REVIEW ARTICLE

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Polyaniline-based adsorbents for removal of hexavalent chromium from aqueous solution: a mini review

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Abstract

Hexavalent chromium (Cr(VI)) is a common hazardous contaminant in the environment and carcinogenic or mutagenic to aquatic animals and human beings. Therefore, the removal and detoxification of Cr(VI) have been attracting increasing attention of researchers. Among various conducting polymers, polyaniline (PANI)-based adsorbents have shown an excellent performance on the removal of Cr(VI) because of their redox properties, eased synthesis, and favorable biocompatibility. In this review, the characteristics of various PANI-based adsorbents were described, including PANI-modified nanofiber mats and membranes, PANI/bio-adsorbents, PANI/magnetic adsorbents, PANI/carbon adsorbents, PANI-modified clay composites, and PANI-inorganic hybrid composites. The mechanisms for the detoxification and adsorption of Cr(VI) were also discussed. The results indicated the potential applications of PANI-based adsorbents for the removal of Cr(VI).

Keywords Adsorbents · Polyaniline (PANI) · Heavy metal ions · Chromium (Cr) · Removal · Adsorption

Introduction

In the past decades, the remarkable progress of science and technology witnessed the applicability of metal and their alloys in various applications (Kalidhasan et al. 2016; Yuan et al. 2011). Chromium (Cr) is widely used in catalyst, electroplating, chrome plating, leather tanning, glass industries, wood preservation, textile industries, etc. (Bhaumik et al. 2013; Kera et al. 2016). However, the improper disposal of the Cr from aqueous solution/wastewater will cause a significant environmental problem and endanger human health due to its toxicity and carcinogenicity.

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Chromium exists in both the trivalent chromium Cr(III) and hexavalent chromium Cr(VI) forms in aqueous solution (Huang et al. 2011). Additionally, the Cr(VI) exists mainly as chromate ion (CrO_4^{2-}), dichromate ion ($Cr_2O_7^{2-}$), hydrogen chromate ion ($HCrO_4^-$), and chromic acid (H_2CrO_4), depending on the total Cr concentration and pH in solution (Bhaumik et al. 2016). CrO_4^{2-} exists at pH above 6.0, $HCrO_4^-$ exists at pH from 1.0 and 6.0, and H_2CrO_4 exists at pH above 1.0. The dichromate ion ($Cr_2O_7^{2-}$) comes into being when the concentration of chromium is more than about 1.0 g/L (Miretzky and Cirelli 2010; Mohan and Pittman 2006). Compared with CrO_4^{2-}, $HCrO_4^-$ possesses a higher redox potential, which makes it more easy to be reduced from toxic Cr(VI) to Cr(III) (Sun et al. 2010b). Cr(VI) is a more poisonous form than Cr(III), which has mutagenic, teratogenic, carcinogenic, and genotoxic effects on living organisms (Aroua et al. 2007; Bhaumik et al. 2012). Moreover, it results in serious health issues, including skin irritation, pulmonary congestion, hepatopathy, and lung cancer (Cancer 1972; Kotaś and Stasicka 2000). The trivalent Cr(III) is less mobile, less bioavailable, less soluble, and less toxic than Cr(VI) due to its limited hydroxide solubility (Krishnani and Ayyappan 2006; Yusof and Malek 2009). However, excessive amounts of Cr(III) can also lead to allergic skin reactions, even cancer (Kotaś and Stasicka 2000). In order to avoid endangering

drinking water and human health, Cr concentration needs to be reduced to a reasonable level in the water. The World Health Organization (WHO) has stipulated a limit of Cr(VI) in drinking water as 50 μg/L (Fawell et al. 1996).

In previous researches, several techniques have been reported for removing Cr(VI) ions from contaminated wastewater, such as adsorption, solvent extraction, ion exchange, membrane filtration, physical and chemical precipitation, and electro-chemical method (Huang et al. 2011; Huang and Chen 2009; Karthik and Meenakshi 2015c; Muthumareeswaran et al. 2017; Owlad et al. 2009; Punrat et al. 2016). By far, adsorption has become the most widely used technology because of its simplicity of design, easy operational conditions, and environmental friendliness (Debnath et al. 2014; Kyzas et al. 2014; Liu et al. 2011; Shao et al. 2017b). Moreover, adsorption process is invertible; therefore, the adsorbents can be readily regenerated through an appropriate desorption process (Liu et al. 2012b, 2017; Shao et al. 2017a). Various adsorbents have been utilized to eliminate Cr(VI) from aqueous solution/wastewaters, including montmorillonite, activated carbon, mesoporous materials, metal and metal oxide, bio-adsorbents, and polymer-based adsorbent (Agrawal and Singh 2016; Chen et al. 2013; Fellenz et al. 2017; Karthik and Meenakshi 2015c; Kera et al. 2016; Sahu et al. 2009).

Among the polymer-based adsorbents, conducting polymer-based adsorbents, such as the polyethylenamine (PEI), polypyrrole (PPy), polyaniline (PANI) and their composites, have been followed with increasing interest for removal of heavy metals owing to the low cost and ease of synthesis, operation, and regeneration; environmental stability; and high content of amine group which can adsorb and chelate heavy metal ions via hydrogen bonding or electrostatic (Agrawal and Singh 2016; Li et al. 2012; Setshedi et al. 2015; Sun et al. 2010a; Tamai et al. 1996; Wei et al. 1993). In addition, these polymer-based adsorbents act as electron donors for the Cr(VI) reduction to Cr(III) and provide the adsorption sites for Cr(III). It is a kind of effective and novel adsorbent through reduction and adsorption simultaneously for the removal of Cr(VI).

PANI, as a unique polymer, has been widely used for various applications including catalysts, energy storage, corrosion inhibitors, chemical and biological sensors, and selective ion-transport switchable membranes (Deshpande et al. 2014; Long et al. 2011; Saikia et al. 2011; Tang et al. 2008; Zhai et al. 2013). Meanwhile, using PANI for the removal of Cr(VI) has gained many benefits in virtue of their facile synthesis, simple acid-base doping-dedoping process, and remarkable environmental stability and reversibility (Bhaumik et al. 2014; Long et al. 2011). It is well-known that polyaniline contains huge amounts of imine and amine functional groups. The imine and amine group of PANI provide various adsorption sites. Moreover, the ratio of imine and amine group

determines the different redox states of PANI, and thoroughly oxidized pernigraniline base (PB), partial oxidized emeraldine base (EB), and completely reduced leucoemeraldine base (LB) (Qiu et al. 2014b). The reversible oxidation-reduction chemistry of PANI is shown in Fig. 1 (Wang et al. 2010b). Therefore, Cr(VI) can be reduced to Cr(III) by the oxidation of the LB and EB forms to PB form. PANI is normally synthesized through the chemical polymerization of oxidative aniline using ammonium peroxydisulfate (APS) as a strong oxidant under acidic condition. Great effort has been expended to synthesis PANI in the presence of various dopants, additive, and the second component to improve the adsorption performance, because the adsorption efficiency major is dependent on the conditions used to synthesize PANI (Karthik and Meenakshi 2015a; Tian et al. 2016; Wang et al. 2014). Olad and Nabavi (2007) have studied the removal performance of Cr(VI) by various forms of PANI, such as powder and film forms, and found that powder form was more effective than film form. PANI also possesses the different performance to get doped by various protonic acids and additives. However, the regeneration of PANI powders from the solution after Cr(VI) adsorption was still a difficult technical constraint. Coating PANI on other substrate materials to synthesize composite materials is one of the strategies to improve the cycle, absorption efficiency, and reuse capability, such as cellulose, biomass, carbon materials, mesoporous materials, metal, and metal oxide.

This article is intended to overview recent literature on the adsorption of Cr(VI) from aqueous solution using various polyaniline-based adsorbents. Different oxidation polymerization processes with aniline can obtain both simple polyaniline and PANI-based adsorbents such as PANI-modified mats and membranes, PANI/bio-adsorbents, PANI/magnetic material, PANI/carbon material, PANI-modified clay composites, and PANI-inorganic hybrid composites. The results indicated the potential application PANI-based adsorbents for Cr(VI) removal and detoxification.

