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REVIEW

Removal of Heavy Metal Ions from Wastewater/Aqueous Solution by Polypyrrole-based Adsorbents: A Review

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Water pollution caused by heavy metal ions is becoming a serious threat for human and aquatic lives day by day. Therefore, treatment of heavy metal ions is of special concern for the environmental scientists and engineers. Historically, various methods such as physical and chemical precipitation, ion-exchange, reverse osmosis, membrane filtration, electrochemical treatment, solvent extraction, adsorption etc. for the removal of these metal ions from aqueous/wastewater have been widely studied. But in past few decades, conducting polymer-based adsorbents have received considerable attention owing to their potential applications in different heavy metal ions especially Cr(VI), Zn (II), Pb (II) etc. Among various conducting polymers, polypyrrole (PPy) based adsorbent plays a major role for removal of various heavy metal ions due to its ease of synthesis, biocompatibility and redox properties. The current review mainly focused on the physico-chemical properties, adsorption characteristics and mechanism of different polypyrrole-based adsorbents like PPy/biosorbents, PPy/Fe₃O₄ nanocomposites, PPy-polyaniline nanofibers, PPy-graphene nanocomposites, exfoliated PPy-organically modified clay nanocomposites, hierarchical porous PPy-nanoclusters etc. as well as their application in the removal of heavy metal ions.

1. Introduction

Nowadays hazardous heavy metal pollution of wastewater is the utmost significant environmental problem and endangers the human being throughout the world. Due to rapid urbanization and industrialization such as metal plating, mining, tanneries, painting, batteries, paper industries, printing and photographic industries, pesticides and fertilizer industries, car radiator manufacturing, etc., 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), Co(II) etc. containing wastewaters are directly or indirectly discharged into the streams, lakes, rivers or oceans increasingly, especially in developing countries.¹⁻⁹ Also, soils in surrounding military bases are offering potential risk of certain heavy metals which can be a threat to ground water 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 amount of different heavy metals are extremely necessary for human beings due to their presence of some vitamins or co-factors, but excessive exposure or intake of them 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 results of heavy metals found in industrial wastewater.⁸⁻¹⁶ According to the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA), the toxicities and the consequences of these heavy metals are highlighted here.

1.1. Arsenic (As)

Although arsenic (As) is a naturally occurring metalloid and common constituent of earth crust, but 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, especially in India, Bangladesh, Vietnam, Cambodia, Thailand, Chile, Southwest USA and Canada.^{13,14,17} Therefore it is categorized as the first priority toxic elements by 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 low concentration of chronic exposure may cause As poisoning.^{13-17,20-22} Thus, WHO and various environmental protection agencies set the permissible limits of As as 0.01 mg/L in drinking water.^{18,19}

1.2. Lead (Pb)

Inorganic lead (Pb) arising 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} The toxic symptoms are anaemia, insomnia,

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headache, dizziness, irritability, weakness of muscles, hallucination and renal damages.²³⁻²⁸ Hence, Pb has been classified as 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 whereas WHO limits it as 0.05 mg/L.^{18,19}

1.3. Chromium (Cr)

Chromium (Cr) is extensively used in electroplating, leather tanning, metal finishing, nuclear power plant, dyeing, photography industries and textile industries.²⁹⁻³³ In aqueous solution it exists in both Cr(III) and Cr(VI) forms. Hexavalent chromium which is more toxic, alters the human physiology, accumulates in 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 to the surface water is 0.1 mg/L and for drinking water is 0.05 mg/L.^{18,37}

1.4. Mercury (Hg)

Mercury (Hg) releases into environments 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 cause 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 priority pollutants, 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, fertilizers etc.⁵⁰⁻⁵² It is well known that chronic cadmium toxicity has been the cause of Japan Itai-Itai disease.⁵¹ Acute or chronic exposures of Cd also cause high blood pressure, kidney damage, destruction of testicular tissue, osteoporosis and destruction of red blood cells.⁵⁰⁻⁵⁸ Cd may replace zinc in some enzymes, thereby altering the stereo-structure of the enzyme and impairing its catalytic activity.⁵⁷ It has been classified by US EPA as a probable human carcinogen and set a safe drinking water limits upto 0.005 mg/L.^{18,19}

1.6. Zinc (Zn)

Tracing amounts of some metal ions such as zinc (Zn), copper (Cu) and cobalt (Co) are required by organisms as cofactors with enzymatic activities.^{59,60} However, the excess of these metal ions will cause serious problems on living organisms due to their higher toxicity, carcinogenic and bioaccumulation.⁵⁹⁻⁶²

Zn is one of the most common pollutants for surface and ground water as its versatile uses.⁶² Again, due to its non-biodegradability and acute toxicity, Zn-containing liquid and solid wastes are considered as hazardous wastes. Excess amount of Zn exposure can cause well-known health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia.⁵⁹⁻⁶² WHO recommended the maximum

acceptable concentration of Zn ions in drinking water as 5.0 mg/L.¹⁸

1.7. Copper (Cu)

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

1.8. Cobalt (Co)

Cobalt (Co) is one of the most important transition metals which plays a double-dealing in both harmful and beneficial impact on human being. 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 contaminate surface and ground water.^{9,61,67-68} Although a minute amount of Co is needed for formation of vitamin B₁₂ but excessive exposure of it 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 be found due to excess Co in wastewater.⁶⁷⁻⁷⁰ The permissible limits of cobalt which is allowed to be in the irrigation water, inland surface water and drinking water are 1, 0.05 and 0.01mg/L respectively.¹⁸

1.9. Nickel (Ni)

The major sources of nickel contamination to 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 known as human carcinogen.⁷¹⁻⁷⁴ According to the WHO guidelines, the maximum permissible concentration of Ni in industrial discharge limit in wastewater is 2 mg/L, while that in drinking water should be less than 0.1 mg/L.¹⁸

The maximum contaminants level or permissible limits of some heavy metal ions in drinking water has been slightly different by the two most authentic international organization such as WHO and US EPA, as can be seen in Table 1.

