# Adsorption of graphene for the removal of inorganic pollutants in water purification: a review

Yong Cao · Xinbao Li

**Abstract** Graphene has aroused widespread attention as a new type of adsorbents due to its outstanding ability for the removal of various pollutants from aqueous solutions. This review summarizes the application of graphene-based nanomaterials as an advanced adsorbent for the removal of inorganic pollutants including anionic and cationic type. The adsorption properties, mechanisms, isotherms, kinetics, thermodynamics and regeneration of adsorbents are all summarized, and the further research trends on graphene-based nanomaterials in the removal of pollutants are also given.

**Keywords** Adsorption · Graphene · Nanomaterials · Inorganic pollutants · Water purification

## 1 Introduction

Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. Clean water is also a critical feedstock in a variety of key industries including electronics, pharmaceuticals and food. However, the rapid pace of industrialization and its resulting by-products have affected water by producing hazardous wastes, which have been released to water directly. Among these hazardous wastes, heavy metal ions, arsenides and fluorides are usual inorganic toxic species. Ingestion of fluoride within the permissible limit is beneficial to human body. When fluoride is present in excess, it causes molting of teeth and

lesion of endocrine glands, thyroid, liver and other organs (Li et al. 2011c). Arsenic is infamous for its marked negative impacts on human health because of its chronic and carcinogenic effects as well as acute lethality (Pontius et al. 1994; Lenoble et al. 2005; Mohan and Pittman 2007). Heavy metal ions are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic (Fu and Wang 2011). Toxic heavy metal ions of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. At present, many techniques have been applied in the removal of these inorganic pollutants, such as flocculation (Karbassi and Nadjafpour 1996), membrane filtration (Soylak et al. 2010), solvent extraction (Makrlik and Vanura 2005), biosorption (Ofomaja et al. 2010), chemical precipitation (Matlock et al. 2002), reverse osmosis (Rao et al. 2009b), ion-exchange (Dabrowski et al. 2004), adsorption (Imamoglu and Tekir 2008), etc. Among these techniques, adsorption is one of the most promising methods for the removal of pollutants because it is simple, highly effective and economical (Stafiej and Pyrzynska 2008; Rao et al. 2007). A lot of adsorbents including clay minerals (Abollino and Aceto 2003), natural and modified zeolites (Oliveira et al. 2004), metal oxides (Zhang et al. 2007), agricultural wastes (Robinson et al. 2002), biomass (Loukidou et al. 2003) and polymeric materials (Atia et al. 2003) have been widely reported to remove pollutants from aqueous solutions. However, the further applications of these materials are limited by their low adsorption capacities or efficiencies.

Historically, thousands of researches focused on prepared carbon-based nanomaterials, such as active carbon (AC) and carbon nanotubes (CNTs), for environmental applications (Rao et al. 2007; Ruparelia et al. 2008; Mauter

Y. Cao (✉) · X. Li
Institute of Environment and Municipal Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045, People's Republic of China
e-mail: caoyangel@126.com

and Elimelech 2008; Petosa et al. 2010; Tawabini et al. 2010; Pyrzynska and Bystrzejewski 2010). However, CNTs with high produced cost usually require special oxidation processes (Kuo 2009; Li et al. 2011a; Ren et al. 2011a) to introduce hydrophilic groups to improve metal ions adsorption capacities. As for AC, a high cost to improve its quality and regenerate is required (Babel and Kurniawan 2003). Therefore, carbon-based nanomaterials with high adsorption ability and low cost are eagerly needed.

Graphene, a two-dimensional (2D) structure consisting of sp$^2$-hybridized carbons with only one atomic thickness, is a rising star in the material science and technology (Rao et al. 2009a; Geim 2009). Due to its large theoretical specific surface area (2,630 m$^2$ g$^{-1}$) (Zhu et al. 2010), remarkable electronic properties and high ability of modification, potential environmental applications of graphene as superior adsorbents have been recognized for the removal of various pollutants from water (Zhao et al. 2011a, b; Wu et al. 2011b; Ramesha et al. 2011; Chandra et al. 2010; Mishra and Ramaprabhu 2011; Chandra and Kim 2011; Ren et al. 2011b). Normally, graphene obtained from graphite exists in two states, i.e., graphene oxide (GO) and reduced graphene oxide (RGO). GO is water-soluble with low conductivity while RGO has good conductivity with poor solubility in water (Park et al. 2009). The oxidation process of graphite to GO can introduce abundant functional groups, such as –COOH, –C=O and –OH on GO surface. These oxygen groups which protrude from its layers can be used as anchoring sites to bind ions by both electrostatic or/and coordinate approaches, especially the multivalent metal ions (Dreyer et al. 2010; Zhang et al. 2010a; Sreeprasad et al. 2011). Moreover, these introduced oxygen groups also make GO hydrophilic, indicating the possibility to apply it in aquatic and biological environments (Fan et al. 2011). Although GO is an ideal adsorbent, the exfoliated graphene nanosheets tend to aggregate to low the specific surface area in water, which is unfavorable for adsorption process. In addition, GO is hard to be separated after adsorption due to its nano-sized particle and hydrophilic property. To overcome these disadvantages, decoration of graphene nanosheets with metal/metal oxide/nonmetallic oxide nanoparticles to form an important kind of graphene-based nanocomposites is an effective and feasible approach. The decoration of nanoparticles on graphene nanosheets is helpful to overcome the aggregation of individual graphene nanosheets and nanoparticles themselves (Williams et al. 2008). Besides, the obtained composites with larger surface area show superior properties, compared with bare nanoparticles (Song et al. 2011).