Polyaniline-based adsorbents

Polyaniline polymer

PANI, a typical conducting polymer, have been a highlighted research because of its outstanding electrical conductivity, electrical/optical capabilities, ion exchange property, and prominent advantages like no toxicity, environmental stability, facile and inexpensive synthesis, high affinity for metal ions, and efficiency to reduced toxic pollutants (Long et al. 2011). PANI prepared in solution with small dopants (i.e., Cl$^-$) exhibits ion exchanging behavior because of these anions of the high mobility HCl in the PANI matrix. Furthermore, PANI has great prospects in the adsorption application because of the

Fig. 1 Oxidation–reduction reaction of PANI (Wang et al. 2010b)

leucoemeraldine base

reduction   oxidation

emeraldine base

reduction   oxidation

Pernigraniline base
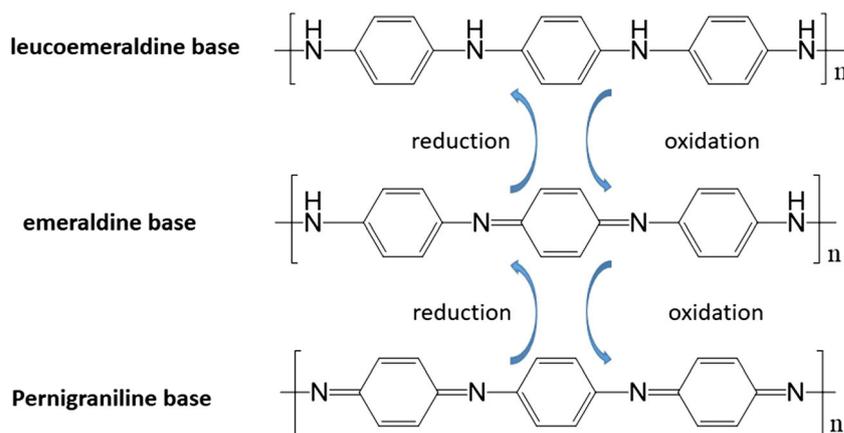
innate cationic amine and imine groups in polymer chains can electrostatically interact with the anionic pollutants. Therefore, the conducting polymers effectively used to eliminate heavy metal ions. The PANI prepared through the chemical polymerization of aniline in the presence of different dopants under different conditions, as the adsorption performance related to the conditions used to synthetic PANI (Zhou et al. 2017a). The different additives and their influence of PANI were shown in Fig. 2. Traditionally, PANI is mostly prepared by ammonium persulfate as an oxidant and polymerization in the strong protonic acids like hydrochloric (HCl) and sulfuric acid (H_2SO_4), and the primary product is aggregated granular (Chowdhury et al. 2008; Zhang et al. 2010). For instance, the hydrochloric doping in PANI was prepared to the elimination of aqueous Cr(VI) in column experiments and its monolayer adsorption capacity was 22.2 mg/g at 25 °C and pH 4.75 (Chowdhury et al. 2008). Similarly, the sulfuric acid-doping PANI was also used to detoxify and remove Cr(VI) ions from aqueous solution. The adsorption experiments showed that a short equilibrium time was about 1.5 h and the maximum adsorption capacity was 95.79 mg/g (Table 1) (Zhang et al. 2010).

Moreover, PANI can be compounded with other addition agents aside from protonic acids to attain better processability and function effectively in adsorption processes (Karthik and Meenakshi 2015a; Li et al. 2011b; Samani et al. 2010). Recently, one of the study revealed that nanostructured PANI was synthesized by a facile sono-assisted oxidation method in aniline monomer with various acid additives like surfulamic acid (SA), hydrochloric acid (HCl), taurine (TA), citric acid (CA), and neutral deionized water (DI) for the removal of Cr(VI) (Wang et al. 2014). The PANI-HCl demonstrated the best maximum adsorption capacity as 182 mg/g at pH 4.0. Other samples followed in the reducing order as PANI-SA (164 mg/g), PANI-CA (145 mg/g), PANI-TA (111 mg/g), and PANI-DI (92 mg/g), respectively. The analysis through the FTIR and XPS spectra showed the possible mechanisms that electrostatic adsorption occurred between PANIs and Cr(VI) as well as the reduction from Cr(VI) to Cr(III) (Wang et al. 2014).

Humic acid (HA) contains various abundant functional groups, like carboxylic, enolic, alcoholic, and phenolic groups (Liu et al. 2016). Recently, some researchers found that HA always modified on particles and heightened the adsorption

Fig. 2 The different additives and their influence on PANI

Additives

Influence

Acid additives

HCl , H_2SO_4 , Surfulamic acid , Citric acid , Taurine, etc.

Surface charges , Molecule structures

Functional additives

Humic acid , Polyvinyl alcohol Poly(ethylene glycol), etc.

Particle size, Morphology, Functional groups

Sacrifice template

MnO_2

Various morphologies

The polymerization process of PANI

Adsorption performance
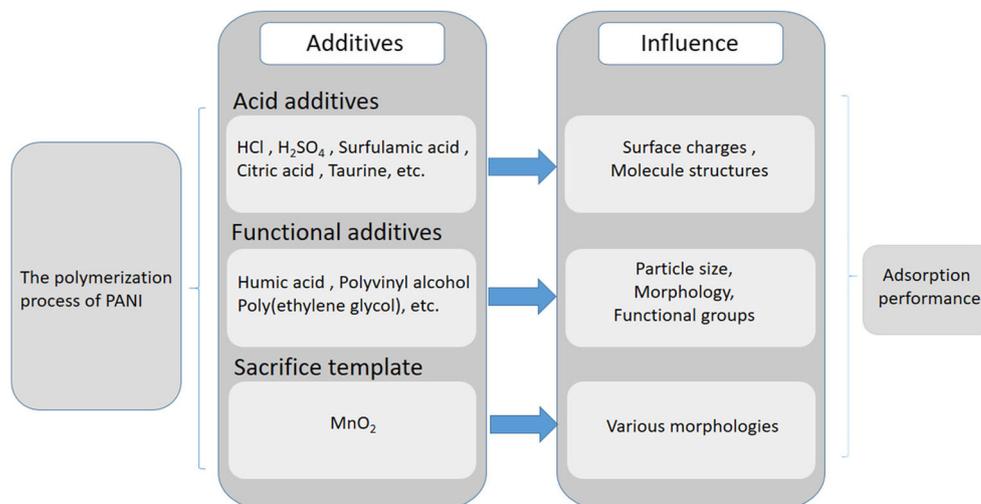
Table 1 Adsorption capacities and experimental conditions of polyaniline-based adsorbents for the removal of Cr(VI) ions