Table 1: Permissible limits of some heavy metal ions in drinking water according to most authentic references

Heavy Metal Ions	Permissible Limits (ppm)	
	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	-

1.10 Suitable techniques for the removal of heavy metal ions

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

Although several methods are being involved for many years to remove heavy metal ions from wastewater but 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 stream/wastewater.^{4,9,15,65,75-82} Up to date, in particular various adsorption methods can be considered as an effective and widely used method due to its simplicity and easy operational conditions.⁸⁰⁻⁸⁶ In addition, adsorption is mostly reversible, thus adsorbents can be easily regenerated by 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, polymer-inorganic hybrid adsorbents and so on.^{15,3347,,83-95} Among polymer-based adsorbents, conducting polymer-based adsorbents like polyaniline (PANI), polyethelenamine (PEI), polypyrrole (Ppy) and their composites have received considerable attention due to their potential applications in adsorbing various heavy metal ions, ease of their synthesis regeneration and operation, environmental and mechanical stability, and low cost. In addition, highly porous structure with specific surface electrochemical properties as well as ion exchange capacities have also drawn much attraction to the researchers.⁸⁹⁻⁹⁶ Moreover, the existence of positively charged nitrogen atoms in polypyrrole provides a good prospect for their applications in adsorption.⁹⁷

This article presents an overview of various polypyrrole-based polymeric adsorbents for the removal of heavy metal ions from aqueous/wastewater sources. These polymeric adsorbents can be produced from different chemical oxidation polymerization of pyrrole to simple polypyrrole formation, multidimensional PPy formation like PPy-bio-adsorbents, PPy-magnetic composites, PPy-nanofibers, PPy-graphene nanocomposites and hierarchical porous PPy-nanomaterials etc. The effects of different parameters such as pH of the solution, adsorbent dosage, initial concentration of heavy metal ions, contact time etc. 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 and

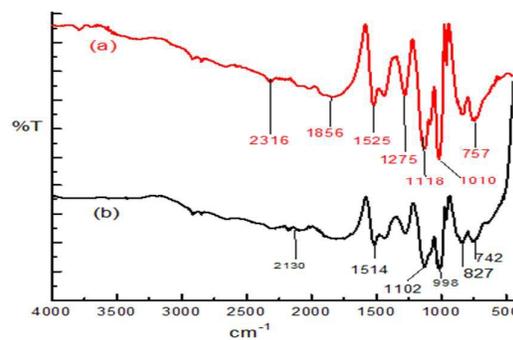
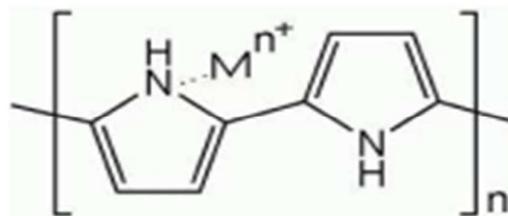


Fig. 1: FTIR spectra of the PPy before (a) and after (b) adsorption of nickel⁹⁷

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^- , NO_3^- , etc., mainly exhibits anion exchanging behavior due to the high mobility of these ions in the polymer matrix. However, under certain conditions, cation exchange was also found to take place with large dopants like polyvinylsulfonate and polystyrenesulfonate, due to immobility of these ions in the polymer matrix.⁹⁸ PPy has also exhibited a good prospect in adsorption application for its nitrogen atoms in the polymer chains. Hence, the removal of heavy metal ions is one of the applications of conducting polymers. A lot of efforts have been made to remove heavy metal ions by polypyrrole conducting polymer prepared by chemical oxidative polymerization of pyrrole in presence of different dopants in different conditions, as the adsorption efficiency largely depends on the preparation conditions of PPy.^{89,100-105}

One of the studies used $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as an oxidant in aqueous solution to form of PPy using the mole ratio of monomer to oxidant as applied 1:1.⁹⁷ The effects of various agents such as pH of solution, dosage of adsorbent and contact time has been investigated and this study has exhibited 100% adsorption efficiency for the removal of Ni ions from aqueous solution at pH 7.0, 8 hours contact time and 0.08g PPy adsorbent dose in 1ppm initial Ni ion concentration. FT-IR spectrum (Fig.1) evidenced that the coordination of Ni ions to nitrogen in amine functional groups of PPy polymer chain involved in the adsorption process and the possible metal ion adsorption is shown in Scheme 1.⁹⁷



Scheme 1: A plausible mechanism of metal ion adsorption on the surface of nitrogen functional groups in PPy conducting polymer⁹⁷

Another study revealed that PPy has been prepared by chemical oxidative polymerization of pyrrole using anhydrous FeCl_3 as an oxidant¹⁰⁰ and various effects such as pH of solution, dosage of adsorbent and contact time were

investigated. This study has shown prepared PPy markedly removes (84%) Ni ions in alkaline pH condition and results compared with other adsorbents (Table 2).