This paper reviews the current state of the application of graphene including GO, RGO, and their corresponding nanocomposites as adsorbents in the removal of inorganic pollutants from aqueous solutions, which involves adsorption effect and impact factors, mechanisms, isotherms, kinetics, thermodynamics and regeneration. This review is not intended to be comprehensive, as our focus is on exploiting the exceptional adsorption properties of graphene-based adsorbents towards the development of novel adsorption materials.

## 2 Adsorption properties of graphene

The adsorption-related applications of graphene to solve environmental pollution problems have received considerable attention since it was discovered. Graphene is a relatively new kind of adsorbents and holds interesting position in carbon-based adsorptive materials for reasons as follow. On one hand, it can be prepared by a simple oxidized method using the common oxidants from cheap and abundant graphite on a large scale. This is a superior advantage compared with CNTs. On the other hand, Graphene is a lamellar material with huge basal planes which provides a high specific surface area. Additionally, this lamellar structure with huge basal plane also provides an excellent location for loading other nanoparticles to form the nanocomposites to enhance the adsorption ability and facilitate the separation from solutions.

Due to its especial structure and strong interactions between graphene and pollutants, the applications of graphene for the removal of hazardous pollutants from aqueous solutions (Jonas et al. 2010; Ramesha et al. 2011; Leenaerts et al. 2008) have been studied extensively via theoretical calculations, experimental measurements and molecular simulations. A large number of experimental studies have already been carried out on the adsorption of small molecules (Romero et al. 2009; Lee et al. 2010), heavy metal ions (Deng et al. 2010; Zhang et al. 2010b; He et al. 2011), noble metals (Liu et al. 2012a, 2013), dyes (Li et al. 2011b; Yao et al. 2012; Liu et al. 2012b), pesticides (Gupta et al. 2012; Maliyekkal et al. 2013; Wu et al. 2011a), antibiotics (Gao et al. 2012) and aromatic pollutants (Zhao et al. 2011a, b) on graphene or its based nanocomposites.

Adsorption properties of graphene depend on the following factors, the first of which is the contribution of individual adsorption site. There are three possible sites in graphene for the adsorption of different pollutants: (1) one is sites on the oxygen functional groups, because the oxygen atoms have a much higher affinity to metal ions than that of the skeleton carbon (Sanchez-Polo and Rivera-Utrilla 2002). There are two major interactions involving electrostatic and coordination between metal ions and oxygen-containing groups on graphene, especially the carboxyl groups. Fig. 1
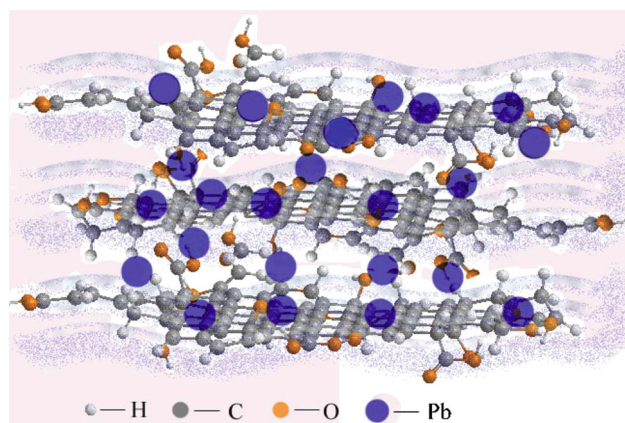
○—H  ●— C  ●—O  ●— Pb

**Fig. 1** A schematic diagram of the formation of the surface coordination of Pb(II) ions on the surfaces of GO "Reprinted from Dalton Transactions, 40, 2011, 10945–10952, Removal of Pb(II) ions from aqueous solutions on few-layered graphene oxide nanosheets, Zhao, G.X., Ren, X.M., Gao, X., Tan, X.L., Li, J.X., Chen, C.L., Huang, Y.Y., Wang, X.K., Copyright (2011), with permission from Royal Society of Chemistry"