Type of adsorbents	Optimum condition/experimental condition	Kinetic model	Isotherm	Adsorption	
				Capacity mg/g	Efficiency %
PANI doped with sulfuric acid (Zhang et al. 2010)	pH 3.0; temp. 293 K; equilibrium time 1.5 h; dose 4 g/L; initial conc. 50 mg/L	Pseudo-second	L	95.79[a]	
PANI-HCL (Wang et al. 2014)	pH 4.0; temp. 298 K; dose 1 g/L; initial conc. varied 10–300 mg/L	–	L、F	182[a]	
PANI-SA (Wang et al. 2014)	pH 4.0; temp. 298 K; dose 1 g/L; initial conc. varied 10–300 mg/L	–	L、F	164[a]	
PANI-CA (Wang et al. 2014)	pH 4.0; temp. 298 K; dose 1 g/L; initial conc. varied 10–300 mg/L	–	L、F	145[a]	
PANI-TA (Wang et al. 2014)	pH 4.0; temp. 298 K; dose 1 g/L; initial conc. varied 10–300 mg/L	–	L、F	111[a]	
PANI-DI (Wang et al. 2014)	pH 4.0; temp. 298 K; dose 1 g/L; initial conc. varied 10–300 mg/L	–	L、F	92[a]	
PANI-HA (Li et al. 2011b)	pH 5.0; temp. 298 K; dose 0.5 g/L; equilibrium time 120 min; initial conc. 15 mg/L	Pseudo-second	F	29.26[b]	
PANI/PEG composite (Samani et al. 2010)	pH 5.0; room temp; dose 1 g/L; equilibrium time 30 min; initial conc. varied 10–100 mg/L	–	L	68.97[a]	
PANI/PVA composite (Karthik and Meenakshi 2015a)	pH 4.0; temp. 303 K; contact time 60 min; dose 2 g/L; initial conc. 200–250 mg/L	Pseudo-second	L、F	111.23[a]	
PANI nanosheets (Tian et al. 2016)	pH 2.0; temp. 298 K; dose 0.2 g/L	Pseudo-second	L	263.2[a]	
PANI nanotubes (Tian et al. 2016)	pH 2.0; temp. 298 K; dose 0.2 g/L	Pseudo-second	L	259.7[a]	
PANI nanofibers (Tian et al. 2016)	pH 2.0; temp. 298 K; dose 0.2 g/L	Pseudo-second	L	248.8[a]	
PAN/PANI nanofibers (Wang et al. 2013)	pH 2.0; temp. 298 K;	Pseudo-second	L	71.28[a]	
Hierarchical Composite (PANI-PS) Fibers (Alcaraz-Espinoza et al. 2015)	pH 4.0; room temp	–	–	58[b]	
PANI-PA/CA composite membrane (Li et al. 2014)	pH 2.0; temp. 303 K	Pseudo-second	L	94.34[a]	
(PANI/EVOH) nanofiber composite membranes (Xu et al. 2016)	pH 2.0; temp. 303 K; initial conc. 25–200 mg/L	Pseudo-second	F	93.09[b]	
(PANI/PI) microfiber membranes (Wang et al. 2017)	pH 1.0; temp. 298 K	Pseudo-second	L、F	70.08[a]	
20.0 wt% PANI/ECs (Qiu et al. 2014b)	pH 1.0; room temp; initial conc. varied 2–200 mg/L;	Pseudo-second	L	38.76[a]	
PANI/jute (Kumar et al. 2008)	pH 3.0; temp. 293 K; dose 2 g/L; contact time 24 h; initial conc. 50 mg/L	Pseudo-second	L、F	62.9[a]	
KF/PANI (Zheng et al. 2012)	pH 4.5; temp. 303 K; dose 2 g/L; initial conc. 100 mg/L	Pseudo-second	R-P	44.05[b]	
SA-PANI (Karthik and Meenakshi 2015d)	pH 4.2; temp. 303 K; contact time 60 min; dose 0.1 g; initial conc. 100 mg/L	Pseudo-second	L	73.34[a]	78.63
PANI/SD (Esfandian et al. 2012)	pH 2.0; temp. 293 K; contact time 20 min; dose 6 g/L; initial conc. 50 mg/L	Morris–Weber equation	F		97%
Chitosan–grafted-polyaniline (Karthik and Meenakshi 2014)	pH 4.2; temp. 303 K; dose 2 g/L; initial conc. varied 200–400 mg/L	Pseudo-second	L、F	165.5[a]	
Cross-linked-chitosan–grafted-polyaniline (Karthik and Meenakshi 2014)	pH 4.2; temp. 303 K; dose 2 g/L; initial conc. varied 200–400 mg/L	Pseudo-second	L、F	179.2[a]	
PANI-Fe/OMC (Yang et al. 2014)	pH 2.0; temp. 298 K; equilibrium time 120 min	Pseudo-second	L	172.33[a]	
PANI–magnetic mesoporous silica composite (Tang et al. 2014)	pH 2.0; temp. 298 K; equilibrium time 430 min	Pseudo-second	L	193.85[a]	
PANI/γ-Fe_2O_3 (Chavez-Guajardo et al. 2015)	pH 2.0; room temp; equilibrium time 35 min	Pseudo-second	L	196[a]	
Polyaniline/akaganéite nanocomposite (Ebrahim et al. 2016)	pH 2.0; room temp; contact time 5 min; dose 0.4 g/L; initial conc. 7.0 mg/L	–	–	17.36[b]	99.2
Fe_3O_4/PANI nanocomposites (Gu et al. 2012)	Contact time 5 min; initial conc. 1.0–3.0 mg/L	Pseudo-first	–		100
Core-shell structured Fe_3O_4/PANI microspheres (Han et al. 2013)	pH 2.0; room temp; equilibrium time 3 h;	Pseudo-second	L	200[a]	90
PANI/Fe_3O_4 nanocomposite (Rezvani et al. 2014)	pH 7.6; room temp; initial conc. 500 mg/L	–	–	54[b]	

Table 1 (continued)

Type of adsorbents	Optimum condition/experimental condition	Kinetic model	Isotherm	Adsorption	
				Capacity mg/g	Efficiency %
10 wt% PANI/CFs (Qiu et al. 2014a)	pH 1.0; room temp; contact time 60 min	Pseudo-second	L	18.1[a]	
DP/MWCNTs (Kumar et al. 2013)	pH 2.0; temp. 303 K; dose 0.02 g initial conc. 100 mg/L	Pseudo-second	F	55.55[a]	
PANI-MWCNT (Wang et al. 2015c)	pH 4.5; temp. 298 K; initial conc. varied 2.5–30 mg/L	Pseudo-second	F	31.75[a]	
PANI/GO (Zhang et al. 2013)	pH 3.0; temp. 298 K; dose 0.2 g/L	Pseudo-second	L、F	1149.4[a]	
PANI-G10 (Harijan and Chandra 2016b)	pH 6.5; temp. 303 K; dose 0.25 g/L; initial conc. 100 mg/L	Pseudo-second	L	192[a]	
Fe$_3$O$_4$/G/PANI composite (Harijan and Chandra 2016a)	pH 6.5; temp. 303 K; dose 0.1 g/L initial conc. varied 40–100 mg/L	Pseudo-second	L	153.5[a]	
PANI@GO-CNT (Ansari et al. 2017)	pH 2.0; temp. 293 K; 1 g/L	Pseudo-second	L	142.9[a]	
Exfoliated PANI/MMT (Chen et al. 2014b)	pH 2.0; room temp; contact time 2.5 h; dose 1 g/L; initial conc. varied 25–250 mg/L	Pseudo-second	L	308.6[a]	
Flake-like PANI/MMT (Chen et al. 2013)	pH 2.0; room temp; contact time 2.5 h; dose 1 g/L; initial conc. varied 25–250 mg/L	Pseudo-second	L	167.5[a]	
PA/PANI composite (Wang et al. 2015b)	pH 5.5; temp. 298 K; initial conc. varied 2.5–30 mg/L	Pseudo-second	L	14.79[a]	
PANI/sepiolite nanofibers (Chen et al. 2014a)	pH 2.0; temp. 298 K	Pseudo-second	L	206.61[a]	
HP/0.5/204%-HCl (Zhou et al. 2017b)	pH 5.07; room temp	Pseudo-second	L	62.9[a]	
PANI@MoS2 (Gao et al. 2016)	pH 3.0; temp. 293 K; dose 0.5 g/L	Pseudo-second	L	526.3[a]	
PANI/LDHs (Zhu et al. 2016) (LDHs/aniline mass ratio of 1:8)	pH 3.0; temp. 288 K; dose 0.2 g/L	Pseudo-second	L	393.7[a]	
PANI/H-TNB (Wen et al. 2016) (H-TNBs/aniline mol ratio of 1: 20)	pH 5.0; temp. 298 K; dose 0.3 g/L	Pseudo-second	L	156.9[a]	
poly(aniline-1,8-diaminonaphthalene) (Li et al. 2011a)	pH 4.0; temp. 298 K; dose 0.5 g/L	Pseudo-second	F	150[b]	
PPy-PANI nanofibers (Bhaumik et al. 2012)	pH 2.0; temp. 298 K; equilibrium time 30–180 min; initial conc. 100–400 mg/L	Pseudo-second	L	227[a]	
PPy-PANI/Fe3O4 (Kera et al. 2017)	pH 2.0; temp. 298 K	Pseudo-second	L	303[a]	

L Langmuir model, *F* Freundlich model, *R-P* Redlich–Peterson

[a] Maximal capacity, calculated from Langmuir isotherm

[b] Maximal capacity, calculated from experimental data

capacity so as to enhance the stability of dispersions (Liu et al. 2016, Yang et al. 2016). A study showed that polyaniline/humic acid (PANI-HA) composite was synthesized via mixing humic acid into oxidizing aniline monomer to polymerization (Li et al. 2011b). This study reported the maximum adsorption capacity for Cr(VI) reached 150.2 mg/g at pH 5.0. The adsorption of Cr(VI) showed a short adsorption equilibrium time about 120 min and also fitted well the pseudo-second-order equation. In the PANI synthesis process, HA played the role of preventing the aggregation, modifying the morphology, and enhancing the adsorption performance. Because of its small-dosage, low-cost, and excellent adsorption capacity, the PANI-HA can be considered as a potential adsorbent.

The poly(ethylene glycol) (PEG), as suitable additives, can influence the morphology of synthesized polymer composite because PEG can be adsorbed on the growing polymer (Eisazadeh 2007; Salehi et al. 2013). PANI/PEG composite was synthesized through adding various concentrations of PEG during chemical polymerization process of oxidative aniline monomers and can be used for toxic Cr(VI) removal (Samani et al. 2010). The adsorption experiments for PANI/PEG composite indicate that the equilibrium time was about 30 min and the maximum removal capacity of Cr(VI) was 68.97 mg/g at pH 5.