Table 2: Heavy metal adsorption capacity on polypyrrole-based materials

Type of adsorbents	Heavy metal ions	Optimum conditions/ Experimental conditions	Adsorption	
			(mg/g)	%
Conducting PPy ⁹⁷	Ni	pH 7.0; contact time 8hrs; dose 0.08g; initial conc. 1ppm	-	100
Conducting PPy ¹⁰⁰	Ni	pH 12.0; contact time 30min; dose 0.5g; initial conc. 100mg/L	-	84
Conducting PPy ¹⁰⁶	As(III)	contact time 30min; dose 0.25g; initial conc. 5mg/L	-	7.4
PPy particles with acetonitrile ¹⁰⁷	Cd (II)	pH 6.6; temp. 45°C; batch adsorption equilibrium time 12 min, initial conc. varied 10-350mg/L	71.4	-
PPy particles with acetonitrile ¹⁰⁷	Co (II)	pH 6.6; temp. 45°C; batch adsorption equilibrium time 12 min, initial conc. varied 10-350mg/L	70.04	-
PPy-PVP ¹⁰⁸	Cd (II)	pH 5; Contact time 45 min; room temp.; dose 0.25g; initial conc. 62.36 mg/L	-	51.41
PPy-PVA ¹⁰⁸	Cd (II)	pH 5; Contact time 45 min; room temp.; dose 0.25g; initial conc. 62.36 mg/L	-	49.98
PPy/SD ⁶²	Zn(II)	pH 3.0; contact time 14 min; temp. 40°C; dose 0.5g; initial conc. 100mg/L aqueous solution	-	94.4
PPy/SD ¹⁰⁹	Cr(VI)	pH 5.0; equilibrium time 15 min; temp. 25°C; dose 0.5g; initial conc. 100mg/L	3.4	-
PPy/Rice hask ash ⁵⁶	Cu (II)	Contact time 25 min; room temp.; dose 0.5g; 700 rpm; textile wastewater containing initial conc. 0.94mg/L	-	96.4
PPy/Rice hask ash ⁵⁶	Cd (II)	Contact time 25 min; room temp.; dose 0.5g; 700 rpm; textile wastewater containing initial conc. 0.28mg/L	-	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; 250 rpm	28.92–35.22	-
PPy-g-Chitin ⁵⁸	Pb (II)	pH 6.0; contact time 60 min; temp. 50°C; dose 0.1g; initial conc. 10mg/L aqueous solution	9.14	-
PPy-g-Chitin ⁵⁸	Cd (II)	pH 6.0; contact time 60 min; temp. 50°C; dose 0.1g; initial conc. 10mg/L 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 hours	217	-
Fe ₃ O ₄ @glycine-doped PPy magnetic nanocomposites ¹¹¹	Cr (VI)	pH 2.0; temp. 25°C; batch adsorption contact time 0.5-3 hours; dose 0.1 g; initial conc. 200 mg/L	238	99.91
PPy/Fe ₃ O ₄ nanocomposites ¹¹²	Cr (VI)	pH 2.0; temp. 25°C; fixed bed column flow rate 3ml/min with 100mg/L	230.17	-
PPy/Fe ₃ O ₄ magnetic nanocomposites ¹¹³	Cr (VI)	pH 2.0; temp. 25°C; batch adsorption contact time 12 hours	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	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 0.11g with initial conc. 100mg/L	-	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 ₃ O ₄ /PPy composites microspheres ¹¹⁷	Cr (VI)	pH 2.0; temp. 25°C; batch adsorption contact time 30 – 180 min	209.2	-

Table 2 (Contd.)

Type of adsorbents	Heavy metal ions	Optimum conditions/ Experimental conditions	Adsorption	
			(mg/g)	%
PPy/ γ -Fe ₂ O ₃ ¹¹⁸	Cr (VI)	pH 2.0; equilibrium time 15min; temp. 25°C	209	-
PPy/ γ -Fe ₂ O ₃ ¹¹⁸	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 hours	497.1	-
PPy-GO NC ¹²⁰	Cr(VI)	pH 2; temp. 25°C; batch adsorption equilibrium time 50 min, dose 0.025g, 200 rpm	625	-
GO- α CD-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 hours	980	-
PPy-Fe ₃ O 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 0.15g; contact time 24 hours	119.34	-
Graphene/Fe ₃ O ₄ @PPy nanocomposites ¹²⁴	Cr (VI)	pH 2.0; temp. 25°C; batch adsorption, magnetic separation	348.4	-
PPy coated Fe ₃ O ₄ nanocomposites ¹²⁵	Cr (VI)	pH 2.0; room temp.; continuous flow rate 0.2 L/min with 20mg/L; 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. 200mg/L aqueous solution	31.64	-
PPy/silica nanocomposites ¹²⁷	Hg(II)	Stirred room temp 10 hours	0.97 mmol/g	
PPy/silica nanocomposites ¹²⁷	Pb(II)	Stirred room temp 10 hours	0.53 mmol/g	
PPy/SB- β /MCM-41 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	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	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	384.61	99.2
Hierarchical porous PPy-nanoclusters ²	Cr(II)	pH 5.0; temp. 20°C; batch adsorption equilibrium time 20 min	3.47mmol/g	

A recent study on the removal of Cd and Co ions from aqueous solutions was done by oxidative polymerization of pyrrole in acetonitrile and this study has shown the maximum monolayer adsorption capacity of Cd and Co ions to be 71.4 and 70.04 mg/g, 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 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 by batch method at pH 5 with the contact time of 45 minutes being the optimum conditions of sorption. The prepared Ppy/PVP and Ppy/PVA showed the adsorption efficiency of 51.41% and 50.64%, respectively.