shows a schematic diagram of the formation of the surface coordination of Pb(II) with the oxygen-containing groups of GO. Mi et al. (2012) pointed out that the adsorption efficiency of RGO for removal of Cu(II) was not good, because most oxygen groups had been removed during the transformation from GO to RGO. Similarly, RGO obtained from the reduced GO also showed a low ability to adsorb Cr(VI) from aqueous solutions (Wu et al. 2013b). In fact, this RGO still kept a small amount of C=O or O=C–OH groups, which could be identified from the results of X-ray photoelectron spectroscopy (XPS). Huang et al. (2011) reported that graphene under a heat treat at a high vacuum demonstrated a high adsorption ability for Pb(II) from aqueous solutions. As we all know, the oxygen functional groups of RGO can be removed after a heat-treated process. Though the total oxygen functional groups showed a significant decrease, the amount of carboxyl groups increased as the increasing heat-treated temperature. In addition to the oxygen functional groups, the site contributed to the high adsorption ability for Pb(II) is the next one. (2) Another is estimated to be sites of C π electrons on graphene sheets (Rivera-Utrilla and San-chez-Polo 2003). In the Lewis definition, acids are electron pair acceptors and bases are electron pair donors. The fundamental reaction between Lewis acid A and Lewis base B is the formation of a complex A-B. In this reaction, the unshared electron pair of the base forms a coordination bond with an electron-deficient atom of the acid. In the case of graphene and a metal ion, graphene is the Lewis base and the heavy metal ion is the Lewis acid. A complex between graphene and the metal ion can occur through Lewis acid–base interaction. Many investigations (Huang et al. 2011;

Zhao et al. 2011c; Hao et al. 2012) demonstrated that the delocalized π electron systems of graphene sheets acted as Lewis bases in aqueous solutions and formed electron donor–acceptor complexes with lead ions; (3) the other is the active site on the outer surface of the decorated nanoparticels on graphene sheets. Many findings indicated that the chemical interactions between metal ions with nanoparticles surface were vitally important to improve the adsorption ability. For example, the decorated $MnO_2$ and Ag nanoparticles on RGO played a role in the adsorption of Hg(II) (Sreeprasad et al. 2011), and the decorated ferric hydroxide was used to adsorb for arsenic (Zhang et al. 2010a). Zhu et al. (2012) synthesized the magnetic graphene nanocomposites decorated with core@double-shell nanoparticles for fast Cr(VI) removal. The Cr(VI) adsorption mechanisms on graphene and the magnetic graphene nanocomposites are illustrated in Fig. 2. From this figure, the outer surface of the decorated nanoparticles acting as active sites for adsorption is clearly being seen.

Secondly, the pore structure of graphene influences the adsorption capacity. As mentioned especial structure before, the real graphene has ultrahigh specific surface and no porosity. However, the adsorption capacities of materials depend on their pore structure and surface properties. In order to enhance adsorption capacity of graphene, introduction of porosity is an effective and feasible method. Combining other porous materials with graphene can introduce porosity. For example, (Zhang et al. 2011) combined chitosan–gelatin with GO to form ordered porous composite for Cu(II) and Pb(II) adsorption. The composite exhibited an extremely high adsorbing ability for both metal ions. Zhang et al. (2013a) presented polyethersulfone enwrapped GO, which showed porous structures inside and a dense skin layers, and displayed well-selective adsorbability to cationic dyes. Additionally, introduction of porosity can also be realized by synthesis of 3D graphene sponges or foams, which have attracted extensive attention due to the high porosity for the practical application of being a high-efficient adsorbent. Wang et al. (2012) fabricated a 3D graphene architectures based on the chemical reduction of GO with the assist of natural phenolic acids and in situ self-assembly of graphene sheets through π-π interaction. The obtained 3D graphene exhibited super hydrophobicity, low density and high porosity, and was proved to have excellent adsorption capacity and fast adsorption rate towards oils and organic solvents. Zhao et al. (2012) prepared spongy graphene by self-assembly of GO sheets under the assistance of thiourea. This graphene had a tunable pore structure and displayed high adsorption capacity to diesel oil. Bi et al. (2012) developed a shape-mouldable spongy graphene which exhibited highly efficient adsorption towards toxic solvents as well as petroleum products and fats, even up to 86 times of its weight.
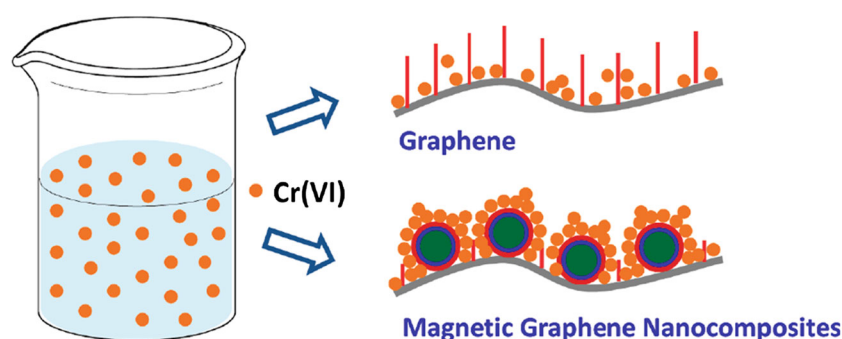
**Fig. 2** Adsorption mechanisms on graphene and the magnetic graphene nanocomposites "Reprinted from Environmental Science & Technology, 46, 2012, 977–985, One-pot synthesis of magnetic graphene nanocomposites decorated with core@double-shell nanoparticles for fast chromium removal, Zhu, J.H., Wei, S.Y., Gu, H.B., Rapole, S.B., Wang, Q., Luo, Z.P., Haldolaarachchige, N., Young, D.P., Guo, Z.H., Copyright (2012), with permission from American Chemical Society"

