure can be hazardous.[9] A lot of physical and mental problems, such as vomiting, nausea, diarrhea, asthma, pneumonia, kidney congestion, skin degeneration and weight loss, can occur due to excess Co in wastewater.[67–70] The permissible limits of cobalt allowed to be in irrigation water, inland surface water and drinking water are 1, 0.05 and 0.01 mg L^{-1}, respectively.[18]

1.9. Nickel (Ni)

The major sources of nickel contamination in water come from industrial process such as electroplating, batteries manufacturing, mining, metal finishing and forging.[71–73] Ni ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization, lung and kidney problems and are a known human carcinogen.[71–74] According to the WHO guidelines, the maximum permissible concentration of Ni in industrial discharge wastewater is 2 mg L^{-1}, while that in drinking water it should be less than 0.1 mg L^{-1}.[18]

The maximum contaminant level or permissible limits of some heavy metal ions in drinking water have been set at slightly different values by the two most authentic international organizations, the WHO and US EPA, as can be observe in Table 1.

1.10. Suitable techniques for the removal of heavy metal ions

Heavy metal ions existing in various aqueous streams/wastewater from multiple sources are currently one of the most important environmental concerns. Therefore, it is necessary to remove heavy metal ions from contaminated wastewater prior to its discharge to the environment to protect the aquatic lives and human beings.

Although several methods have been used for many years to remove heavy metal ions from wastewater, achieving the most effective treatment is still challenging for environmental scientists/engineers. Physical and chemical precipitation, ion-exchange, reverse osmosis, membrane filtration, electrochemical treatment, solvent extraction and adsorption processes are the widely used methods for removing heavy metal ions from aqueous streams/wastewater.[4,9,15,65,75–82] To date, various adsorption methods have been considered as effective and widely used methods due to their simplicity and easy operational conditions.[80–86] In addition, adsorption is mostly reversible, thus the adsorbents can be easily regenerated using a suitable desorption process.[83–85]

Several inorganic and organic adsorbents have been utilized for the adsorption method, including zeolites, montmorillonite, clay minerals, trivalent and tetravalent metal phosphates, biosorbents, activated carbon, polymer-based adsorbent, and polymer-inorganic hybrid adsorbents.[15,33,47,83–95] Among the polymer-based adsorbents, conducting polymer-based adsorbents, such as polyaniline (PANI), polyethylenamine (PEI), polypyrrole (PPy) and their composites, have received considerable attention due to their potential applications in adsorbing various heavy metal ions, ease of synthesis, regeneration and operation, environmental and mechanical stability, and low cost. In addition, their highly porous structures with specific surface electro-chemical properties as well as ion exchange capacities have also drawn much attraction from researchers.[89–96] Moreover, the existence of positively charged

Table 1 The permissible limits of some heavy metal ions in drinking water

	Permissible limits (ppm)	
Heavy metal ions	WHO[18]	US EPA[19]
As(III)/As(V)	0.05	0.01
Pb(II)	0.05	0.015
Cd(II)	0.005	0.005
Cr(VI)/Cr(III)	0.05	0.05
Hg(II)	0.001	0.002
Zn(II)	5.0	5.0
Cu(II)	1.5	1.3
Co(II)	0.01	—
Ni(I)	0.1	—

nitrogen atoms in polypyrrole provides a good prospect for their applications in adsorption.[97]

This article presents an overview of the various polypyrrole-based polymeric adsorbents used for the removal of heavy metal ions from aqueous streams/wastewater sources. These polymeric adsorbents can be produced from different chemical oxidation polymerization processes from pyrrole to obtain simple polypyrroles and multi-dimensional PPy formation such as PPy-bio-adsorbents, PPy-magnetic composites, PPy-nanofibers, PPy–graphene nanocomposites and hierarchical porous PPy-nanomaterials. The effects of different parameters, such as the pH of the solution, adsorbent dosage, initial concentration of heavy metal ions, and contact time, on the removal efficiency and adsorption capacity of the adsorbents are also discussed in this section.

2. Polypyrrole-based adsorbents

2.1. Polypyrrole conducting polymer

Polypyrrole (PPy) conducting polymer has been extensively researched due to its varied potential applications, environmental stability, high conductivity, redox properties and ease of synthesis.[89,90,93–97] PPy synthesized in solutions with small dopants, such as Cl^-, ClO_4^-, and NO_3^-, mainly exhibits anion exchanging behavior due to the high mobility of these ions in the polymer matrix. However, under certain conditions, cationic exchange was also found to occur with large dopants, such as polyvinylsulfonate and polystyrenesulfonate, due to immobility of these ions in the polymer matrix.[98] PPy has also exhibited good prospects in adsorption applications because of the nitrogen atoms present in the polymer chains. Therefore, the removal of heavy metal ions is one of the applications of conducting polymers. A lot of effort has been made to remove heavy metal ions using polypyrrole conducting polymers prepared *via* the chemical oxidative polymerization of pyrrole in the presence of different dopants under different conditions, as the adsorption efficiency largely depends on the conditions used to prepare PPy.[89,99–105]

One of the studies used $FeCl_3 \cdot 6H_2O$ as an oxidant in an aqueous solution to form PPy using a molar ratio of monomer to oxidant of 1 : 1.[97] The effects of various parameters, such as the pH of the solution, dosage of the adsorbent and contact time, have been investigated and this study exhibited a 100% adsorption efficiency for the removal of Ni ions from aqueous solution at pH 7.0, 8 h of contact time and 0.08 g PPy adsorbent dose with a 1 ppm initial Ni ion concentration. The FT-IR spectrum (Fig. 1) showed that the coordination of Ni ions to the nitrogen atoms in the PPy polymer chain were involved in the adsorption process and a possible mechanism of metal ion adsorption is shown in Scheme 1.[97]

Another study revealed that PPy has been prepared *via* the chemical oxidative polymerization of pyrrole using anhydrous $FeCl_3$ as an oxidant[100] and various parameters such as the pH of the solution, dosage of the adsorbent and contact time were investigated. This study has shown the prepared PPy markedly removes (84%) Ni ions under alkaline pH conditions and the results compared with other adsorbents (Table 2).