Polyvinyl alcohol (PVA) can also be considered to be one of the proper additive agents to improve the Cr(VI) adsorption performance by PANI for it contains huge amounts of reactive hydroxyl groups (Lv et al. 2013). In recent years, it has been reported that PVA, as surfactant, can control the particle size of PANI to enhance the adsorption performance of heavy metal ions (Hasani and Eisazadeh 2013; Karthik and Meenakshi 2015a). PANI/PVA composite composed of 2% *w/v* polyvinyl alcohol and 0.2 mol/L aniline was fabricated via in situ polymerization technique. It has been reported that PANI/PVA used as adsorbents to remove Cr(VI) ions from aqueous solution with the adsorption capacity of Cr(VI) as 111.23 mg/g

(Karthik and Meenakshi 2015a). XPS and FTIR spectra studies demonstrated the electrostatic adsorption of Cr(VI) with the PANI/PVA composite simultaneously that the reduction of Cr(VI) to Cr(III) occurred (Karthik and Meenakshi 2015a).

Different morphology of polyaniline have different adsorption capacity. The study indicated three different morphology of PANI nanostructures as absorbent for Cr(VI) (Tian et al. 2016). Among them, the PANI nanosheets and nanotubes synthesized using MnO_2 as the sacrificial templates. Compared to PANI nanofibers with no templates, the template-guided PANIs demonstrated better adsorption efficiency. The maximum Cr(VI) adsorption capacities calculated by the Langmuir isotherm are 263.2, 259.7, and 248.8 mg/g on PANI nanosheets, PANI nanotubes, and PANI nanofibers, respectively.

Polyaniline-modified mats and membranes

The inherent properties of PANI to reduce toxic Cr(VI) allow PANI and its modified materials to apply to eliminate Cr(VI) from wastewater (Alcaraz-Espinoza et al. 2015; Bhaumik et al. 2012). But the agglomeration of bare PANI particles easily occurred in the process of application and preparation, which is expected to result in slow kinetics and low adsorption capacity. PANI composites are widespreadly prepared by in situ polymerization method. Because this method can overcome the aggregation of PANI particles and increase the amount of amine groups on adsorption material in a large extent. The synthesis of PANI-based adsorbents via in situ polymerization of aniline was shown in Fig. 3. Polymer nanofiber mats attained through electrospinning have been adopted as adsorbent due to their ease of preparation and small diameter. For example, the study showed that PAN/PANI core/shell nanofiber mat as an absorbent of Cr(VI) were synthesized through in situ polymerization of aniline on the surface of the electrospun PAN (Wang et al. 2013). This adsorption experiments showed that the maximum adsorption capacity of Cr(VI) calculated by Langmuir model was 71.28 mg/g at pH 2.0 and 25 °C. Meanwhile, the adsorption capacity would increase with temperature. This adsorption equilibrium time was 30 min and it could effectively reduce 86.2% of Cr(VI) to Cr(III).

Recently, studies reported the possibility of using polyaniline-modified nonwoven (NW) electrospun PS mats polyaniline via in situ chemical polymerization to successfully synthesize polyaniline-(electrospun polystyrene) (PANI-PS) fibers which was used as an adsorbent for Cr(VI), Cd(II), Hg(II), Cu(II), and Pb(II) ion removal and the adsorption capacities were 58, 124, 148, 171, and 312 mg/g at pH 4.0, respectively (Alcaraz-Espinoza et al. 2015).

The composite membrane adsorbent, phytic acid doped PANI/cellulose acetate (PANI-PA/CA), successfully synthesized via preparation of aniline in cellulose acetate solution and followed the phase-inversion process (Li et al. 2014). This method used phytic acid doping into PANI to improve the pore volume and surface area of the composite membrane. The maximum adsorption capacity of Cr(VI) and Hg(II) reached 94.34 and 280.11 mg/g, respectively (Li et al. 2014).

The adsorbents loaded with proper substrates could increase their adsorption capacity, prevent the aggregation of particles, separated easily the adsorbents from water, and expand their practical application. Polymer nanofiber membranes have drawn more and more attention due to high surface area, high porosity, and small pore size, which affords high adsorption active sites. A recent study described a novel fabrication method for polyaniline/poly(ethylene-co-vinyl alcohol) (PANI/EVOH) nanofiber composite membranes production via a combination of high-speed flow deposition subsequent in situ polymerization growth (Xu et al. 2016). The study of adsorption experiment showed that adsorption

Fig. 3 The synthesis of PANI-based adsorbents via in situ polymerization of aniline

Aniline Various substrate In situ polymerization

Mats and membranes	Bio-adsorbents	Magnetic material	Carbon material	Clay and mineral
• Nanofiber mats	• Cellulose fiber	• Magnetic mesoporous material	• Carbon fabrics	• Palygorskite
• Membranes	• Natural fiber		• Carbon nanotubes	• Sepiolite
• Nanofiber membranes	• Sawdust	• Magnetic iron oxide	• Graphene oxide	• Montmorillonite
	• Biopolymer		• Graphene	• Halloysite
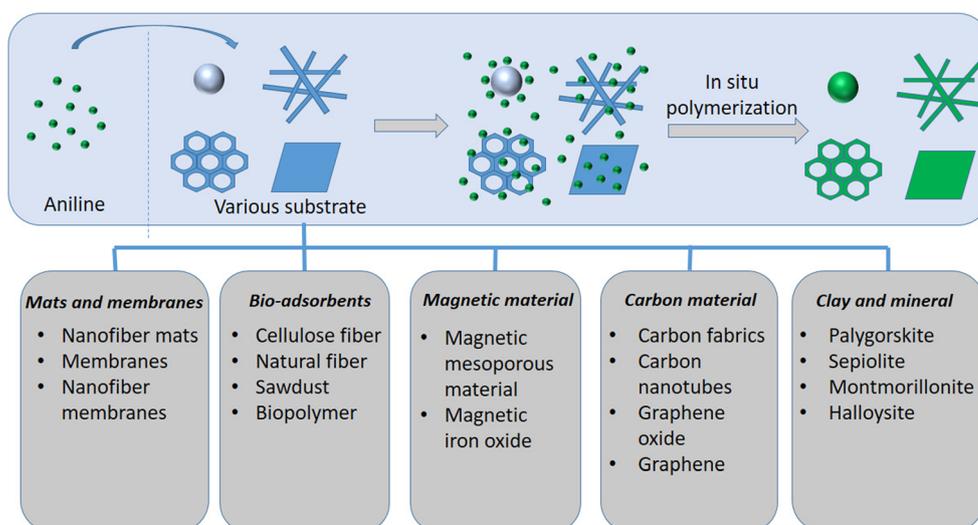
equilibrium time was less than 100 min and the maximum adsorption capacity of Cr(VI) was 93.09 mg/g. It is noteworthy that the excellent reusability of (PANI/EVOH) nanofiber composite membranes. The removal efficiency reached up to 92.79% in the first 5 cycles, and still held on 76.7% after 25 cycles.

A novel polyaniline/polyimide (PANI/PI) microfiber membranes fabricated by solution blowing and followed by in situ polymerization of aniline on the surface of PI nanofiber membranes (Wang et al. 2017). In the process of polymerization of polyaniline, dodecylbenzene sulfonic acid acted as acid additives to enhance the performance of PANI. Its maximum adsorption capacity of Cr(VI) was 70.08 mg/g (Table 1).

Polyaniline modified bio-adsorbents

The use of bio-adsorbents is a green option for removal of heavy metals due to their biodegradability, biocompatibility, and non-toxicity (Boamah et al. 2015; Huang et al. 2008; Karthik and Meenakshi 2015e; Leng et al. 2015). Several studies reported that adsorption of metal ions by various PANI-based bio-adsorbents was an effective method in term of eco-friendly, renewable sources and easy and inexpensive synthesis (Karthik and Meenakshi 2015e; Yavuz et al. 2011). The main advantages of these bio-adsorbents are their wide range of effectiveness. PANI can be modified Fe_3O_4/G/PANI, such as cellulose, jute fiber, kapok fiber, sodium alginate, sawdust, chitosan, etc. to improve the adsorption performance of aqueous Cr(VI).

Cellulose have been tried as an adsorbent to remove many environmental pollutants from wastewater because of the existence of abundant hydroxyl groups that can afford adsorption sites for heavy metal or organic dye adsorption (Chen et al. 2016). Cellulose also can play the role of an electron donor for the Cr(VI) reduction to Cr(III) via the hydroxyl groups (Dong et al. 2016). However, these materials are suffering with disadvantages related to lower adsorption capacity and removal rate. Modified with polymers containing amine groups, such as PANI, was one useful method to improve the removal rate and removal capacity of cellulose (Hanif et al. 2016).