Thirdly, the pH of aquatic environments can greatly influence the adsorption property of graphene. Solution pH is one of the most important parameters to determine the adsorption property of an adsorbent due to its effect not only on surface charge of the adsorbent, but also on the degree of ionization and speciation of adsorbate. The pH dependence of ionic pollutants adsorption on graphene can be explained by point of zero charge ($pH_{PZC}$) of the adsorbent (Chandra et al. 2010). At $pH < pH_{PZC}$, the surface of graphene is positively charged, which can attract anionic pollutants effectively and repulse cationic pollutants strongly by electrostatic interaction. Whereas at a $pH > pH_{PZC}$, the surface of graphene is negatively charged, which can attract cationic pollutants and repulse anionic pollutants strongly. Deng et al. (2010) prepared the functionalized graphene for the removal of Pb(II) and Cd(II). The results indicated that the uptake of Pb(II) or Cd(II) by the functionalized graphene was tiny at pH <3, the reason was that more hydrogen ions tended to occupy the surface active sites at low pH and resist nearness of metal ions due to electrostatic force, which led to fewer binding sites being available to bind metal ions, so the adsorption capacity of Pb(II) or Cd(II) was very little. With the pH increased, there were fewer hydrogen protons in solution, this meant that there were less competition of binding sites and more binding sites were released, the surface charges of graphene became more negative, which caused electrostatic interaction and resulted in that the adsorption of Pb(II) or Cd(II) increased dramatically in the range of pH value from 3.0 to 6.0.

Additionally, the contact time between absorbent and adsorbate can influence the adsorption property of graphene. As an ideal adsorbent, the adsorption on graphene mainly occurs on its planar surface (external surface), escaping from intraporous diffusion like that in porous carbons but only controlled by external diffusion since graphene with randomly aggregated structures have open ion channels, which results in a short period to reach adsorption equilibrium.

# 3 Application as adsorbents

In this review, our focus is on exploiting the exceptional adsorption properties of graphene and its based nanocomposites towards the development of novel adsorption materials in the removal of inorganic pollutants from wastewater. So we do not lay emphasis on the synthesis approaches of graphene and its based nanocomposites, which can be referred to other literatures (Kuilla et al. 2010; Prashant 2010; Xiang et al. 2012; Bai and Shen 2012; Avouris and Dimitrakopoulos 2012; Edwards and Coleman 2013). Next, the inorganic pollutants as adsorbates can be divided into two categories, anionic and cationic, to be discussed.
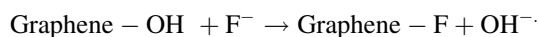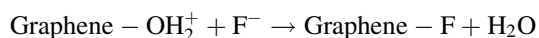
## 3.1 Adsorption of anionic pollutants

Fluoride, arsenic and chromium are common anionic pollutants in wastewater. For fluoride, $F^-$ is the main species in aqueous solution. Inorganic arsenic species, arsenate (As(V)) and arsenite (As(III)) are believed to be more toxic than the organic forms. As(V) is predominate in surface water, while As(III) is dominant in groundwater systems (Cullen and Reimer 1989). Under most pH conditions, As(III) is present in negative ionic form ($H_2AsO_3^-$). As(V) in solution exist mainly as $H_3AsO_4$ at pH<2.2, $H_2AsO_4^-$ at pH 2.2–6.98, $HAsO_4^{2-}$ at pH 6.98–11.5 and $AsO_4^{3-}$ at pH>11.5 (Zhu et al. 2009a; Chang et al. 2010). Chromium exists in two main oxidation states in the environment, Cr(VI) and Cr(III). Compared with Cr(III), Cr(VI) is more toxic (Liu et al. 2011b). At low pH, the predominant Cr(VI) species is $HCrO_4^-$, but as the pH increases, this form shifts to $Cr_2O_7^{2-}$ or $CrO_4^{2-}$.

For these anionic pollutants, a low pH value is facilitated for adsorption. This because the low pH leads to the surface of the adsorbent become highly protonated and positively charged (i.e., Surface-OH + H$^+$ → Surface-OH$_2^+$), which favors the uptake of anionic pollutants through electrostatic attraction. An increase in the solution pH will make the surface negatively charged, greatly weakening the electrostatic attraction between the adsorbent and negatively charged anionic pollutants, thus reducing the removal efficiency. Moreover, as the pH increases, there is competition between OH$^-$ and anionic contaminants, especially at high pH levels.