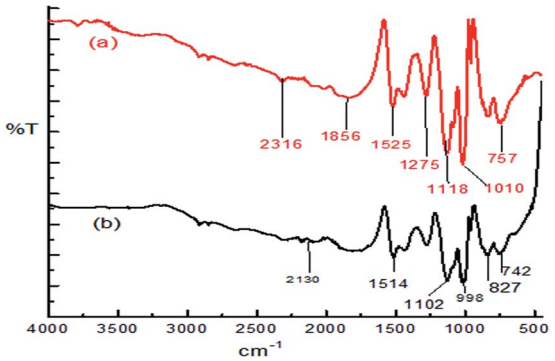


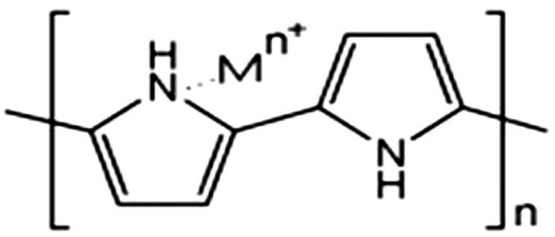
Fig. 1 The FTIR spectra of the PPy before (a) and after (b) the adsorption of nickel.[97]

A recent study on the removal of Cd and Co ions from aqueous solutions was carried out using the oxidative polymerization of pyrrole in acetonitrile and this study showed the maximum monolayer adsorption capacity of Cd and Co ions to be 71.4 and 70.04 mg g^{-1}, respectively (Table 2).[107] Their findings suggest that Cd and Co could be used as suitable agents for doping polypyrrole conducting polymers. Another recent study also showed the successful synthesis of polypyrrole using ferric chloride as an oxidant in the presence of poly(vinyl pyrrolidone) (PPy/PVP) and poly(vinyl alcohol) (PPy/PVA) as surfactants in aqueous media.[108] The role of the various surfactants on controlling the particle size and homogeneity of the polymer for its use as adsorbents for various heavy metals from aqueous solution has been reported. The removal percentage of Cd(II) was carried out using a batch method at pH 5 with a contact time of 45 minutes as the optimum conditions of sorption. The prepared PPy/PVP and PPy/PVA showed an adsorption efficiency of 51.41% and 50.64%, respectively.

2.2. Polypyrrole bio-adsorbents

The adsorption of different heavy metal ions using various PPy-based bio adsorbents is a very promising process in terms of low cost, renewable sources and ecofriendly. The major benefits of these types of bio-adsorbents are their wide range of effectiveness. Different forms of inexpensive materials, such as sawdust, rice husks, and chitin, have been studied as potential bio-adsorbents for heavy metals.

2.2.1. Polypyrrole sawdust (PPy/SD) composites. Sawdust (SD) obtained from wood industry is an abundant by-product,



Scheme 1 A plausible mechanism for metal ion adsorption on the surface of nitrogen functional groups in PPy conducting polymer.[97]

Table 2 Heavy metal adsorption capacity on polypyrrole-based materials

Type of adsorbents	Heavy metal ions	Optimum conditions/experimental conditions	Adsorption ($mg\ g^{-1}$)	Adsorption %
Conducting PPy[97]	Ni	pH 7.0; contact time 8 h; dose 0.08 g; initial conc. 1 ppm	—	100
Conducting PPy[100]	Ni	pH 12.0; contact time 30 min; dose 0.5 g; initial conc. 100 mg L^{-1}	—	84
Conducting PPy[106]	As(III)	Contact time 30 min; dose 0.25 g; initial conc. 5 mg L^{-1}	—	7.4
PPy particles with acetonitrile[107]	Cd(II)	pH 6.6; temp. 45 °C; batch adsorption equilibrium time 12 min, initial conc. varied 10–350 mg L^{-1}	71.4	—
PPy particles with acetonitrile[107]	Co(II)	pH 6.6; temp. 45 °C; batch adsorption equilibrium time 12 min, initial conc. varied 10–350 mg L^{-1}	70.04	—
PPy–PVP[108]	Cd(II)	pH 5; contact time 45 min; room temp.; dose 0.25 g; initial conc. 62.36 mg L^{-1}	—	51.41
PPy–PVA[108]	Cd(II)	pH 5; contact time 45 min; room temp.; dose 0.25 g; initial conc. 62.36 mg L^{-1}	—	49.98
PPy–SD[62]	Zn(II)	pH 3.0; contact time 14 min; temp. 40 °C; dose 0.5 g; initial conc. 100 mg L^{-1} aqueous solution	—	94.4
PPy–SD[109]	Cr(VI)	pH 5.0; equilibrium time 15 min; temp. 25 °C; dose 0.5 g; initial conc. 100 mg L^{-1}	3.4	—
PPy/rice husk ash[56]	Cu(II)	Contact time 25 min; room temp.; dose 0.5 g; 700 rpm; textile wastewater containing initial conc. 0.94 mg L^{-1}	—	96.4
PPy/rice husk ash[56]	Cd(II)	Contact time 25 min; room temp.; dose 0.5 g; 700 rpm; textile wastewater containing initial conc. 0.28 mg L^{-1}	—	92.4
Polypyrrole functionalized chitin[110]	Cr(VI)	pH 4.8; temp. 30–50 °C; batch adsorption contact time 60 min; dose 0.1 g; initial conc. 50 mg L^{-1}; 250 rpm	28.92–35.22	—
PPy-*g*-chitin[58]	Pb(II)	pH 6.0; contact time 60 min; temp. 50 °C; dose 0.1 g; initial conc. 10 mg L^{-1} aqueous solution	9.14	—
PPy-*g*-chitin[58]	Cd(II)	pH 6.0; contact time 60 min; temp. 50 °C; dose 0.1 g; initial conc. 10 mg L^{-1} aqueous solution	6.49	—
PPy-glycine doped composites[38]	Cr(VI)	pH 2.0–5.0; temp. 25 °C; batch adsorption contact time 0.5–3 h	217	—
Fe_3O_4@glycine-doped PPy magnetic nanocomposites[111]	Cr(VI)	pH 2.0; temp. 25 °C; batch adsorption contact time 0.5–3 h; dose 0.1 g; initial conc. 200 mg L^{-1}	238	99.91
PPy/Fe_3O_4 nanocomposites[112]	Cr(VI)	pH 2.0; temp. 25 °C; fixed bed column flow rate 3 mL min^{-1} with 100 mg L^{-1}	230.17	—
PPy/Fe_3O_4 magnetic nanocomposites[113]	Cr(VI)	pH 2.0; temp. 25 °C; batch adsorption contact time 12 h	169.4	—
Bamboo-like PPy nanotubes[114]	Cr(VI)	pH 2.0; room temp.	482.6	—
MWCNT–PPy nanotubes[115]	Pb(II)	pH 6.0; room temp. continuous column; flow rate 1.5 mL min^{-1}	25.0	—
PPy–PANI nanofibers[33]	Cr(VI)	pH 2.0; equilibrium time 30–180 min; temp. 25 °C	227	—
PANI–PPy copolymer[9]	Co(II)	pH 7.0; equilibrium time 11 min; dose 0.11 g with initial conc. 100 mg L^{-1}	—	99.68
PAN/PPy core/shell nanofiber mat[116]	Cr(VI)	pH 2.0; equilibrium time 30–90 min; temp. 25 °C	62	—
Orange-like Fe_3O_4/PPy composites microspheres[117]	Cr(VI)	pH 2.0; temp. 25 °C; batch adsorption contact time 30–180 min	209.2	—
PPy/γ-Fe_2O_3 (ref. 118)	Cr(VI)	pH 2.0; equilibrium time 15 min; temp. 25 °C	209	—
PPy/γ-Fe_2O_3 (ref. 118)	Cu(II)	pH 5.5; equilibrium time 35 min; temp. 25 °C	171	—
PPy–GO nanosheets[119]	Cr(VI)	pH 3.0; temp. 25 °C; batch adsorption contact time 24 h	497.1	—
PPy–GO NC[120]	Cr(VI)	pH 2; temp. 25 °C; batch adsorption equilibrium time 50 min, dose 0.025 g, 200 rpm	625	—
GO–αCD–PPy nanocomposites[121]	Cr(VI)	pH 2; temp. 25–45 °C; batch adsorption equilibrium time 30–200 min	606–666	—
PPy–rGO[47]	Hg(II)	pH 3.0; temp. 20 °C; batch adsorption contact time 3 h	980	—