2.2. Polypyrrole bio-adsorbents

Adsorption of different heavy metal ions by various PPy-based bio adsorbents is a very promising process in terms of low cost, renewable sources and ecofriendly. The major

benefits of this type of bio-adsorbents are its wide range of effectiveness. Different forms of inexpensive materials such as sawdust, rice husks, chitin etc. 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, low cost and easily available. It contains various organic compounds with polyphenolic groups¹⁰³ that could 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 was conducted by some scientists.^{62,109, 131-133}

Omeraei *et al.* showed PPy/SD composite has considerable potential for the removal of Zn(II) from aqueous solution by batch method.⁶² The optimum conditions of sorption has been found to be PPy/SD dose of 0.5 g in 100 mL, contact time of 14 min, pH 3.0 and temperature 40°C and at this condition the maximum removal efficiency of PPy/SD was 94.4%. Again, this study also exhibits in effective adsorption in wastewater that containing 328, 32.5 and 15.2 mg/L Cr (VI), Ni and Zn (II) respectively. The removal efficiency has been 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 where FeCl_3 was used as chemical oxidant for oxidation of pyrrole into polymer (PPy/Cl).¹⁰⁹ This study has exhibited PPy/SD was used both batch and column adsorption as an efficient sorbent for removal of Cr(VI) ion from aqueous solutions. In batch system, the removal of 98% Cr(VI) has been found in the optimum conditions of sorption (PPy/SD dose 1.0g in 25 mL; 100ppm initial Cr(VI) concentration, contact time 15 minutes, pH 5.0 and temperature 25°C). Again, in column system, the maximum 98.6% removal efficiency of Cr(VI) has been found in uniformly packed 1.0g PPy/SD in glass column at 2ml/min and other factors remained constant.

2.2.2. Polypyrrole-rice husk ash (PPy/RHA) composites

Rice husk ash (RHA) is a solid obtained after burning of rice husk which is another natural abundant by-product of rice mill, low cost and easily available. Polypyrrole/rice husk ash nanocomposite was prepared by coating the rice husk ash substrate with pyrrole using the chemical oxidative polymerization.⁵⁶ Their ability in the removal of heavy metals from wastewater were investigated by few researchers^{56,134} Ghorbani and Eisazadeh studied continuous mode fixed bed column with a flow rate of 1.0 mL/min with different bed depths such as 10, 20 and 30 cm and found that PPy/RHA can be used as an effective adsorbent in the wastewater treatment⁵⁶. Another study reported the percentage efficiency of Cu and Cd ions removal as 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 by *in-situ* polymerization and the batch experiments were carried out to examine the adsorption of Cr(VI) ions at certain conditions.¹¹⁰ This study exhibited the maximum adsorption capacity of 35.22 mg/g for an initial concentration of 50 mg/L at 50 °C and 4.8 pH with 60 minutes 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 poor solubility in common solvents, low sorption capacity and poor stability. Therefore, it has been introduced to polypyrrole structure to enhance the sorption capacity of this conducting polymer-based bio-adsorbent. Another study was carried out on 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 aqueous solution.⁵⁸ The maximum removal was obtained at pH 6 for both Pb(II) and Cd(II) ions with the adsorption capacity of 9.14 and 6.49 mg/g, respectively. The 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 contamination in high industrial areas in developing countries due to its versatile uses.^{33-38,111} Therefore, environmental scientists are

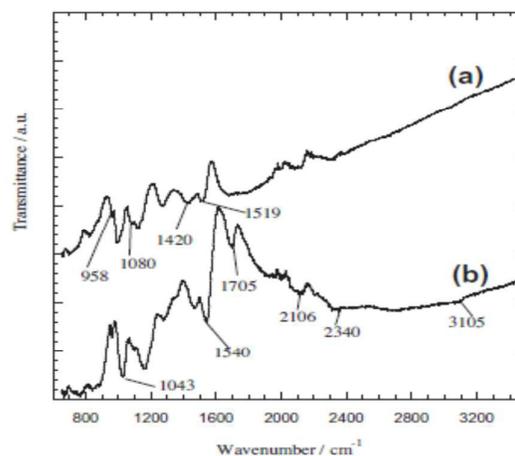


Fig.2: ATR-FTIR spectra of (a) PPy homopolymer and (b) PPy-gly³⁸

more concerned to remove this Cr ion efficiently and a lot of polymeric adsorption techniques were applied.^{33,38, 111-114,116} In this continuation, a high efficient removal of Cr(VI) using glycine doped polypyrrole from aqueous solution has been investigated which was prepared via *in situ* polymerization of pyrrole monomer in the presence of glycine.³⁸ Formation of PPy homopolymer and inclusion of glycine in the PPy matrix were confirmed by ATR-FTIR and XRD, respectively (Fig.2 and 3).³⁸

The adsorption of Cr(VI) onto the PPy-gly adsorbent was highly pH dependent and removal efficiency by PPy-gly was much higher compared to other PPy homopolymer (Table 2). The maximum adsorption capacity of PPy-gly was found to be 217 mg/g at pH 2.0 and 25°C. It is much better than other reported polymer-based materials. It is much better than other reported polymer-based materials. The adsorption mechanism has shown the ionic interaction between amine

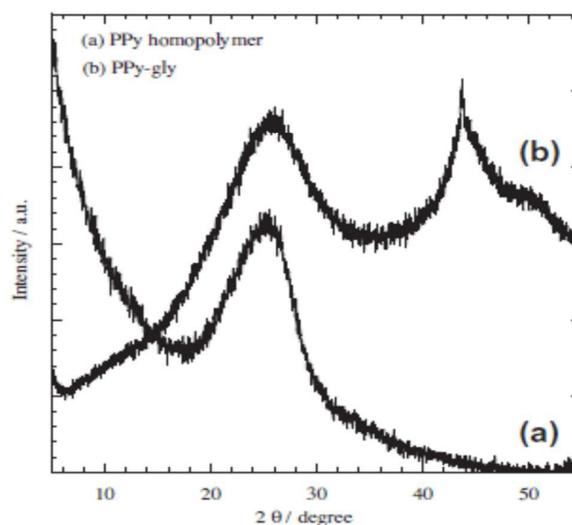
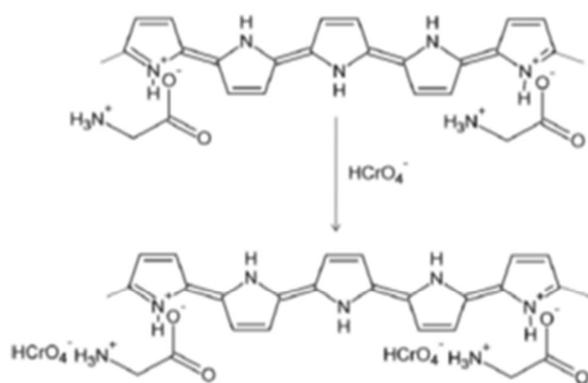