### 3.1.1 Adsorption of fluoride

Anions have been proposed to be adsorbed on adsorbents through specific and/or nonspecific adsorption (Reyes Bahena et al. Bahena 2002; Rude and Aller 1993). The specific adsorption involves ligand exchange reactions, where the anions displace –OH groups from the surface (Reyes Bahena et al. Bahena 2002). The nonspecific adsorption involves the electrostatic forces and mainly depends on the pH$_{PZC}$ of the adsorbent (Rude and Aller 1993). Li et al. (2011c) used graphene to adsorb of fluoride from aqueous solutions. Under the same condition, the maximum adsorption capacity for graphene was 35.59 mg g$^{-1}$, while the value for the aligned CNTs was only 1.99 mg g$^{-1}$. Their investigations suggested that adsorption of fluoride by graphene was mainly a specific process, which indicated that the adsorption mechanism for the graphene was ion exchange between fluoride ions in solution and hydroxyl ions on graphene. Thus, fluoride ions were predominantly adsorbed by the following surface-exchange reactions (Lopez-Valdivieso et al. 2006):

Graphene $-$ OH$_2^+$ + F$^-$ → Graphene $-$ F + H$_2$O

Graphene $-$ OH $+$ F$^-$ → Graphene $-$ F + OH$^-$.

### 3.1.2 Adsorption of As(III) and As(V)

Graphene has an excellent adsorption property toward various pollutants. However, some pollutants, such as arsenate, can not be removed effectively by using graphene solely to adsorb. In this case, graphene-based nanocomposites need to be developed. Iron minerals have been recognized as an effective media to remove various pollutants (Kharisov et al. 2012), especially for heavy metals such as As(III) and As(V) (Chandra et al. 2010), Cr(VI) (Hu et al. 2005) and Pd(II) (Shin and Jang 2007). More recently, iron and iron oxide nanostructures have been proved as higher efficient materials for the heavy metal ions removal by reduction or adsorption (Zhang 2003; Hu et al. 2008). However, these iron-based adsorbents are
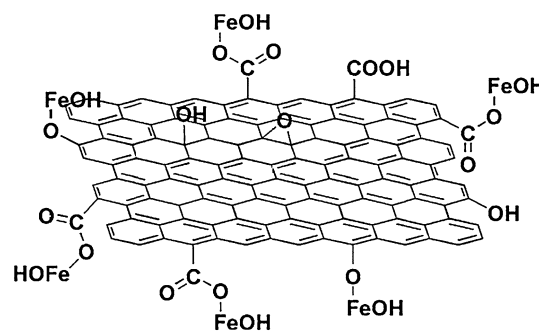


**Fig. 3** A diagram of the composites based on GO cross-linked with ferric hydroxide "Reprinted from Journal of Hazardous Materials, 182, 2010, 162–168, Graphene oxide/ferric hydroxide composites for efficient arsenate removal from drinking water. Zhang, K., Dwivedi, V., Chi, C.Y., Wu, J.S., Copyright (2010), with permission from Elsevier"

difficult to use in continuous flow systems due to small particle size and instability, since magnetite is highly susceptible to oxidation when exposed to the atmosphere (Jolivet et al. 2004). To overcome these challenges, combining iron minerals and graphene to form composites is a feasible way. The composites have following two main advantages: firstly, the absorption capacity is enhanced obviously. This is because the composites formed to overcome the aggregation of individual graphene nanosheets and iron-based nanoparticles themselves. As a result, both the specific surface area and the number of adsorption site have been increased, which leads to enhance the absorption capacity. Secondly, the separation of the composites from aqueous solution can be easy to realize using magnetic separation method due to the intrinsic magnetic property of iron-based nanoparticles. The magnetic separation is energy-saving and environment-friendly. Recently, many composites that iron-based nanoparticles decorated on the planar surface of graphene have been developed to remove As(III) and As(V) (Zhang et al. 2010a; Chandra et al. 2010; Wu et al. 2011c; Debabrata and Kaushik 2012; Sheng et al. 2012), Cr(VI) (Zhu et al. 2012; Jabeen et al.), Pb(II) (Yang et al. 2012; Fan et al. 2013) and Co(II) (Liu et al. 2011a) from wastewater. Zhang et al. (2010a) produced a series of composites based on GO cross-linked with ferric hydroxide, which were used to remove arsenate effectively from contaminated drinking water. The structure of the composites can be referred to Fig. 3.

(Chandra et al. 2010); (Sheng et al. 2012) investigated the Fe$_3$O$_4$/RGO and Fe$_3$O$_4$/GO composites as adsorbents to remove As(III) and As(V) from aqueous solutions. The results showed both the composites having a high adsorption capacity compared with bare Fe$_3$O$_4$ particles. The high adsorption capacity was due to the increased adsorption sites in the composites which occurred by reducing the
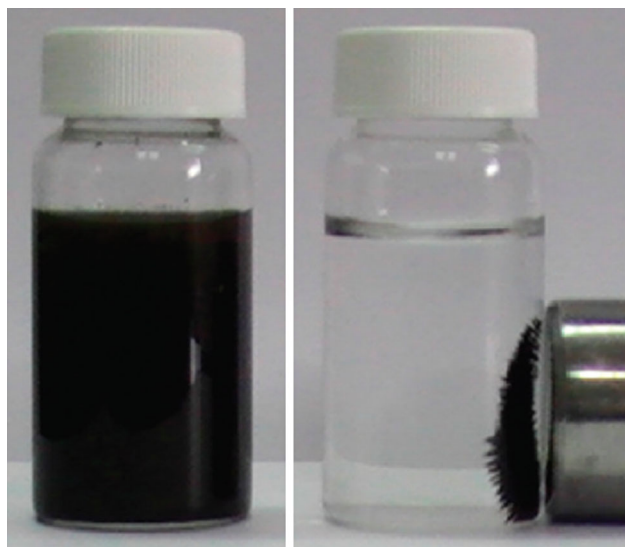
**Fig. 4** A diagram of the magnetic separation of $Fe_3O_4$/RGO from aqueous solution "Reprinted from ACS Nano, 4, 2010, 3979–3986, Water dispersible magnetite-reduced graphene oxide composites for arsenic removal, Chandra, V., Park, J., Chun, Y., Lee, J.W., Hwang, I.C., Kim, K.S., Copyright (2010), with permission from American Chemical Society"