Table 2 (*Contd.*)

Type of adsorbents	Heavy metal ions	Optimum conditions/experimental conditions	Adsorption ($mg\ g^{-1}$)	Adsorption %
PPy–Fe_3O_4/rGO[122]	Cr(VI)	pH 3; temp. 30–45 °C; batch adsorption equilibrium time 720 min	293.3	—
PPy-OMMTNC[123]	Cr(II)	pH 2.0; temp. 20 °C; batch adsorption dose 0.15 g; contact time 24 h	119.34	—
Graphene/Fe_3O_4@PPy nanocomposites[124]	Cr(VI)	pH 2.0; temp. 25 °C; batch adsorption, magnetic separation	348.4	—
PPy coated Fe_3O_4 nanocomposites[125]	Cr(VI)	pH 2.0; room temp.; continuous flow rate 0.2 L min^{-1} with 20 mg L^{-1}; residence time 30 min	—	80–98
PPy–TP nanocomposite[126]	Cr(VI)	pH 2; temp. 25–45 °C; batch adsorption equilibrium time 19 min, dose 0.2 g; initial conc. 200 mg L^{-1} aqueous solution	31.64	—
PPy/silica nanocomposites[127]	Hg(II)	Stirred room temp 10 h	0.97 mmol g^{-1}	
PPy/silica nanocomposites[127]	Pb(II)	Stirred room temp 10 h	0.53 mmol g^{-1}	
PPy/SH-beta/MCM-41 (ref. 49)	Hg(II)	pH 8.0; temp. 25–45 °C; batch adsorption contact time 10 min; dose 0.11 g; initial conc. 400 mg L^{-1}	157.43	—
PPy/SBA-15 nanocomposite[128]	Hg(II)	pH 8.0; temp. 25–45 °C; batch adsorption contact time of 60 min dose 0.1 g; initial conc. 60 mg L^{-1}	200	—
PANI/PPy/HMS[129]	Cd(II)	pH 8.0; room temp.; batch adsorption contact time of 8 min dose 0.04 g; initial conc. 50 mg L^{-1}	384.61	99.2
Hierarchical porous PPy-nanoclusters[2]	Cr(II)	pH 5.0; temp. 20 °C; batch adsorption equilibrium time 20 min	3.47 mmol g^{-1}	

low cost and easily available. It contains various organic compounds with polyphenolic groups[103] that could be easily coated with PPy and form PPy/SD composites, which can bind heavy metal ions through different conditions and mechanisms.[130] Several experiments on the efficiency of PPy/SD for the removal of Zn(II), Ni and Cr(VI) ions have been conducted by researchers.[62,109,131–133]

Omraei *et al.* showed the PPy/SD composite has considerable potential for the removal of Zn(II) from aqueous solution using a batch method.[62] The optimum conditions for sorption were been found to be a PPy/SD dose of 0.5 g in 100 mL, a contact time of 14 min, pH 3.0 and temperature 40 °C, and under these conditions the maximum removal efficiency of PPy/SD was 94.4%. Again, this study also demonstrated its effective adsorption in wastewater containing 328, 32.5 and 15.2 mg L^{-1} of Cr(VI), Ni and Zn(II), respectively. The removal efficiency was found to be 96.4%, 93.5% and 92.8% for Cr(VI), Ni and Zn(II), respectively.[62] Ansari and Fahim also prepared PPy/SD wherein $FeCl_3$ was used as the chemical oxidant for the oxidation of pyrrole into the polymer (PPy/Cl).[109] This study demonstrated that PPy/SD can be used in both batch and column adsorption as an efficient sorbent used for the removal of Cr(VI) ion from aqueous solutions. In the batch system, the removal of 98% Cr(VI) was found under the optimum conditions for sorption (PPy/SD dose 1.0 g in 25 mL; 100 ppm initial Cr(VI) concentration, contact time 15 min, pH 5.0 and temperature 25 °C). Again, in the column system, a maximum 98.6% removal efficiency for Cr(VI) was found using a uniformly packed 1.0 g PPy/SD in glass column at 2 mL min^{-1} with the other factors remaining constant.

2.2.2. Polypyrrole–rice husk ash (PPy/RHA) composites. Rice husk ash (RHA) is a solid obtained after burning rice husk, which is another natural abundant by-product of rice milling, low cost and easily available. A polypyrrole/rice husk ash nanocomposite was prepared by coating the rice husk ash substrate with pyrrole using chemical oxidative polymerization.[56] Their ability in the removal of heavy metals from wastewater were investigated by several researchers.[56,134] Ghorbani and Eisazadeh studied a continuous mode fixed bed column with a flow rate of 1.0 mL min^{-1} using different bed depths such as 10, 20 and 30 cm and found that PPy/RHA can be used as an effective adsorbent in wastewater treatment.[56] Another study reported the percentage efficiency of Cu and Cd ions removal was 96.4% and 92.4%, respectively, using 0.5 g adsorbent dosage with only 25 minutes of contact time at room temperature.[134]