Recent studies indicated that the PANI-bioadsorbent obtained by PANI coating with cellulose was successfully synthesized via in situ oxidative polymerization and quite effective in reduction and adsorption of Cr(VI) on the polyaniline/cellulose fiber composite (Liu et al. 2013). In this polymerization process, ammonium persulfate (APS) acted as an oxidant to polymerization of aniline on the surface of cellulose. One-gram adsorbent was added to 100 mL Cr(VI) solution with the initial concentration 100 mg/L at pH 4.8. The treatment experiment of Cr(VI)-contaminated solution showed a high adsorption efficiency that almost 100% of Cr(VI) could be removed at 25 °C (Liu et al. 2013). It was also found that

ferric chloride ($FeCl_3$) could be used as activator and hydrogen peroxide (H_2O_2) as the oxidant to synthesize PANI-cellulose adsorbent, instead of using relatively expensive chemicals such as persulfate salts as oxidants (Liu et al. 2012a).

A novel composite of ethyl cellulose (EC) modified with PANI (PANI/EC) were prepared as a potential absorbent via similarly mixing the EC and PANI solution with various weight ratio of PANI loading range from 5 to 20 wt% and have showed a higher Cr(VI) removal capacity than that of pure EC (Qiu et al. 2014b). The Freundlich isotherm was a very good fit for this Cr (VI) adsorption. The absorption capacities of PANI/ECs with 20.0, 10.0, 5.0, and 0 wt% PANI were 38.76, 26.11, 19.49, and 12.2 mg/g, respectively. About the adsorption rate, the PANI/ECs (20.0% PANI loading) were demonstrated to entirely eliminate 2.0 mg/L Cr(VI) within 5 min, which was faster than the pure EC (> 1 h) (Qiu et al. 2014b).

Kumar et al. found a short chain polyaniline/jute (PANI-jute) fiber composite using the 1,4-phenylenediamine as chain terminating agent (Kumar et al. 2008). Optimum amount of chain terminating agent and jute fiber were 3.05 mmol and 5 g, respectively, for 21.5 mmol of aniline. According to the batch data, maximum monolayer capacity of PANI-jute was 62.9 mg/g at pH 3 and the adsorption equilibrium was accomplished within 40–120 min with the initial concentration of 50–500 mg/L (Kumar et al. 2008). The fixed-bed column with the PANI-jute adsorbent for the elimination of Cr(VI) in the sustaining mode was also studied (Kumar and Chakraborty 2009). The data obtained for total chromium were well described by bed depth service tome (BDST) equation till 10% breakthrough. Adsorption rate constant and dynamic bed capacity at 10% breakthrough was noticed as 0.01 L/mg × h and 1069.46 mg/L, respectively (Kumar and Chakraborty 2009).

It was reported the Kapok fiber (KF) was modified with PANI through in situ polymerization method (Zheng et al. 2012). The pseudo-second-order equation was used to describe the adsorption capacity and rate. The results showed that the adsorption capacity of KF/PANI was 44.05 mg/g at pH 4.5 and 30 °C (Zheng et al. 2012). At lower initial Cr(VI) concentration, compared to crude PANI, KF/PANI exhibited comparable adsorption capacity (55.05 mg/g) and faster adsorption rate due to the intrinsic large lumen of KF. The rate constant of KF/PANI was twice of that of crude PANI (Zheng et al. 2012).

Sawdust (SD), a kind of industrial by-product, contains varieties of organic compounds that can be readily modified with PANI and prepare PANI/SD composites. It can bind metal ions under various conditions and mechanisms. Recently, the efficiency of removing Cr(VI) from aqueous solutions with polyaniline coated on sawdust (PANI/SD) has been studied (Ansari 2006; Esfandian et al. 2012; Yanovska et al. 2014). Esfandian et al. (2012) found the as-prepared PANI/SD

composite for removing Cr(VI) via the batch experiment. The optimum adsorption conditions were found to be 6 g/L adsorbent in Cr(VI) solution (50 mg/L) at pH 2 and 20 °C, and the increasing temperature resulted in the decrease of removal efficiency of Cr(VI) (Esfandian et al. 2012). In these conditions, the PANI/SD maximum removal efficiency for Cr(VI) reached 97% with contact time of 20 min.

Sodium alginate (SA), a linear biopolymer, to which has been paid more attention as an adsorbent for heavy metals removing due to its hydrophilicity biodegradability, non-toxic, low cost, and abundance in nature (Lim et al. 2009). Moreover, polymers were used to modify SA and enhance its adsorption performance of heavy metals (Lim et al. 2009). For example, Karthik and Meenakshi have prepared the sodium alginate-polyaniline (SA-PANI) nanofibers via in situ polymerization technique as an adsorbent for removing Cr(VI) ions from aqueous solution (Karthik and Meenakshi 2015d). The maximum adsorption capacity was 73.34 mg/g at pH 4.2 and 30 °C (Table 1).

Natural eco-friendly biopolymer, chitosan, and its derivatives are generally procured by deacetylation of chitin. Chitosan have been used as a bio-adsorbent to remove various heavy metal ions from wastewater due to its non-toxicity biodegradability and biocompatibility (Jayakumar et al. 2005, Miretzky and Fernandez Cirelli 2009). Furthermore, chitosan is abundant in nature and contains abundant active sites, i.e., amine ($-NH2$) and hydroxyl ($-OH$) groups (Yavuz et al. 2011). These functional groups can make chitosan anchoring and binding heavy metal ions by hydrogen bonding or electrostatic attraction (Karthik and Meenakshi 2014). However, raw chitosan are suffering with drawbacks related to low mechanical strength and unsatisfactory sorption capacity. Therefore, some researchers have studied the application of polymer to modify the characteristics of chitosan (Hena 2010; Karthik and Meenakshi 2015b).

Cross-linking is an effective way for chemical modification of chitosan, which enable to form network or body type polymer from linear or branched polymer chain via covalent bond connection. In the recent study, the novel cross-linked chitosan-grafted polyaniline composite (CCGP) has been fabricated via in situ polymerization of aniline in the cross-linking chitosan (Karthik and Meenakshi 2014). It was found that the strength of cross-linking composite could improve the adsorption efficiency of Cr(VI). The adsorption capacity attributed for CCGP composite was 179.2 mg/g higher than without cross-linking agent in the adsorbent synthesis process (165.5 mg/g) at pH 4.2.

Polyaniline modified magnetic material

Magnetic separation has been certified as an absorbing technique for the high efficiency, easy separation, and simple experimental operation (Wang et al. 2015a; Xu et al. 2012).

Recently, magnetic mesoporous adsorbents binding the multiple superiority of sufficient magnetization and mesoporous structure has received widespread attention in pollutant adsorption due to the narrow pore size distribution, ordered mesoporous structure, and distinct large surface area (Vunain et al. 2016; Wang et al. 2010a). Composite materials that combine the advantages of PANI and nanostructured magnetic material are also effective on remediation of Cr(VI) from wastewater (Chavez-Guajardo et al. 2015; Gu et al. 2012).

Recently, a kind of adsorbent based on PANI-modified magnetic mesoporous carbon (PANI-Fe/OMC) was prepared via polymerization of oxidative aniline on the Fe/OMC matrix (Yang et al. 2014). The novel functional adsorbent was developed for reduction performance and improving adsorption efficiency of Cr(VI). The maximum adsorption capacity calculated by Langmuir model was 172.33 mg/g at pH 2.0. In addition, the exhausted adsorbent could be effectively recycling. The inorganic interferents from PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^- were almost insignicant at low concentrations of each of them (less than 25 mg/L). However, as the concentration of interferents increased, the Cr(VI) adsorption capacity showed a slight decrease under PO_4^{3-} and SO_4^{2-}, while almost remains steady under NO_3^- and Cl^-. The existence of humic and fulvic acids (as the organic interferents) at lower concentrations (less than 300 mg/L) can enhance the Cr(VI) adsorption capacity, while the reduction on Cr(VI) adsorption capacity occurs at higher concentrations of humic and fulvic acids. Furthermore, three different real water environments, including river, tap, and ultrapure water were applied to the fixed-bed column adsorption. Various Cr(VI) samples with an initial concentration of 80 mg/L at pH 2.0 were added into an polyethylene columns (10-mm diameter and 200-mm length) with the desired flow rate of 8 mL/min. The uptake capacities of Cr(VI) were slightly increased in river water samples whereas there was a deceleration in tap water compared with ultrapure water.