aggregation of bare $Fe_3O_4$. The adsorption capacity of the composites decreased with ascending pH due to electrostatic interaction. After adsorption, the composites could be separated by an external magnetic field, which referred to Fig. 4.

Layered double hydroxides (LDHs) are a large class of lamellar inorganic materials. The existence of cationic brucite-like layers and exchangeable interlayer anions of LDHs make them excellent adsorbents for water treatment (Zhao et al. 2010). Combined LDHs with GO to form the LDHs/GO composite has been found to possess an efficient

removal of As(V) from aqueous solutions (Wen et al. 2013). Moreover, wu et al. (2011c) applied the composite of $Fe_3O_4$/LDHs/RGO, which was shown in Fig. 5, to remove As(V) from aqueous solutions. The maximum adsorption capacities were 37.73 mg g$^{-1}$ for LDHs and 73.14 mg g$^{-1}$ for the composite, demonstrating a higher adsorption capacity for the composite. The high adsorption capacity was owing to its high surface area and nano-crystalline property. The mechanism might include the following, one attributed to the strong electrostatic interaction between As(V) and the LDHs layered structure. Another was due to ion exchange between the intercalated anions of LDHs and As(V). In addition, the magnetic nanoparticles and graphene also provided extra adsorption sites for As(V) removal. This composite could also be easily separated by magnetic separation process.

Exception for the magnetic $Fe_3O_4$ nanoparticles, the magnetic $Mn_x^{2+}Fe_{2-x}^{3+}O_4^{2-}$ nanoparticles were also decorated on RGO to remove As(III) from the contaminated groundwater (Debabrata and Kaushik 2012). This composite with a high adsorbing capacity compared to bare $Mn_x^{2+}Fe_{2-x}^{3+}O_4^{2-}$ particles owing to its high specific surface area. As the magnetic properties of $Mn_x^{2+}Fe_{2-x}^{3+}O_4^{2-}$ particles, the composite could also be separated by an external magnetic field.

### 3.1.3 Adsorption of Cr(VI)

Chromium exists in two main oxidation states in the environment, Cr(VI) and Cr(III). Compared to much less soluble Cr(III), Cr(VI) is soluble, toxic and carcinogenic (Liu et al. 2011b). Therefore, the removal of Cr(VI) is imperative to meet the discharge levels. Zero valent iron nanoparticles (Fe) have high reducing power for Cr(VI),