Fig.3: XRD curves of (a) PPy homopolymer and (b) PPy-gly³⁸



Scheme 2: Plausible adsorption mechanism for the removal of Cr(II) ions by the PPY-gly adsorbent³⁸

groups of gly and 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, Fe_3O_4 coated glycine doped polypyrrole magnetic nanocomposite (Fe_3O_4 @gly-PPy NC) was prepared. An adsorption capacity of 238 mg/g has been reported with a maximum removal efficiency of 99.91%. The adsorption is highly pH dependent and the adsorbent can be separated by external magnetic field.

2.4. Polypyrrole/ Fe_3O_4 nanocomposites

Various forms, size and shape of PPy/ Fe_3O_4 Nanocomposites are recently advanced used for the adsorption of heavy metal ions from wastewater or aqueous solution.^{111-113,117,118,135-137} Fe_3O_4 coated PPy magnetic nanocomposite has been prepared via in situ polymerization of pyrrole monomer for the removal of highly toxic Cr(VI).¹¹³ Batch experimental result showed upto 100% adsorption with 200 mg/L Cr(VI) aqueous solution at pH 2. Adsorption results showed that Cr(VI) removal efficiency by 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 at about 577.5 eV and 587.2 eV corresponding to the binding energies of Cr (2p3/2) and Cr (2p1/2) orbital's, respectively, are 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 is consistent with the sorption of Cr(VI) ions due to the anion exchange property 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 adsorbed Cr(VI) was reduced to Cr(III) by a reduction process. The reduction process may be due to the presence of electron rich polypyrrole moieties in the nanocomposite.

Another study showed the similar PPy/ Fe_3O_4 nanocomposite has been synthesized via in situ chemical oxidative polymerization technique for 9 hours preparation time.¹¹² Fixed-bed column with continuous flow has been also

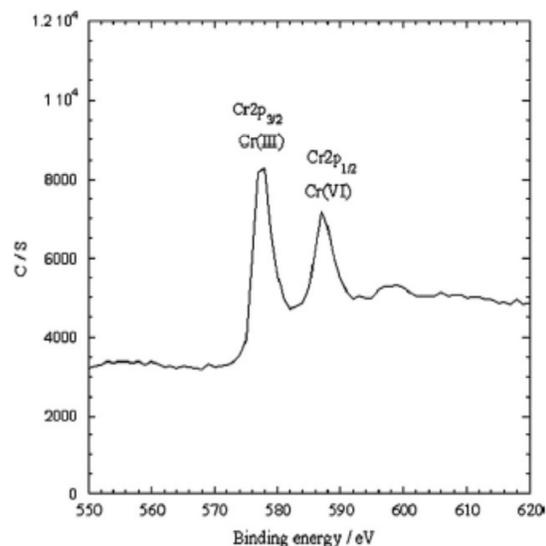
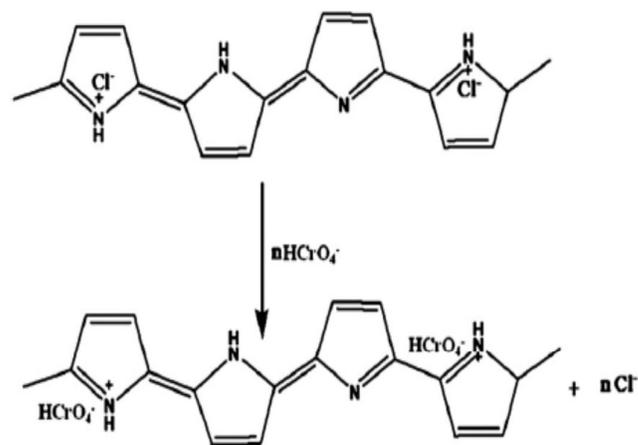


Fig.4: XPS spectra of the PPy/ Fe_3O_4 nanocomposites after Cr(VI) adsorption¹¹³

selected at a flow rate of 3 mL/min with 100 mg/L of Cr(VI). From this experiment, it has been confirmed that the breakthrough curve is dependent on bed mass, initial Cr(VI) concentration, pH and flow rate. The Efficiency of PPy/ Fe_3O_4 nanocomposite in environmental water to remove Cr(VI) ion is effective as below acceptable level by processing 5.04 L water with initial 76.59 mg/L Cr(VI) concentration using only 2g of adsorbent mass. An alternative method in magnetic adsorption separation (MAS) process for extracting Cr(VI) ions from aqueous solution using polypyrrole coated Fe_3O_4 nanocomposites has been reported very recently.¹²⁵ The sorption capacity is influenced by Fe_3O_4 nanoparticles loading. The separation process was aided by mechanical and magnetic filtration mechanism by introducing steel wool into the separation chamber. This special arrangement yielded 100% absorption capacity of Cr(VI) ions from aqueous solution.