Magnetic mesoporous silica incorporated with PANI was developed to improve reduction and adsorption of toxic Cr(VI) (Tang et al. 2014). The magnetic mesoporous silica composite was synthesized via $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (FAS), F-127, and tetraethyl orthosilicate (TEOS), evenly using H_2O_2 as oxidant, and finally PANI grafting to functionalize the composite. The grafting PANI containing many imine and amine groups, which could be as active sites for the adsorption of metals ions, with the adsorption capacity of 193.85 mg/g for Cr(VI) (Tang et al. 2014). The adsorption process meets the pseudo-second-order kinetics model and Langmuir isotherm. Moreover, the results indicated the adsorbent could be great recyclable and sustain above 83% Cr(VI) adsorption ratio in three cycles. The effects of common ions (Na^+, K^+, Ca^{2+}, SO_4^{2-}, NO_3^-, and Cl^-) on the adsorption of Cr(VI) was proved to be insignificant with the concentration of common ions increase from 0 to 100 mg/L.

Recently, various magnetic nanoparticles, such as akaganéite (β-FeOOH), magnetite (Fe_3O_4), and maghemite (γ-Fe_2O_3), have also been adopted for the heavy metal ions removal, mainly owing to their excellent characteristics such as high saturation magnetization, large surface area, and large number of active adsorption sites for contaminants (Cui et al. 2015; Xie et al. 2014; Xin et al. 2012). PANI applied to modify the surface of the magnetic nanoparticles can enhance the adsorption of heavy metal ions because of its activity as chelating agents (Chávez-Guajardo et al. 2015). The recent study examined the use of polyaniline/maghemite (PANI/γ-Fe_2O_3) nanocomposites for the adsorption of Cr(VI) from wastewater (Chavez-Guajardo et al. 2015). The magnetic nanoparticles were synthesized via chemical co-precipitation methods. Subsequently, magnetic nanoparticles grafted with PANI to functionalize the magnetic nanoparticles via emulsion polymerization of aniline with sodium dodecyl sulfate (SDS) as an emulsifier. It was showed the maximum adsorption capacity was 196 mg/g at pH 2.0 and adsorption process achieved balance within 35 min (Table 1).

Recent study on removing Cr(VI) ions from aqueous solutions was conducted by PANI/akaganéite (PANI/β-FeOOH) nanocomposite which was synthesized through a mechanical mixture of PANI and akaganéite nanoparticles (Ebrahim et al. 2016). The composite has showed removal capacity of 17.36 mg/g in a short contact time (5 min) and the removal percentage reached 99.2% for 7.0 mg/L Cr(VI) wastewater at pH 2.0.

Different methods used for synthesis of Fe_3O_4/PANI nanocomposites have been employed for adsorption of pollutants from aqueous solution or wastewater (Gu et al. 2012; Han et al. 2013; Li et al. 2013; Rezvani et al. 2014). The feasibility of Cr(VI) removal through the core-shell structured Fe_3O_4/PANI microspheres synthesized via an interfacial polymerization without surfactant was reported (Han et al. 2013). Fe_3O_4/PANI microspheres have Cr(VI) ion adsorption capacity of 200 mg/g (Han et al. 2013). The nanocomposites showed rapid removal rate from water in about 30 min (Han et al. 2013). The Fe_3O_4/PANI microspheres demonstrated fine regeneration that adsorption capacity could retain 90% of the initial value after reuse five times.

Fe_3O_4 was modified into PANI to synthesis the PANI/Fe_3O_4 nanocomposite by chemical polymerization of oxidative aniline grafted to the surface of Fe_3O_4 nanoparticles (Rezvani et al. 2014). It was applied to the rapid determination and extraction of trace quantities of Cr(VI) in spiked water samples. The limit of detection was 0.1 μg/L, the maximum adsorption capacity was 54 mg/g, and all the relative standard deviation were < 6.3% (Rezvani et al. 2014). Another magnetic PANI/Fe_3O_4 nanocomposites has been prepared via the surface initiated polymerization method (Gu et al. 2012). A complete removal efficiency can be found on the 20.0 mL

neutral solution with adsorbent load of 0.5 g/L and Cr(VI) concentration was 1.0–3.0 mg/L after 5-min contact time.

PANI/Fe_3O_4 was another nanocomposite synthesized by in situ polymerization method, where Fe_3O_4 nanoparticle were prepared by the microwave irradiation technique (Ramachandran et al. 2017). Groundwater samples treated with PANI/Fe_3O_4 indicated that the Cr concentration was reduced from 0.295 to 0.144 mg/L.

Polyaniline modified carbon material

It is well-known that many investigations paid attention to the carbon materials, which were used as substrate for fabricating composite adsorbents for contaminant removal. Carbon materials have great potential as adsorbents to remove dye, heavy metal, and tetracycline from wastewaters (Tang et al. 2012). Various forms of carbon and their composites were investigated to enhance the adsorption performance (Wu et al. 2014). One way to enhance the adsorption performance is the modification of carbon materials, using polymer containing functional groups (Setshedi et al. 2015; Wu et al. 2014). The polyaniline contains abundant imine and amine nitrogen groups which can be adopted as modifying agent to synthesis functional adsorbent. It was reported the carbon fabrics (CFs) loaded with various weight percentage of PANI (PANI/CFs) synthesized via soaking carbon fabrics in PANI m-cresol solution have been indicated greater removal efficiency than the as-received CFs for Cr(VI) ion (Qiu et al. 2014a). The Langmuir maximum sorption capacity of the 10.0 wt% PANI/CFs was 18.1 mg/g at pH 1.0. The adsorption equilibrium time of the 10.0 wt% PANI/CFs was about 15 min for the initial Cr(VI) concentration of 1.0 mg/L. It was much better than the as-received CFs (> 1 h) and the classical active carbon (6 h) (Qiu et al. 2014a).

Among the carbon material adsorbents, carbon nanotubes (CNTs) are used in extensively applications for the removal of contaminants because of their small size, good electrical conductivity, hollow/layered structures, and high specific surface area (Chen et al. 2017b; Kumar et al. 2013). However, in the adsorption application, bare CNTs always show a slight reduction ability and limited adsorption capacity, because of the easy agglomeration in the aqueous solution. There is also lack of enough hydrophilic surface and functional groups. Hu et al. found that the maximum adsorption capacity was 4.26 mg/g onto oxidized multiwalled carbon nanotubes and the adsorption equilibrium time was about 30 h at the initial concentrations of 1.0 mg/L Cr(VI) solution (Hu et al. 2009). Atieh (2011) reported that activated carbon coated with carbon nanotubes was used to adsorb Cr(VI) with the adsorption capacity of 9 mg/g. One way to overcome this drawback is using polymer or surfactant to modify the surface of CNTs. In this field, the polyaniline/multiwalled carbon nanotube (PANI-MWCNT) was obtained by coating polyaniline medicate on

the surface of MWCNT (Wang et al. 2015c). The maximum adsorption capability for Cr(VI) was 31.75 mg/g at pH 4.5. The equilibrium adsorption time was 24 h, which was faster than oxidized multiwalled carbon nanotubes (30 h) (Hu et al. 2009). As Cr(VI) exists in water as oxyanions, amino adsorbents with positively charged nitrogen-containing functional groups have been shown to be effective for Cr(VI) removal (Wang et al. 2015c). Therefore, modification of CNT with PANI can be able to enhance both the adsorption capacity and rate.

Recent study also showed the polyaniline/ MWCNTs dope with dodecyl benzene sulfonic acid (DBSA) to prepare the nanocomposite used to remove Cr(VI) ions and the maximum monolayer adsorption capacity was 55.55 mg/g (Table 1) (Kumar et al. 2013). DP/MWCNTs were synthesized via in situ oxidative polymerization oxidative aniline with MWCNTs in the previous solution of DBSA. The increase in temperature and contact time promoted the diffusion of Cr(VI) ions into the internal adsorption sites resulting in the increase of adsorption efficiency. The kinetics results demonstrated that the equilibrium time of DP/MWCNTs was about 10 h which was faster than those of the PANI-MWCNT and oxidized multiwalled carbon nanotubes (30 h) (Hu et al. 2009).

Graphene oxide (GO), a member of the family of carbon, is versatile materials employed in varied applications for the removal of pollutants (Chen et al. 2017a; Wu et al. 2016b; Yuan et al. 2016). The interaction of GO with PANI are very useful in heavy metal ions removal due to its nitrogen-contain functional groups and high theoretical surface area. In this regard, conducting PANI (1D nanorods) arrays grown vertically on GO (2D nanosheets) by dilute polymerization to prepare a novel hierarchical nanocomposite using to remove Cr(VI) (Zhang et al. 2013). They exhibited high adsorption capacity of 1149.4 mg/g (Zhang et al. 2013). The formation mechanism of PANI/GO composites was speculated. Firstly, the electrostatic attraction between functional groups and aniline ions led to many active sites were produced on GO in the early stages of the polymerization process of PANI. Aniline ions started to polymerize in these active sites and formed many tiny PANI protuberances on the nanosheets after $(NH_4)_2S_2O_8$ was added to the reaction system. The homogeneous nucleation was suppressed because the low concentration of aniline cannot reach a supersaturation state. PANI nanorods would further grow along the initial nuclei, and consequently, aligned PANI nanorods on GO nanosheets were generated.