**Fig. 5** Schematic illustration of the formation of $Fe_3O_4$/LDHs/RGO composite. The *solid balls* represent magnetite nanoparticles and the *hexagonal plate* represents LDHs "Reprinted from Journal of Materials Chemistry, 21, 2011, 17353–17359, Water-dispersible magnetite-graphene-LDH composites for efficient arsenate removal, Wu, X.L., Wang, L., Chen, C.L., Xu, A.W., Wang, X.K., Copyright (2011), with permission from Royal Society of Chemistry"
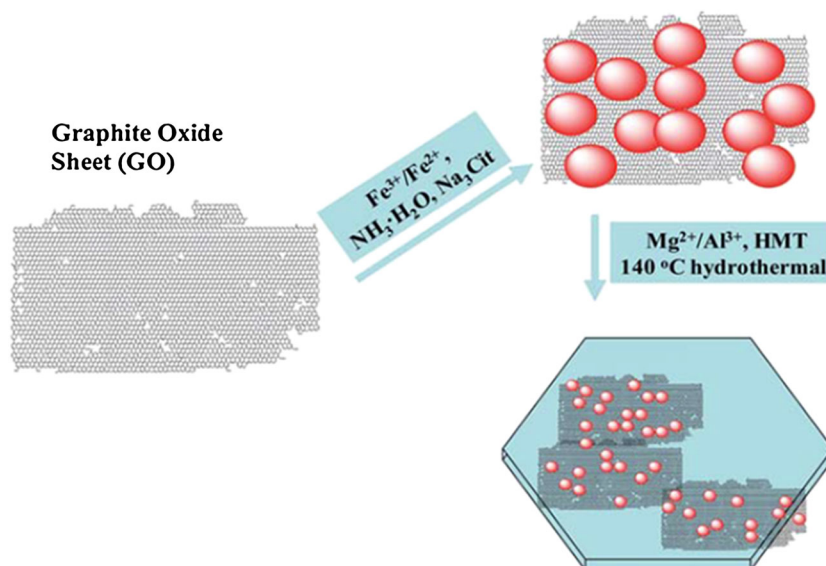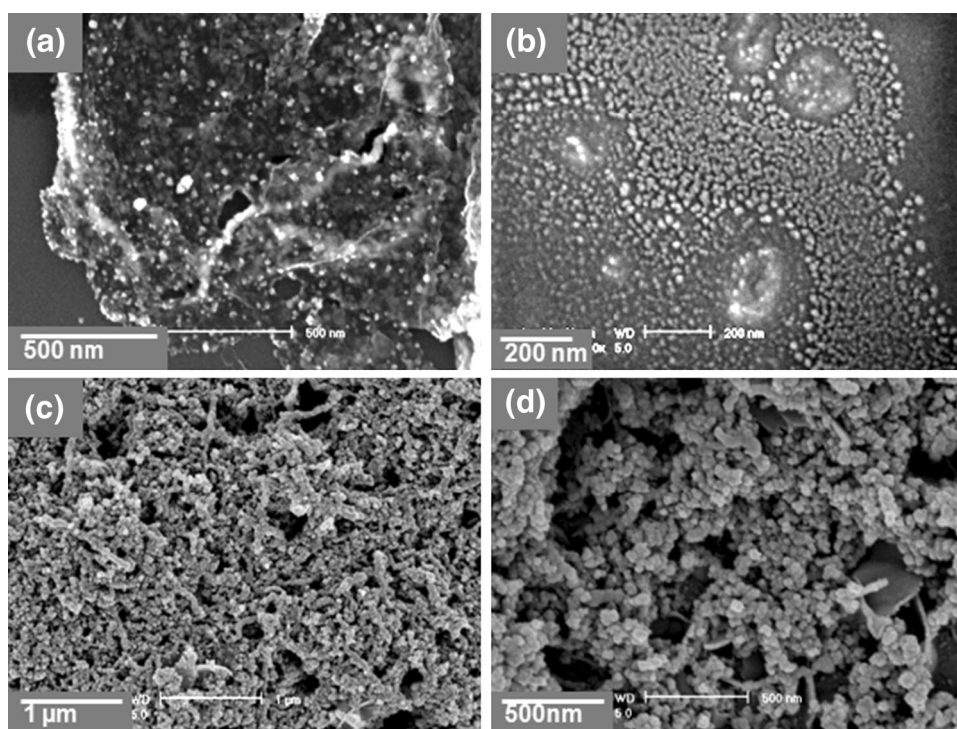
**Fig. 6** SEM images of (a–b) Fe nanoparticles decorated RGO and (c–d) bare Fe naoparticles "Reprinted from Nanoscale, 3, 2011, 3583–3585, Enhanced Cr(VI) removal using iron nanoparticle decorated graphene, Jabeen, H., Chandra, V., Jung, S., Lee, J.W., Kim, K.S., Kim. S.B., Copyright (2011), with permission from Royal Society of Chemistry"



and thus have been used as effective adsorbent for Cr(VI), which facilitates magnetic removal of Cr(VI) (Li et al. 2008). However, bare Fe nanoparticles tend to rapidly agglomerate to form larger aggregates and oxide/dissolve especially in acidic solutions. So decorating Fe nanoparticles on graphene is a powerful method to solve these problems. Jabeen et al. (2011) decorated Fe nanoparticles on RGO to remove Cr(VI) from aqueous solutions. The SEM images of Fe/RGO can be seen in Fig. 6. The maximum adsorption capacities for Fe and Fe/RGO were 148 and 162 mg $g^{-1}$. The Fe decorated on RGO had small size and high surface area (170 $m^2$ $g^{-1}$) than bare Fe nanoparticles (56 $m^2$ $g^{-1}$). The decreased size and increased surface area of Fe nanoparticles in RGO sheets enhanced the catalytic and adsorption sites for chromium, hence the adsorption capacity. Zhu et al. (2012) decorated core@double-shell structure, with Fe as the core, $Fe_2O_3$ as the inner shell and amorphous Si–S–O compound as the outer shell, on RGO for Cr(VI) removal. This composite demonstrated an extremely fast Cr(VI) removal from the wastewater with high removal efficiency and an almost complete removal of Cr(VI) within 5 min. The adsorption mechanism of Cr(VI) on pure graphene was a single-layer adsorption just like AC, while on the composite it was a combined process of surface complexation between sulfur on the outer shell and Cr(VI) together with the single layer adsorption on the bare area of graphene. Besides the difference in adsorption mechanism, the large difference between pure graphene and the composite also came from the greater surface area (pure graphene 36.4 $m^2$ $g^{-1}$;

composite 42.1 $m^2$ $g^{-1}$), which contributed to the extension of the active surface for adsorption. Subsequently, more efficient utilization of the respective adsorption sites could be achieved by this new adsorbent. The Cr(VI) adsorption mechanisms on graphene and the composite are illustrated in Fig. 2. As introducing the magnetic Fe, the formed composite could be separated by an external magnetic field.