Scheme 3: A plausible mechanism for the removal of Cr(II) ions from aqueous solution¹¹³

2.5. Polypyrrole - nanofibers

The inherent features of PPy which include ease of chemical and electrochemical polymerization, capacity to form adhesive coating at different substrates, ease of chemical substitution to modify its properties and porous structure enables exchange of ions with the surrounding medium provides its application to heavy metal ions removal from aqueous solution/ wastewater.^{33,118,135-138} The use of other conducting polymers like polyaniline (PANI) and polyacrylonitrile (PAN) has been used with PPy in different nature for heavy metal ions removal from aqueous solution due to the presence of imine and amine groups which can chelate metal ions and also can adsorb anionic metal species through electrostatic 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 Hence, few studies have been adapted by both PPy and PANI as a nanofiber in adsorption technology^{9,33} and PAN with PPy.¹³⁷ One of the pioneer studies showed that PPy-PANI nanofibers as adsorbent of Cr(VI) were prepared without template *via* coupling of propagating PPy^{••} and PANI^{••} free radicals by simultaneous polymerization of pyrrole and aniline monomers in presence of FeCl₃ oxidant. Inclusion of both polymeric moieties PPy and PANI in the fibers has been confirmed by the ATR-FTIR (Fig. 5) and polymeric formation are shown in Scheme-4.

The experiments were carried out in 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 (Table 2).³³ Again, selective adsorption of Cr(VI) from aqueous solution has been 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 the Cr(VI) ion adsorption compared to its polypyrrole homopolymer counterpart and as well overcome the limitations of the rareness of new conjugated bond-containing monomers.¹³⁹ Another recent study showed that, PANI/PPy copolymer nanofibers are synthesized by in situ chemical polymerization method and its capacity for the removal of Co(II) from aqueous solutions.⁹ In optimum condition of batch method, the sorption of Co(II) ions showed 99.68% removal efficiency for 100 mg/L Co(II) solution (Table 2).

Another study reported on bamboo-like PPy nanotubes that has been successfully prepared *via* reactive-template vapor phase polymerization for Cr (VI) ions removal.¹¹⁴ The adsorption capacity of bamboo-like PPy nanotubes (482.6 mg/g) was much higher than that of traditional PPy nanoparticles (Table 2).

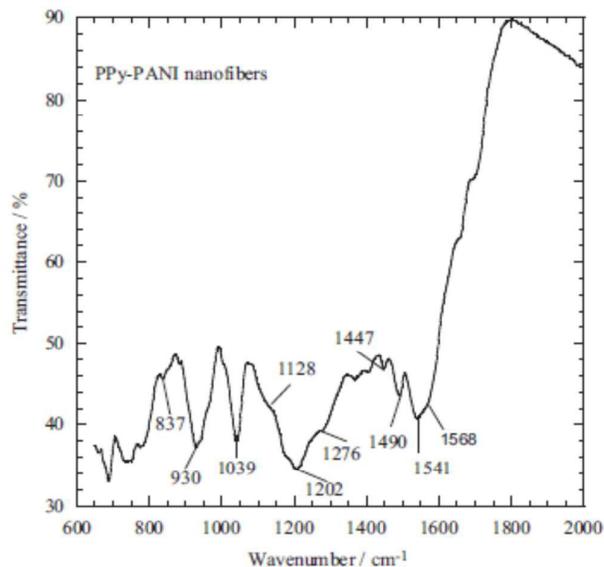
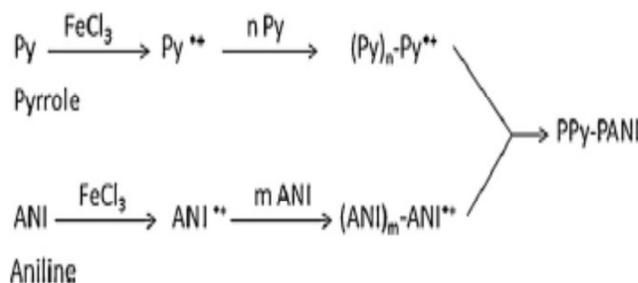


Fig.5: ATR-FTIR spectrum of the PPy-PANI nanofibers³³

A recent study of multi-walled carbon nanotubes-polypyrrole conducting polymer nanocomposite (MWCNT-PPy nanotube composite) has been successfully synthesized and applied to the removal of Pb(II) ions.¹¹⁵ The adsorption capacity of the nanocomposite was reported as 25.0 mg/g at 6.0 pH and room temperature. Because of the uniform structure of MWCNT and the higher affinity for heavy metals, it has been incorporated to PPy to realize the enhanced adsorption capacity of the prepared nanotube composites.

2.6. Polypyrrole – graphene nanocomposites

Due to optimal transformation of life, the demand for higher performance applications of nanoadsorbent materials has dramatically raised in the last few years. Different nanoparticles like zeolites, Fe₂O₃, TiO₂, carbon nanotubes (CNT), graphene oxide nanosheets or nanoplatelets etc. are employed to characterize the nanocomposites at different stages of polymerization.¹⁴⁰⁻¹⁴³ Graphene is a two-dimensional monoatomic thin sheet with a large lateral dimension sp²-hybridized carbon nanostructure, has unique properties of high tensile strength and Young's modulus, good electrical and thermal conductivities, high aspect ratio.¹⁴²⁻¹⁴⁴



Scheme 4: Polymerization of pyrrole and aniline monomers and formation of PPy-PANI nanofibers³³

Theoretical and experimental results show that single-layered graphene sheets are the strongest materials developed thus far,¹⁴² as a result, it has made possible novel applications, for example removal of heavy metal ions by nano-adsorbents. Recently, some work has been done on the preparation of PPy/graphene oxide (PPy/GO) and PPy/graphene nanocomposites for their applications in supercapacitor, transparent electrodes and environmental field.¹⁴²⁻¹⁴⁹ There are some reports on hierarchical PPy/GO nanosheets by combining 2D nanosheets of GO and 3D nanoflowers of PPy has been also established.¹⁴⁴⁻¹⁴⁷ Very recently, a study has been attempted to fabric PPy/GO nanocomposite sheets by using a simple and reliable sacrificial template polymerization method to remove Cr(VI) from 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, polypyrrole graphene oxide nanocomposite (PPy-GO NC) were synthesized via *in-situ* polymerization of Py monomer in GO dispersion for Cr(VI) ions adsorption from aqueous solutions by using both batch and packed-bed column modes.¹²⁰ The results showed that in a batch mode at 25°C and pH 2, the maximum sorption capacity was 625 mg/g.