2.2.3. Polypyrrole with chitin (PPy/ch) composites. Polypyrrole functionalized chitin (PPy-Ch) was synthesized *via in situ* polymerization and batch experiments were carried out to examine the adsorption of Cr(VI) ions under certain conditions.[110] This study showed a maximum adsorption capacity of 35.22 mg g^{-1} for an initial concentration of 50 mg L^{-1} at 50 °C and pH 4.8 with 60 min of contact time and 0.1 g adsorption dosage. The use of chitin alone as an adsorbent for heavy metals appears to be unsatisfactory due to its poor solubility in common solvents, low sorption capacity and poor stability. Therefore, it has been introduced to the polypyrrole structure to enhance the sorption capacity of this conducting polymer-based bio-adsorbent. Another study was carried out to investigate the

possibility of using chemically modified chitin with polypyrrole (PPy-*g*-Ch) as an adsorbent for the removal of Pb(II) and Cd(II) ions from an aqueous solution.[58] The maximum removal was obtained at pH 6 for both Pb(II) and Cd(II) ions with an adsorption capacity of 9.14 and 6.49 mg g^{-1}, respectively. Ion-exchange and electrostatic attraction followed by complexation have been found as the plausible mechanism for the removal of Pb(II) and Cd(II) ions from aqueous solution.

2.3. Glycine-doped polypyrrole and its magnetic nanocomposites

Chromium is the top most heavy metal ion contaminant found in highly industrial areas in developing countries due to its versatile uses.[33–38,111] Therefore, environmental scientists are more concerned to remove Cr ions efficiently and a lot of polymeric adsorption techniques have been applied.[33,38,111–114,116] In this continuation, a highly efficient removal of Cr(VI) using glycine doped polypyrrole from an aqueous solution has been investigated, which was prepared *via* the *in situ* polymerization of pyrrole monomer in the presence of glycine.[38] Formation of the PPy homopolymer and the inclusion of glycine in the PPy matrix were confirmed using ATR-FTIR spectroscopy and XRD analysis, respectively (Fig. 2 and 3).[38]

The adsorption of Cr(VI) onto the PPy-gly adsorbent was highly pH dependent and the removal efficiency of PPy-gly was much higher compared to other PPy homopolymers (Table 2). The maximum adsorption capacity of PPy-gly was found to be 217 mg g^{-1} at pH 2.0 and 25 °C. It is much better than the other reported polymer-based materials. It is much better than the other reported polymer-based materials. The adsorption mechanism was shown to be the ionic interactions between the amine groups of gly and the $HCrO_4^-$ ions (Scheme 2).[38] In another attempt, a very similar study was conducted by Ballav *et al.* for the removal Cr ions.[111] In this study, a Fe_3O_4 coated glycine doped polypyrrole magnetic nanocomposite (Fe_3O_4@-gly-PPy NC) was prepared. An adsorption capacity of 238 mg g^{-1} was reported with a maximum removal efficiency of 99.91%. The adsorption is highly pH dependent and the adsorbent can be separated using an external magnetic field.

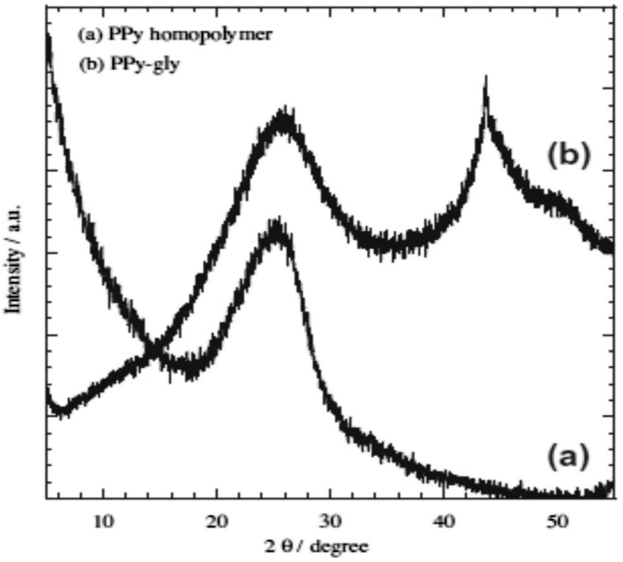


Fig. 3 XRD curves of (a) PPy homopolymer and (b) PPy-gly.[38]

2.4. Polypyrrole/Fe_3O_4 nanocomposites

Various forms, size and shapes of PPy/Fe_3O_4 nanocomposites have recently been used for the adsorption of heavy metal ions from wastewater or an aqueous solution.[111–113,117,118,135–137] A Fe_3O_4 coated PPy magnetic nanocomposite has been prepared *via* the *in situ* polymerization of pyrrole monomer for the removal of highly toxic Cr(VI).[113] The batch experimental results showed upto 100% adsorption with a 200 mg L^{-1} Cr(VI) aqueous solution at pH 2. The adsorption results showed that the Cr(VI) removal efficiency using the nanocomposite decreased with an increase in pH. XPS studies also suggested that ion exchange and reduction on the surface of the nanocomposite may be the possible mechanism for Cr(VI) removal by the PPy/Fe_3O_4 nanocomposite (Fig. 4).[113] Two energy bands

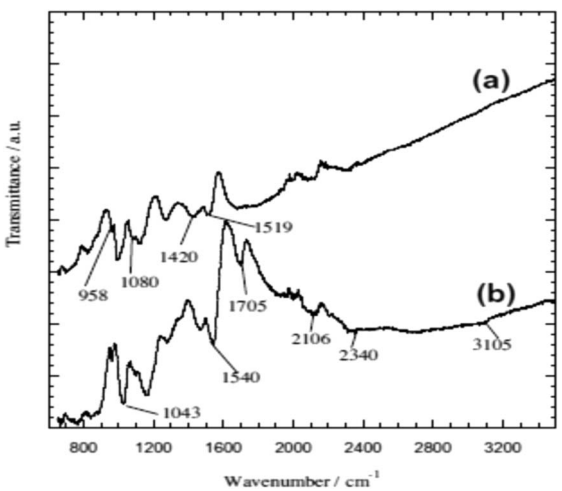
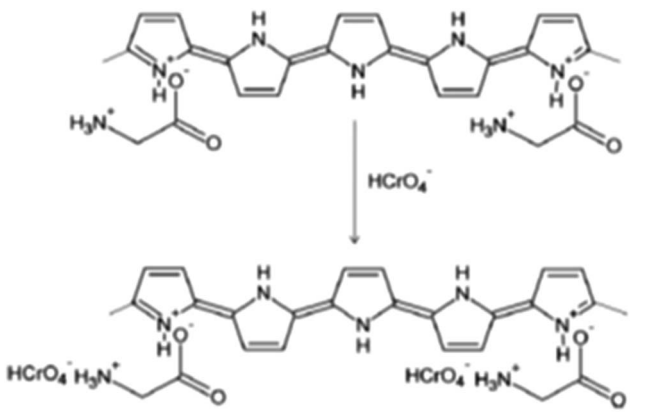