Another study used the reduced graphene oxide and PANI motivated the synthesis of a PANI functionalized graphene sheets (PANI-G) used for the removing Cr(VI) ions from wastewater (Harijan and Chandra 2016b). The synthesis process was achieved via polymerizing aniline in the presence of graphene oxide with various loading and reducing it with sodium borohydride. The Cr(VI) removal capacity increases with graphene oxide loading and shows maximum for 10% loading (PANI-G10) was 192 mg/g at pH 6.5 and 30 °C. However, the equilibrium adsorptions data show the equilibration time within 20 min onto PANI-G10.

The recent study showed the generation of PANI@GO-CNT using the PANI combining with the GO composite and multiwalled CNT by oxidative polymerization aniline (Ansari et al. 2017). PANI@GO-CNT composite finally doped with para toluene sulphonic acid (pTSA) to form the pTSA-PANI@GO-CNT. The maximum adsorption of Cr(VI) was 142.86 mg/g at pH 2 and 30 °C. CNTs provided adequate substrate and high surface area for the further attachment of polyaniline and GO. The presence of polyaniline can provide sites for pTSA functionalization and adhesion of components on CNTs.

The study has been attempted to synthesize Fe_3O_4/G/PANI composite containing PANI, graphene sheets (G), and magnetite nanoparticles (Fe_3O_4) through chemical route for removing toxic Cr(VI) from wastewater (Harijan and Chandra 2016a). The G-PANI nanocomposite was obtained by polymerizing aniline on the surface of G. Then, iron precursors were added to synthesis Fe_3O_4/G/PANI composite (Harijan and Chandra 2016a). The equilibrium adsorptions revealed maximum adsorption capacity 153.54 mg/g at pH 6.5 and 30 °C and the adsorption saturation limit was 40 min. The adsorption capacity of bare PANI was lower than G/PANI due to the G with advantages of electron transport and high surface area which can improve electro reductive capacitance and adsorptive sites of the PANI. The magnetic Fe_3O_4/G/PANI composite indicates weak Cr (VI) adsorption performance in comparison with the G/PANI because of poor surface area and low adsorptive capacity of Fe_3O_4 component (Harijan and Chandra 2016a).

Polyaniline-modified clay and mineral

Clay minerals are widely applied to adsorption removal of heavy metal ions. Meanwhile, adsorbent supported with clay minerals has been widely researched for the hexavalent chromium removal due to its special surface area, high exchange capacity, and enrichment ability of heavy metal ions (Zhou et al. 2017a).

The palygorskite (PA) were used as clay with a fibrous morphology and negatively charged surface which were modified by polyaniline (Wang et al. 2015b). The maximal adsorption capacity of PA/PANI composite was 14.79 mg/g for Cr(VI) at pH 5.5, while untreated PA almost did not adsorb Cr(VI). The repeated removal rate of PA/PANI composite just keeps 57% removal efficiency after first cycle.

Recent studies reported that the PANI/sepiolite nanofibers were synthesized with sepiolite served as template to orient the growth of PANI nanofibers at room temperature which

uses to remove Cr (VI) by adsorption (Chen et al. 2014a). This study showed the maximum adsorption capacity was 206.61 mg/g at 25 °C and PANI/sepiolite nanofibers can be reused for two treatment cycles remained almost same removal efficiency (100%).

The flake-like polyaniline/montmorillonite (PANI/MMT) composite was synthesized via the in situ polymerization method and used as an adsorbent to remove toxic Cr(VI) (Chen et al. 2013). In this synthesis system, the pristine MMT was modified with polymer acid as poly(2-acrylamido-2-methylpropanesulfonic acid), which could be regarded as a "bridge" role to combine clay and PANI. Then, the polymerization of aniline occurred. In batch adsorption studies, the results showed that the flake-like PANI/MMT showed the adsorption capacity of 167.5 mg/g. Similarly, another study found anther amphoteric polymer, the copolymer consisting of methacrylate acid and (2-methacryloyloxyethyl)trimethyl ammonium chloride, which was used to modify MMT to synthetize the exfoliated (PANI/MMT) composites exhibiting an higher adsorption capacity of 308.6 mg/g than the flake-like PANI/MMT (Chen et al. 2014b).

As clay minerals, halloysite (HA) nanotubes (chemical composition of $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) with massive surface hydroxyl groups, which can induce the growth of PANI on the HA in situ (Zhou et al. 2017a). Recent studies showed the effect of various dopant acids (HCl, H_2SO_4, HNO_3, and H_3PO_4) with the same acidity in synthesis process and redoping on the adsorption capacity of HA@PANI hybrid nanotube. The HA@PANI synthesized with HCl tuning the pH to 0.5 and 204% apparent weight proportion for aniline and HA (denote as HP/0.5/204%-HCl) showed the highest adsorption capacity (62.9 mg/g) due to the highest doping degree of PANI (Zhou et al. 2017a). Furthermore, the preparation of a variety of HP/A/204%-HCl under various concentrations of HCl and redoping HP/0.5/204%-HCl by HNO_3, H_2SO_4 and H_3PO_4 indicated that the optimum HCl concentration was 1 M in the synthesis process.

Other composites with polyaniline

Recently, the organic-inorganic hybrid material gained extensive attention in the field of adsorption and photocatalysis due to their multifunctional properties and enhanced adsorption efficiency (Samiey et al. 2014; Wu et al. 2016a). In this area, various preparations of organic-inorganic hybrid materials using inorganic materials and conducting polymers have been studied. For example, the PANI@MoS2 composite fabricated by PANI was modified to 3D flower-like MoS_2 (Gao et al. 2016). Under UV irradiation, the maximum removal capacity of Cr(VI) by PANI@MoS_2 was 526.3 mg/g at pH 3.0. PANI@MoS2 composite exhibited a higher removal capacity than bare MoS2 and bare PANI. Firstly, Cr(VI) was adsorbed

on the surface of PANI@MoS_2 and further reduced to Cr(III) due to the adsorption/photocatalytic reduction under UV irradiation.

However, another study showed that a novel adsorbent of Mg/Al layered double hydroxides (LDHs) with ployaniline were prepared via in situ polymerization method (Zhu et al. 2016). Various ratios of LDHs/aniline mass for the removing toxic Cr(VI) ions from water was studied. The PANI/LDHs sample with the LDHs/aniline mass ratio of 1:8 showed the maximum adsorption capacity of 393.701 mg/g.

Whereas, complicated fabrication procedures and the regeneration of the hybrid absorbents greatly limited absorbents practical applications (Wen et al. 2016). The study showed the polyaniline/hydrogen-titanate nanobelt (PANI/H-TNB) composites presented satisfactory reusability and regeneration performance in the adsorption of Cr(VI) and humic acid (HA). The PANI/H-TNB composites prepared with the H-TNBs/aniline molar ratio of 1:20 exhibited high adsorption capacity of Cr(VI) and HA was 156.94 and 339.46 mg/g, respectively (Wen et al. 2016). The PANI/H-TNB composites were synthesized via adding phytic acid in the polymerization process. Phytic acid played an important role in the regeneration and formation of PANI (Wen et al. 2016). The removal efficiency of Cr(VI) could be still up to 70.5% in 10 use cycles. The PANI/H-TNB composites were used to treat the natural groundwater, the contaminated simulated water, and the Milli-Q water with 10 mg/L Cr(VI). The removal rate of Cr(VI) by PANI/H-TNB in the natural groundwater, the contaminated simulated water and the Milli-Q were 78, 90, and 96%, respectively.

However, copolymerization also is an effective method to enhance the quantity of functional groups on polymer chains. Diaminonaphthalene (DAN) have abundant amine and secondary amino groups (Huang et al. 2005). Therefore, the copolymer of 1,8-diaminonaphthalene (1,8-DAN) and aniline (AN) is regarded as an economical and effective adsorbent for removing heavy metal ions. The novel composite materials poly(aniline-1,8-diaminonaphthalene) (PANDAN) was fabricated via chemical oxidation method and applied as adsorbent to remove Cr(VI) (Li et al. 2011a). The adsorption capacity of PANDAN for Cr(VI) ions was 150 mg/g at pH 4 and 298 K and with adsorbent dosage of 0.5 g/L. The column adsorption studies indicated that the greater breakthrough adsorption capacity was mainly depended on the higher inlet Cr(VI) concentration and the lower feed flow rate (Li et al. 2011a).