A novel graphene oxide-alpha cyclodextrin-polypyrrole nanocomposites (GO-αCD-PPY NC) has been successfully synthesized and applied for toxic hexavalent chromium removal from 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 the advantage of this material as an adsorbent, it has been used to form nanocomposite with graphene oxide and polypyrrole for the synergetic adsorption effect on hexavalent chromium ions removal. The maximum adsorption capacity was found to be 666.67 mg/g at certain optimum conditions (Table 2). Another novel hybrid nanocomposite prepared via anchoring the Fe₃O₄@polypyrrole nanospheres with hierarchical porous structure on graphene nanosheets (graphene /Fe₃O₄ @ PPy, GFP) have been reported for the removal of Cr(VI) ions.¹²⁴ The GFP exhibits excellent adsorption capability (348.4mg/g) for

Cr(VI) removal due to the combined effect of graphene and Fe₃O₄@polypyrrole.

Again, a short communication reported a facile chemical route to synthesize the polypyrrole-reduced graphene oxide composite showing a highly selective Hg²⁺ ions removal capacity.⁴⁷ Usually, materials functionalized with sulphur, nitrogen or oxygen have shown high binding affinity to mercury. Conducting polymers incorporating these functional groups, interfaced with carbon and carbon-based derivatives have shown enhanced removal of mercury and other toxic materials from water, but their surface area is not large¹⁵⁰ which has shown their major drawbacks. Thus, the higher surface area of reduced graphene oxide (rGO) and higher stability as well as non-toxicity of PPy motivated the synthesis of the PPy-rGO composite for the removal of mercury (II) ions. The synthesis has been achieved via 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 m² g⁻¹) influences the morphology of the PPy and increases the surface area from 6.18 m² g⁻¹ (PPy) to 166 m² g⁻¹ (PPy-rGO). The large surface area of the PPy-rGO composite increases the binding sites for mercury ions in the 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) compared to other traditional adsorbents (Table 2) with a characteristic features of higher desorption capacity showing a good practical applications for the treatment of wastewater.¹⁵¹

Fig. 6 shows another facile synthesis of polypyrrole decorated rGO-Fe₃O₄ magnetic composites (PPy-Fe₃O₄/rGO) by two steps for the removal of Cr(VI) ions.¹²² The results showed that the ternary PPy-Fe₃O₄/rGO nano-hybrid exhibited excellent performance for chromium (VI) removal from aqueous solution. The maximum adsorption capacity for Cr(VI) onto PPy-Fe₃O₄/rGO was 293.3 mg/g. 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.

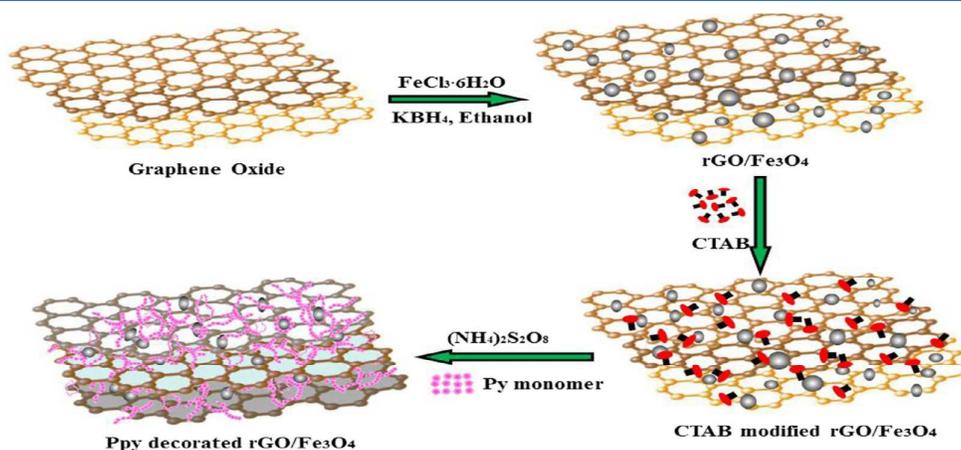


Fig. 6: Schematic illustration of the ternary composites preparation¹²²

2.7. Polypyrrole and other nanocomposites

Not only graphene, a lot of other synthetic nano-adsorbents or organically modified clay nanocomposites or hierarchical porous polypyrrole nanoclusters act as a potential adsorbent for heavy metal ions especially for more abundant Cr(VI) ions.^{2,49,126-128} As a synthetic adsorbent, polypyrrole-titanium(IV) phosphate nanocomposite (PPy-TIP) was prepared by *in-situ* oxidative polymerization.¹²⁶ The adsorption process based on the thermodynamic parameters was spontaneous and endothermic. The maximum adsorption capacity for Cr(VI) ions removal has been found to be 31.64 mg/g at 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 on colloidal nanocomposites as adsorbents that formed when pyrrole or aniline was oxidatively polymerized in the presence of silica (SiO₂) or tin (IV) oxide.¹⁵² Recently, a short communication described a simple fabrication method for PPy/silica nanocomposites with a cratered surface by a modified silica-templated oxidation/polymerization of pyrrole in the presence of FeCl₃ oxidant.¹²⁷ The PPy/silica nanocomposites were examined with regard to removing heavy metals from water. It showed a relatively high adsorption capacity for Hg²⁺ and Pb²⁺ compared to Cd²⁺ and Cr³⁺ and most likely due to the complexation reaction between the secondary amine of the pyrrole and the heavy metal ions (Table 2). However, another study shows the enhancing adsorption of Cd²⁺ ions by nanostructure composite of modified hexagonal type mesoporous silica with polyaniline/polypyrrole nanoparticles (PANI/PPy/HMS).¹²⁹ The adsorption efficiency has been found to be 99.91% at only 8