Fig. 2 The ATR-FTIR spectra of (a) PPy homopolymer and (b) PPy-gly.[38]



Scheme 2 The plausible adsorption mechanism for the removal of Cr(II) ions using the PPy-gly adsorbent.[38]

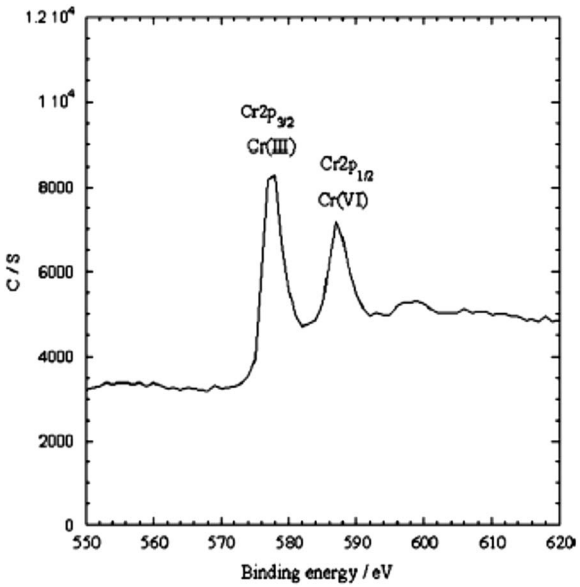
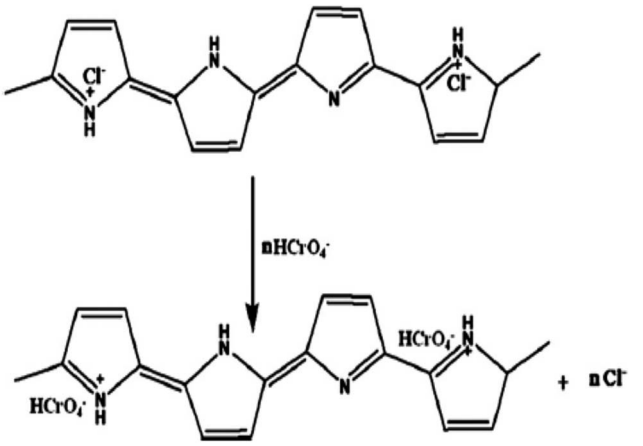


Fig. 4 The XPS spectra of the PPy/Fe_3O_4 nanocomposites after Cr(VI) adsorption.[113]

at about 577.5 eV and 587.2 eV corresponding to the binding energies of the Cr (2p3/2) and Cr (2p1/2) orbitals were observed.[113] This observation suggests the existence of both Cr(III) and Cr(VI) on the adsorbent surface. The existing of Cr(VI) species on the surface of the adsorbent are consistent with the sorption of Cr(VI) ions due to the anion exchange properties of PPy by replacing the doped Cl^- ions, as shown in Scheme 3. The presence of Cr(III) on the nanocomposite surface suggests that some fraction of the adsorbed Cr(VI) was reduced to Cr(III) *via* a reduction process. The reduction process may be due to the presence of electron rich polypyrrole moieties in the nanocomposite.

Another study showed that a similar PPy/Fe_3O_4 nanocomposite has been synthesized *via* an *in situ* chemical oxidative polymerization technique with 9 h of preparation time.[112] A fixed-bed column with continuous flow was also selected at a flow rate of 3 mL min^{-1} with 100 mg L^{-1} of Cr(VI). From this experiment, it has been confirmed that the breakthrough curve was dependent on the bed mass, initial Cr(VI) concentration, pH and flow rate. The efficiency of the PPy/Fe_3O_4 nanocomposite in environmental water to remove Cr(VI) ions was effective to give below acceptable levels of Cr(VI) upon processing 5.04 L of water with an initial 76.59 mg L^{-1} Cr(VI) concentration using only 2 g of adsorbent. An alternative method using a magnetic adsorption separation (MAS) process for extracting Cr(VI) ions from aqueous solution with polypyrrole coated Fe_3O_4 nanocomposites has been reported very recently.[125] The sorption capacity is influenced by the Fe_3O_4 nanoparticles loading. The separation process was aided by a mechanical and magnetic filtration mechanism by introducing steel wool into the separation chamber. This special arrangement yielded a 100% absorption capacity for Cr(VI) ions from an aqueous solution.



Scheme 3 A plausible mechanism for the removal of Cr(II) ions from aqueous solution.[113]

2.5. Polypyrrole-nanofibers

The inherent features of PPy, which include ease of chemical and electrochemical polymerization, a capacity to form an adhesive coating with different substrates, ease of chemical substitution to modify its properties and porous structure enables the exchange of ions with the surrounding medium, allow its application to heavy metal ions removal from an aqueous solution/wastewater.[33,118,135–138] The use of other conducting polymers, such as polyaniline (PANI) and polyacrylonitrile (PAN), have been used with PPy for heavy metal ions removal from an aqueous solution due to the presence of imine and amine groups, which can chelate metal ions and also adsorb anionic metal species through electrostatic interactions or hydrogen bonding.

Nowadays, nanotubes, nanowires, nanobelts or nanofibers structure based materials have been extensively used in medical, filtration, barrier, drug delivery, energy storage and many other sophisticated purposes due to their high aspect ratio and uniqueness.[9,11,33,118] The existence of nitrogen atoms in polyaniline and polypyrrole provides a good prospect for their applications in adsorption separation.[138] Therefore, a few studies have been adapted using both PPy and PANI as a nanofiber in adsorption technology[9,33] and PAN with PPy.[137] One of the pioneering studies showed that PPy–PANI nanofibers as an adsorbent of Cr(VI) were prepared without a template *via* the coupling of propagating $PPy^{\bullet+}$ and $PANI^{\bullet+}$ free radicals *via* the simultaneous polymerization of pyrrole and aniline monomers in the presence of $FeCl_3$ as an oxidant. The inclusion of both polymeric moieties, PPy and PANI, in the fibers was confirmed by ATR-FTIR spectroscopy (Fig. 5) and the polymeric process is shown in Scheme 4.