PANI and polypyrrole (PPy) containing abundant amine and imine groups provide the main adsorption sites for heavy metal ions. Therefore, the recent study on removing Cr(VI) from wastewater was carried out using the PPy-PANI nanofibers and the maximum adsorption capacity was 227 mg/g at pH 2.0 (Table 1) (Bhaumik et al. 2012). PPy-PANI nanofibers were fabricated with no template by coupling of propagating PANI•+ and PPy•+ free radicals via the coinstantaneous

polymerization of aniline and pyrrole monomers using $FeCl_3$ as an oxidant (Bhaumik et al. 2012). Synthesizing PPy-PANI nanofibers mainly aims to the corporation of PANI into the growing polymer chain of PPy, which offers an enhanced surface area that may improve the adsorption of Cr(VI) compared to its polypyrrole homopolymer counterpart (Fusalba and Bélanger 1999). One similar study had showed a Fe_3O_4 coated PPy-PANI/magnetic nanocomposite (PPy-PANI/Fe_3O_4), whose adsorption capacity of Cr(VI) was 303 mg/g at pH 2.0 (Afshar et al. 2016). The adsorption process was not significantly affected by the Ni^{2+}, Zn^{2+}, Cu^{2+}, Cl^-, NO_3^-, and SO_4^{2-} in solution and showed the adsorbent could maintain the 100% adsorption capacity after three treatment cycles.

The removal mechanisms of Cr(VI)

For evaluating removal performance through polyaniline-based adsorbents, the illumination of the possible mechanisms of the adsorption process is needed. The adsorption behavior of polyaniline-based adsorbents correlated with the conditions of solution (i.e., pH, temperature, and co-existing interferents). In addition, the adsorption mechanisms of the composite adsorbent depend on the properties of PANI and various substrates. However, there are certain characteristics in common for polyaniline-based adsorbents to remove Cr(VI) from aqueous solution or wastewater. Lower pH usually shows a better adsorption capacity due to stronger electrostatic attraction between aqueous Cr(VI) oxyanions and protonated imine groups. The decrease of adsorption capacity with the increase of original solution pH was mainly due to the weakening electrostatic interaction between adsorbent and Cr(VI) and the competition between Cr(VI) anions and OH^- for adsorption sites on the polyaniline-based adsorbents (Wen et al. 2016). For testing whether any chemical redox reaction occurred during the Cr(VI) adsorption process, it is necessary to perform the analysis of chemical bond and elemental on the adsorbent. The possible adsorption mechanisms are usually demonstrated using FTIR and XPS techniques for adsorbent before and after Cr(VI) adsorption (Qiu et al. 2014b; Wang et al. 2014).

The removal of hexavalent chromium by polyaniline-modified materials was mainly depended on the substrate materials as well as the functional groups of PANI. The adsorption performances and adsorption mechanisms may change with type of PANI-based adsorbents, which are related closely to the properties of the various substrate materials. The adsorption capacity of each kind of polyaniline-based adsorbent on the corresponding experimental conditions has been listed in Table 1. However, the removal mechanisms of polyaniline-modified various substrate materials remained to be studied further in depth. The adsorption mechanisms of polyaniline-based adsorbents seem to be happened with the reduction of Cr(VI) species to Cr(III) species at acidic conditions. Meanwhile, the amine group (−NH−) of PANI is partially changed into imine group (−N=) after adsorption of Cr(VI) (Ebrahim et al. 2016). The adsorption process is related to ion exchange, surface, electrostatic attraction, complexation reactions with protonated sites, and the reduction coupled adsorption. In all, the adsorption process can be divided into three parts depending on the characteristics of PANI: Firstly, under the acidic conditions, surface complexation occurs between negatively charged aqueous Cr(VI) oxyanions and protonated imine groups by electrostatic attraction or ion exchange between doped aqueous Cr(VI) oxyanions and anion (i.e., Cl^-) doped in PANI, resulting in Cr(VI) adsorption on PANI surface. Secondly, some Cr(VI) oxyanions are reduced to Cr(III) cations while amines are oxidized to quinoid amine, which indicates that PANI is partially oxidized from EB to PB. Thirdly, the oxidated state of PANI functional groups (quinoid amines) are strongly bound partial Cr(III) cations as other possible functional groups (i.e., hydroxyl group) on various substrates also can bound Cr(III). The pathway of the removal mechanisms of Cr(VI) was showed in Fig. 4.

Fig. 4 Proposed mechanisms of Cr(VI) removal with PANI-based adsorbents
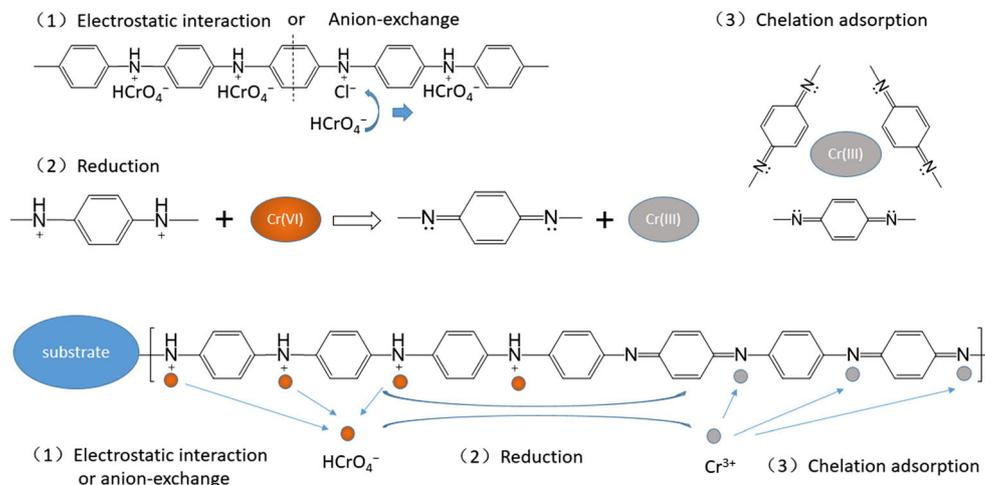
Meanwhile, kinetics models indicate the potential rate-controlling step in the adsorption process. As shown in Table 1, most of the PANI-based adsorbents fit well with the pseudo-second-order model, which shows that adsorption process seems to be chemical adsorption. Meanwhile, for the majority of PANI-based adsorbent, Langmuir model, an isotherm model, means the adsorption process is limited with monolayer coverage, fits better than Freundlich model for the adsorption of Cr(VI).

Conclusions and prospects

In this review, the extensive information on Cr(VI) removing from wastewater effluents or aqueous solutions using the PANI-based adsorbents were introduced. Various affecting factors related to the adsorption of Cr(VI) via PANI-based adsorbents from wastewater effluents or aqueous solutions were discussed and compiled. Polyaniline homopolymer have been readily synthesized by chemical oxidative polymerization with different additives to modify the morphology or enhance the absorption efficiency. The PANI coating can raise the hydrophilicity of adsorbents, enhance the adsorption rate and adsorption capacity of adsorbent, and strengthen the detoxification if Cr(VI) species to Cr(III) species. These polyaniline-based adsorbents exhibit faster kinetics, higher capacity, and preferably adsorption. The results demonstrate that the PANI-based adsorbents can be effective for Cr(VI) removal from aqueous solutions. For example, PANI-bioadsorbents can be easily prepared and always be regarded as economic and effective adsorbents for Cr(VI) treatment. The PANI-based nanomaterials show a better adsorption efficiency for Cr(VI) removal in virtue of the presence of highly specific active surface sites and surface area in adsorbents. The PANI-modified magnetic materials, nanofiber mats, and nanofiber membranes can be easily separated from water. Nevertheless, there are still some technical challenges needed to be conquered in promote practical application of PANI-based adsorbent. Under the acid condition, PANI-based adsorbents show better adsorption performance than alkaline condition. Therefore, the composite adsorbent can effectively work in wide pH range. However, there is a lack of large commercial application on the conducting PANI-based adsorbents. Massive researches are still needed to achieve the commercial practical application of PANI-based adsorbent, which will be explored as a new direction in adsorption technology alleviating the Cr(VI) contaminated water. Various PANI-based adsorbents should be sourced out and focus on improving the recovery rate to minimize the cost of their commercial applications, and can be effective in removal efficiency. The adsorption study is mainly forced on the synthetic solutions. There is a lack of researches on real wastewater. Therefore, more researches are still needed on real wastewater in the future.

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