minutes (Table 2). Mesoporous M41S silicate groups including MCM-41 and SBA-15 are considered as suitable adsorbents due to 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 Hg²⁺ onto PPy/SH-Beta/MCM-41 is an endothermic and spontaneous process and is potentially able to remove Hg²⁺ ions from aqueous solutions at even high concentrations (400 mg/L) with the adsorption capacity of 157.43mg/g. Another composite of PPy/SBA-15 was synthesized via chemical oxidation with FeCl₃ for 5 hours.¹²⁸ The maximum adsorption capacity of Hg (II) removal (200 mg/g) was observed at the optimal conditions of pH 8, contact time of 60 min and absorbent dosage of 1 g/l at room temperature (Table 2).

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

It has been already reported that for the adsorption of Cr(VI) onto PPy based materials, ion-exchange mechanism was involved *via* replacement of doped Cl⁻ by HCrO₄⁻ ions.¹¹³ However, some of Cr(VI) ions has been reduced to Cr(III) by electron rich PPy polymer after starting adsorption. The whole

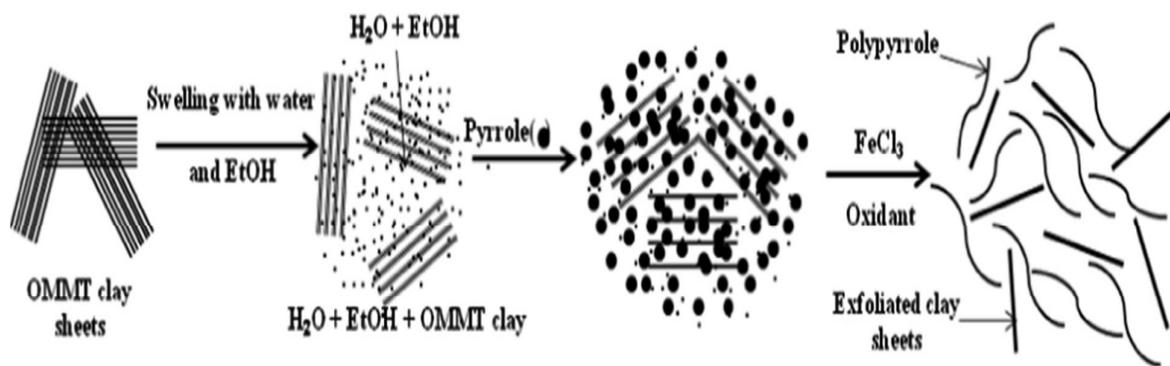
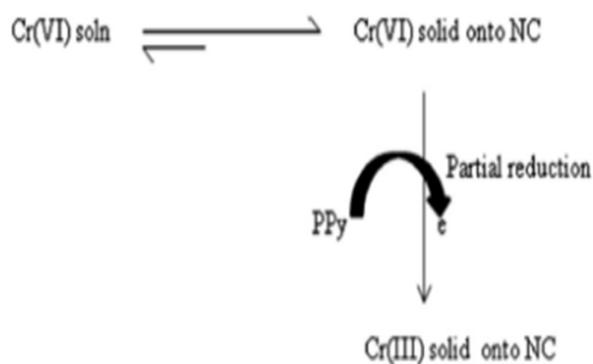


Fig. 7: Formation of Exfoliated PPy-OMMTNC nanocomposites¹²³

REVIEW



Scheme 5: Mechanism for adsorption and Partial reduction of Cr(VI) onto PPy-OMMTC Nanocomposites¹²³

adsorption and reduction of Cr(VI) onto the exfoliated Ppy-OMMTNC has been shown in 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 has been based on hierarchical porous polypyrrole nanoclusters which has been synthesized by a reactive-template method where Fe₃O₄ nanoclusters acted as both the template for shaping the PPy nanostructures and the oxidant source simultaneously.²

The prepared PPy-nanoclusters have been exhibited a wide surface area as high as 104 m²g⁻¹ and due to their special hierarchical porous structures it has been 3.5 times larger than that of traditional PPy. The maximum removal amount of Cr(VI) ions for PPy-nanoclusters was 3.47 mmol/g in 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/wastewater effluents by a wide range of polypyrrole-based adsorbents. Effects of various parameters associated with the adsorption of heavy metal ions from aqueous solutions are compiled and discussed. They have some potential advantages and limitations. Polypyrrole homopolymer and PPy-bio-adsorbents have been readily synthesized and carried out for the removal of different heavy metal ions for its inexpensive and simplicity processes. 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 adsorbents. Among

the available polymeric adsorbents, PPy-based nanomaterials are widely explored as a highly efficient adsorbents for removal of different heavy metal ions from different aqueous/wastewater sources due to their presence of highly active surface sites of the nano-adsorbents. They exhibit various advantages such as fast kinetics, high capacity, and preferable sorption toward heavy metal ions in aqueous/wastewater. Nevertheless, to further promote the practical application of PPy-based polymers in the abatement of heavy metal pollution, there still exist some technical constraints to be solved. So far, from the commercial point of view, no greater success has been achieved using conducting polymer-based adsorbents, particularly, polypyrrole and its composites. Extensive research are 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/nano-composites/bio-composites should be sourced out and focused on regeneration to minimize the cost involved for its commercial applications.

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Declaration

Authors declare no conflict of financial interest or any others.

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