The experiments were carried out in a batch system to investigate the effect of pH, adsorbent dose, contact time, temperature and concentration of Cr(VI) ions. The adsorption of Cr(VI) ions on the nanofibers surface has been shown highly pH dependent and the maximum adsorption capacity of the PPy–PANI nanofibers for Cr(VI) was found to be 227 mg g^{-1} (Table 2).[33] Again, selective adsorption of Cr(VI) from an aqueous

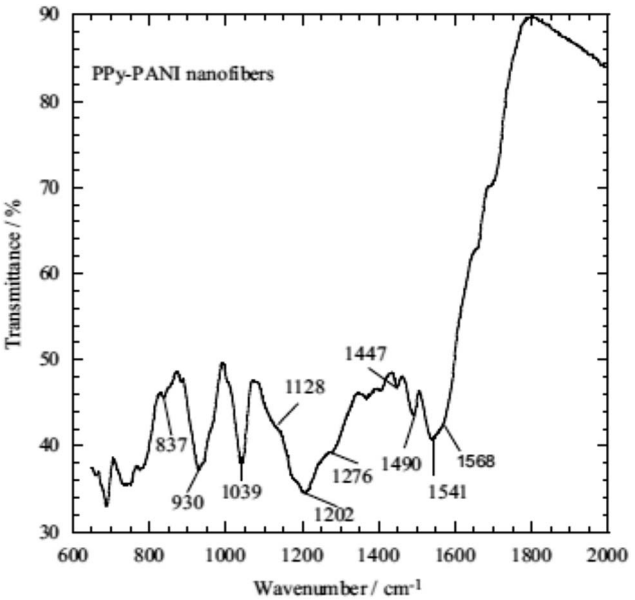
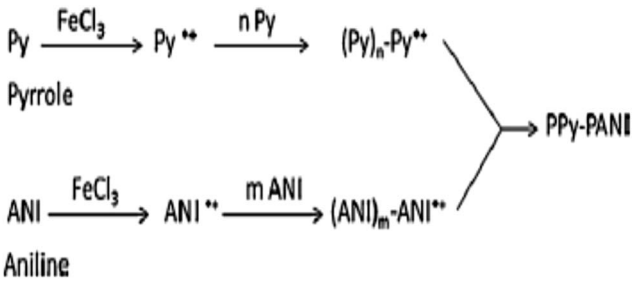


Fig. 5 The ATR-FTIR spectrum of the PPy–PANI nanofibers.[33]

solution was achieved in the presence of other co-existing ions. The main inspiration for synthesizing the nanofibers lies in fact that the incorporation of PANI into the growing polymer chain of PPy provides an increase in surface area that may enhance Cr(VI) ion adsorption when compared to its polypyrrole homopolymer counterpart and also overcome the limitations of the rareness of the new conjugated bond-containing monomers.[139] Another recent study showed that PANI/PPy copolymer nanofibers can be synthesized *via* an *in situ* chemical polymerization method and demonstrated its capacity for the removal of Co(II) from aqueous solutions.[9] Under the optimum conditions of the batch method, the sorption of Co(II) ions showed 99.68% removal efficiency for a 100 mg L^{-1} Co(II) solution (Table 2).

Another study reported on bamboo-like PPy nanotubes that were successfully prepared *via* reactive-template vapor phase polymerization for Cr(VI) ion removal.[114] The adsorption capacity of the bamboo-like PPy nanotubes (482.6 mg g^{-1}) was much higher than that of traditional PPy nanoparticles (Table 2).

A recent study showed a multi-walled carbon nanotubes–polypyrrole conducting polymer nanocomposite (MWCNT–PPy nanotube composite) could be successfully synthesized and applied to the removal of Pb(II) ions.[115] The adsorption capacity of the nanocomposite was reported to be 25.0 mg g^{-1} at pH 6.0 and room temperature. Because of the uniform structure of the MWCNT and its higher affinity for heavy metals, the material has been incorporated into PPy to realize the enhanced adsorption capacity of the prepared nanotube composites.



Scheme 4 The polymerization of pyrrole and aniline monomers, and the formation of PPy–PANI nanofibers.[33]

2.6. Polypyrrole–graphene nanocomposites

Due to optimal transformation of life, the demand for higher performance applications of nanoadsorbent materials has dramatically increased in the last few years. Different nanoparticles, such as zeolites, Fe_2O_3, TiO_2, carbon nanotubes (CNT), graphene oxide nanosheets or nanoplatelets, have been employed to characterize the nanocomposites at different stages of polymerization.[140–143] Graphene is a two-dimensional monoatomic thin sheet with a large lateral dimensional sp^2-hybridized carbon nanostructure and has unique properties of high tensile strength and Young's modulus, good electrical and thermal conductivities, and high aspect ratio.[142–144]

Theoretical and experimental results show that single-layered graphene sheets are the strongest materials developed to date,[142] and as a result, it has made possible novel applications, for example, the removal of heavy metal ions by nanoadsorbents. Recently, some study has been carried out on the preparation of PPy/graphene oxide (PPy/GO) and PPy/graphene nanocomposites for their applications in supercapacitor, transparent electrodes and environmental fields.[142–149] There are some reports on hierarchical PPy/GO nanosheets that combine the 2D nanosheets of GO and 3D nanoflowers of PPy.[144–147] Very recently, a study has been attempted to fabricate PPy/GO nanocomposite sheets using a simple and reliable sacrificial template polymerization method to remove Cr(VI) from an aqueous solution.[119] The adsorption capacity of the PPy/GO composite nanosheets is about two times as large as that of conventional PPy nanoparticles. Again, in another study, a polypyrrole graphene oxide nanocomposite (PPy–GO NC) was synthesized *via* an *in situ* polymerization of Py monomer in GO dispersion and used for Cr(VI) ion adsorption from aqueous solutions using both batch and packed-bed column methods.[120] The results showed that in the batch mode at 25 °C and pH 2, the maximum sorption capacity was 625 mg g^{-1}.

A novel graphene oxide–alpha cyclodextrin–polypyrrole nanocomposite (GO–αCD–PPy NC) has been successfully synthesized and applied for toxic hexavalent chromium removal from an aqueous solution.[121] Having both hydrophilic and hydrophobic characteristics, alpha cyclodextrin appeared to be useful in adsorbing organic and inorganic pollutants from wastewater forming inclusion complexes. To take advantage of this material as an adsorbent, it has been used to form a nanocomposite with graphene oxide and polypyrrole for a synergetic adsorption effect for hexavalent chromium ions removal. The maximum adsorption capacity was found to be 666.67 mg g^{-1} under optimum conditions (Table 2). Another novel hybrid nanocomposite prepared *via* anchoring the Fe_3O_4@polypyrrole nanospheres with hierarchical porous

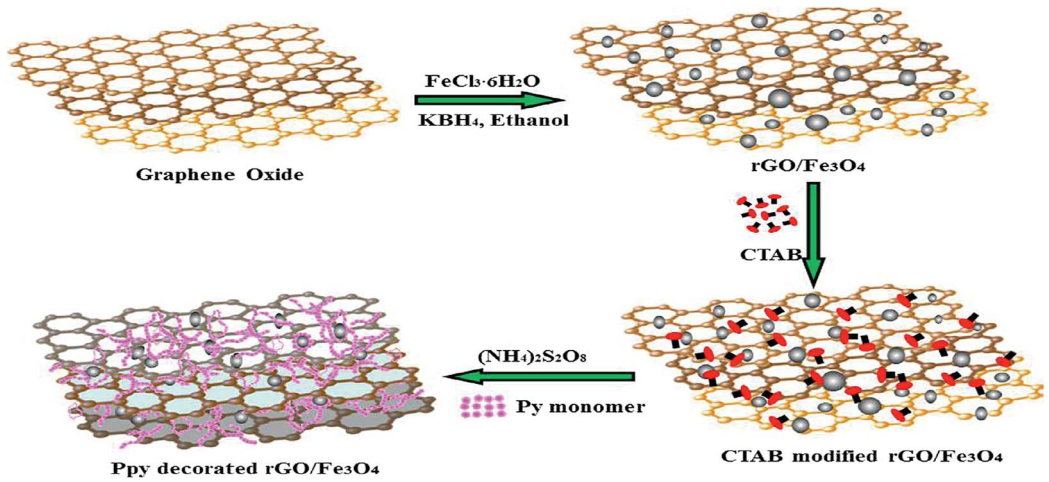


Fig. 6 Schematic of the preparation of the ternary composites.[122]

structure on graphene nanosheets (graphene/Fe_3O_4@PPy, GFP) has been reported for the removal of Cr(VI) ions.[124] The GFP exhibits an excellent adsorption capability (348.4 mg g^{-1}) for Cr(VI) removal due to the combined effect of graphene and Fe_3O_4@polypyrrole.

Again, a short communication reported a facile chemical route to synthesize a polypyrrole–reduced graphene oxide composite that showed a highly selective Hg^{2+} ion removal capacity.[47] Usually, materials functionalized with sulphur, nitrogen or oxygen have shown a high binding affinity to mercury. Conducting polymers incorporating these functional groups, interfaced with carbon and carbon-based derivatives have shown the enhanced removal of mercury and other toxic materials from water, but their surface area is not large,[150] which has been shown to be their major drawback. Thus, the higher surface area of reduced graphene oxide (rGO) and higher stability as well as non-toxicity of PPy motivated the synthesis of a PPy–rGO composite used for the removal of mercury(II) ions. The synthesis was achieved *via* the chemical exfoliation of graphite to graphene oxide and its subsequent reduction to rGO in the presence of PPy. The high BET surface area of the rGO (280.7 m^2 g^{-1}) influences the morphology of the PPy and increases the surface area from 6.18 m^2 g^{-1} (PPy) to 166 m^2 g^{-1} (PPy–rGO). The large surface area of the PPy–rGO composite increases the binding sites for mercury ions in solution. On the other hand, this prepared adsorbent is more stable and environmentally friendly. The adsorption capacity of PPy–rGO was much higher (980 mg g^{-1}) when compared to other traditional adsorbents (Table 2) with a characteristic feature of higher desorption capacity and good practical applications in the treatment of wastewater.[151]

Fig. 6 shows another facile synthesis of polypyrrole decorated rGO–Fe_3O_4 magnetic composites (PPy–Fe_3O_4/rGO) in two steps, which is used for the removal of Cr(VI) ions.[122] The results showed that the ternary PPy–Fe_3O_4/rGO nano-hybrid exhibited excellent performance for chromium(VI) removal from an aqueous solution. The maximum adsorption capacity for Cr(VI) on PPy–Fe_3O_4/rGO was 293.3 mg g^{-1}. The removal process was found to be pH dependent, exothermic and spontaneous. Both the electrostatic attraction and ion-exchange properties of the prepared nanocomposites were involved in the adsorption process of Cr(VI) ions.

2.7. Polypyrrole and other nanocomposites

Not only graphene, many other synthetic nano-adsorbents or organically modified clay nanocomposites or hierarchical porous polypyrrole nanoclusters act as a potential adsorbents for heavy metal ions especially for the more abundant Cr(VI) ions.[2,49,126–128] As a synthetic adsorbent, a polypyrrole–titanium(IV) phosphate nanocomposite (PPy–TiP) was prepared *via* an *in situ* oxidative polymerization process.[126] The adsorption process was based on thermodynamic parameters and was spontaneous and endothermic. The maximum adsorption capacity for Cr(VI) ion removal was found to be 31.64 mg g^{-1} under the optimum conditions (Table 2).

For the last few years, various fabrications of nanocomposite materials using conducting polymers and inorganic materials have been introduced in the nanotechnology area. For example, Maeda and Armes reported colloidal nanocomposites as adsorbents that were formed when pyrrole or aniline was oxidatively polymerized in the presence of silica (SiO_2) or tin(IV) oxide.[152] Recently, a short communication described a simple fabrication method for PPy/silica nanocomposites with cratered surfaces using a modified silica-templated oxidation/polymerization of pyrrole in the presence of $FeCl_3$ as the oxidant.[127] The PPy/silica nanocomposites were examined with regard to removing heavy metals from water. The results showed a relatively high adsorption capacity for Hg^{2+} and Pb^{2+} compared to Cd^{2+} and Cr^{3+}, which was most likely due to a complexation reaction between the secondary amine of pyrrole and the heavy metal ions (Table 2). However, another study showed the enhanced adsorption of Cd^{2+} ions using a nanostructured composite of modified hexagonal type mesoporous silica with polyaniline/polypyrrole nanoparticles (PANI/PPy/HMS).[129] The adsorption efficiency was found to be 99.91% after only 8 min (Table 2). Mesoporous M41S silicate groups,

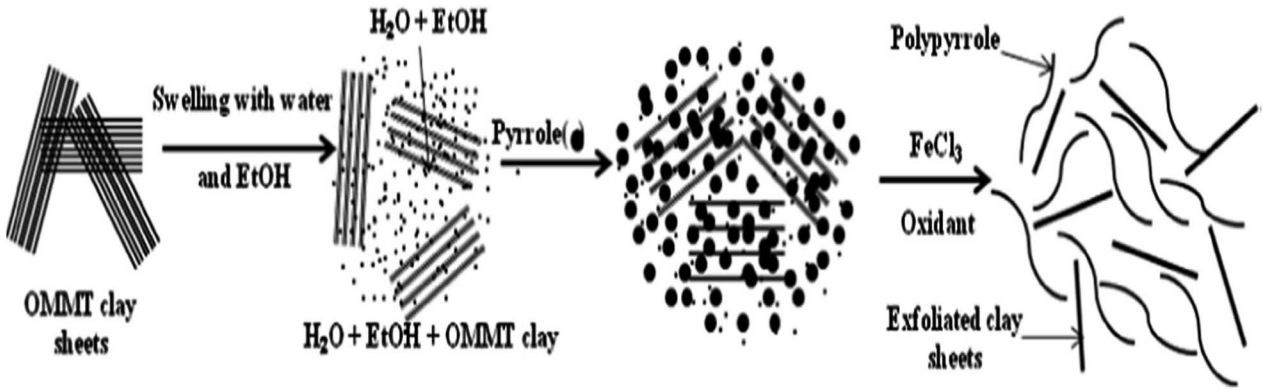


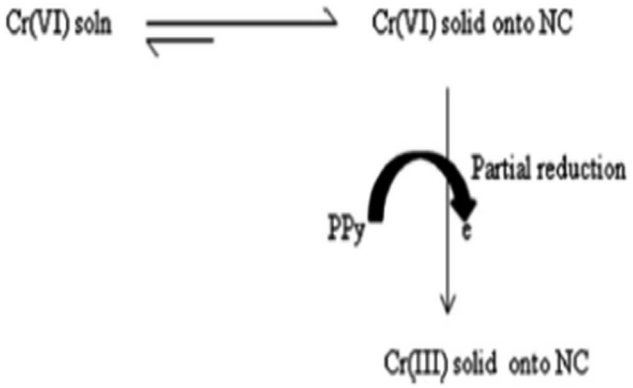
Fig. 7 The formation of exfoliated PPy-OMMTC nanocomposites.[123]

including MCM-41 and SBA-15, are considered as suitable adsorbents due to their high surface area, high pore volume and ordered structure to functionalize its surface.[153–156] A composite of polypyrrole/thiol-functionalized beta/MCM-41 (PPy/SH-beta/MCM-41) was prepared *via in situ* polymerization of pyrrole in the presence of SH-beta/MCM-41.[49] This study revealed that the adsorption of Hg^{2+} onto PPy/SH-beta/MCM-41 is an endothermic and spontaneous process, and is potentially able to remove Hg^{2+} ions from aqueous solutions at even high concentrations (400 mg L^{-1}) with an adsorption capacity of 157.43 mg g^{-1}. Another composite of PPy/SBA-15 was synthesized *via* chemical oxidation with $FeCl_3$ for 5 h.[128] A maximum adsorption capacity of Hg(II) removal (200 mg g^{-1}) was observed under the optimal conditions of pH 8, contact time of 60 min and absorbent dosage of 1 g L^{-1} at room temperature (Table 2).

An exfoliated PPy-organically modified montmorillonite clay nanocomposite (PPy-OMMTNC) was prepared as a potential adsorbent *via* the *in situ* polymerization of pyrrole monomer (Fig. 7) and used for the adsorption of toxic Cr(VI) from an aqueous solution.[123] In batch adsorption studies, it has been found that the removal efficiency was dependent on the pH, contact time, temperature and initial concentration, and the optimum removal of Cr(VI) ions was achieved at pH 2 wherein the maximum adsorption capacity was found to be 119.34 mg g^{-1} at 25 °C (Table 2).

It has been already reported that for the adsorption of Cr(VI) onto PPy based materials, an ion-exchange mechanism was involved *via* replacement of the doped Cl^- by the $HCrO_4^-$ ions.[113] However, some of Cr(VI) ions were reduced to Cr(III) by the electron-rich PPy polymer after adsorption. The whole adsorption and reduction of Cr(VI) onto the exfoliated PPy-OMMTNC has been shown to occur *via* another mechanism (Scheme 5).

Hierarchical porous nanomaterials have drawn more attention due to their higher surface area compared to traditional nanoparticles, nanocapsules or nanofibers.[2,157] A recent study was based on hierarchical porous polypyrrole nanoclusters, which were synthesized *via* a reactive-template method wherein Fe_3O_4 nanoclusters acted as both the template for shaping the PPy nanostructures and the oxidant.[2]



Scheme 5 The mechanism for adsorption and partial reduction of Cr(VI) onto the PPy-OMMTC nanocomposite.[123]

The prepared PPy-nanoclusters exhibited a wide surface area as high as 104 m^2 g^{-1} and due to their special hierarchical porous structures it was 3.5 times larger than that of traditional PPy. The maximum removal amount of Cr(VI) ions for the PPy-nanoclusters was 3.47 mmol g^{-1} in an aqueous solution at pH 5.0 (Table 2).

3. Conclusions and prospects

This review article offers the extensive information on the removal of different heavy metal ions from aqueous streams/wastewater effluents using a wide range of polypyrrole-based adsorbents. The effects of various parameters associated with the adsorption of heavy metal ions from aqueous solutions were compiled and discussed. They have some potential advantages and limitations. Polypyrrole homopolymer and PPy-bio-adsorbents have been readily synthesized and used for the removal of different heavy metal ions due to their low cost and simplicity. PPy-bio-adsorbents are recognized as effective and economic adsorbents for low concentration heavy metal ions treatment. However, the adsorption capacity is low and largely depends on the type of adsorbent. Among the available polymeric adsorbents, PPy-based nanomaterials have been widely explored as highly efficient adsorbents used for removal of

different heavy metal ions from different aqueous/wastewater sources due to the presence of highly active surface sites in the nano-adsorbents. They exhibit various advantages, such as fast kinetics, high capacity and preferable sorption, towards heavy metal ions in aqueous streams/wastewater. Nevertheless, to further promote the practical applications of PPy-based polymers in the abatement of heavy metal pollution, there still exist some technical constraints to be solved. To date, from a commercial point of view, no greater success has been achieved using conducting polymer-based adsorbents, particularly, polypyrrole and its composites. Extensive research is imperative to materialise the commercial success of conducting polymer-based adsorbents, which will provide a new dimension in adsorption technology towards mitigating the environmental pollution problem. Various polypyrrole-based composites/nanocomposites/bio-composites should be sourced out and focus on regeneration to minimize the cost involved for their commercial applications.

4. Conflict of interest

The authors declare no conflict of financial interest or any others.

Acknowledgements

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