Recently, other graphene-based nanocomposites were also developed to remove Cr(VI). Ma et al. (2012) prepared ethylenediamine (ED)/RGO by simple refluxing of GO with ED. It was speculated that the mechanism of Cr(VI) removal by ED/RGO involving three steps (Fig. 7): (1) Cr(VI) bound to ED/RGO by electrostatic interaction between the negatively charged Cr(VI) species and the protonated amine groups; (2) Cr(VI) was reduced to Cr(III) with the assistance of π electrons on the carbocyclic six-membered ring of ED/RGO; (3) the release of Cr(III) into solution by electrostatic repulsion between the protonated amine groups and Cr(III), or the binding of Cr(III) on ED/RGO by the electrostatic attraction between Cr(III) and negatively charged groups (–$COO^-$) of ED/RGO. Based on these, an improved ED/dimethyl formamide (DMF)/RGO was prepared by refluxing of GO with ED using DMF as solvent (Zhang et al. 2013b). The ED/DMF/RGO could remove 75.6 % of Cr(VI) after being mixed with Cr(VI) solution for 15 min, which was much higher than that of ED/RGO (59.4 %). The improvement in the Cr(VI) removal efficiency was attributed to the higher content of amine groups. The Cr(VI) removal capacity of ED/DMF/
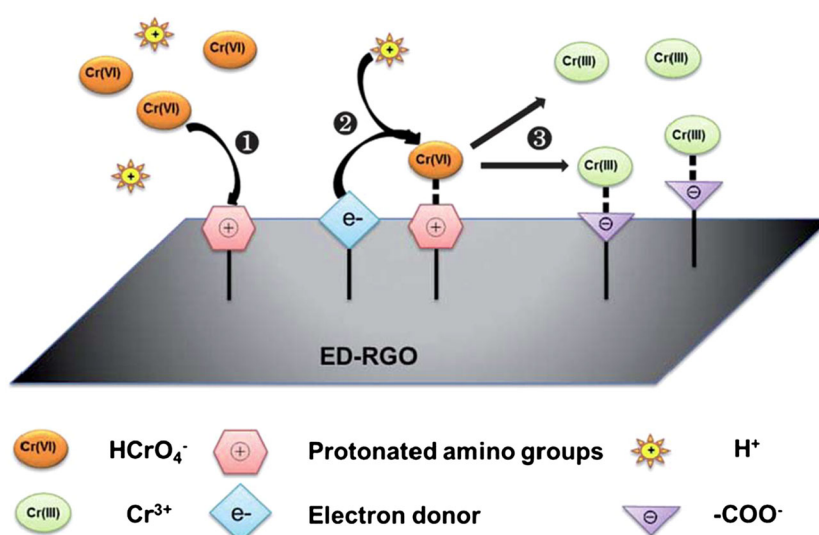
RGO was 92.15 mg g$^{-1}$, which was about 27 times higher than that of AC (3.46 mg g$^{-1}$), even nearly 4–8 times higher than that of various modified AC. The removal mechanism was the same as ED/RGO composite. In addition, cetyltrimethylammonium bromide (CTAB) was chosen to modify graphene to form composite for the removal of Cr(VI) in aqueous solutions (Wu et al. 2013b). CTAB groups together with –OH and –COOH groups on the RGO surface could make CTAB/RGO an excellent adsorbent. The adsorption process was rapid within the first 5 min and reached equilibrium in about 40 min.

### 3.2 Adsorption of cationic pollutants

Pb(II), Hg(II), Cd(II), Cu(II), Ni(II), Co(II) and Zn(II) are common cationic pollutants in wastewater. Generally speaking, the adsorption of metal ions is based on the three adsorption mechanisms: electrostatic interaction, ion exchange and complex formation (Moreno-Castilla et al. 2010). The abundant oxygen groups protruded from GO sheets can be used as anchoring sites to bind ions by electrostatic, ion exchange, and coordinate approaches. For those cationic contaminants, a high pH value is facilitated for adsorption. This is because there are some competitions on –COO$^-$ and –O$^-$ sites between proton and metal ions in a low pH condition, which will result in a lower adsorption capacity. The increase in the pH values of the solutions will convert more of above groups to –COO$^-$ and –O$^-$ (i.e., Surface-OH → Surface-O$^-$ + H$^+$), and provide electrostatic interaction that are favorable to adsorb cationic species.

#### 3.2.1 Adsorption of Pb(II)

RGO (Huang et al. 2011), GO (Zhao et al. 2011c), and their based composites (Hao et al. 2012; Yang et al. 2012; Fan et al.
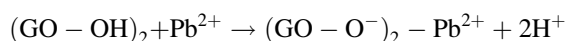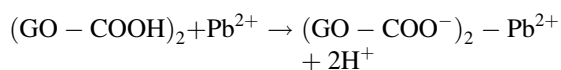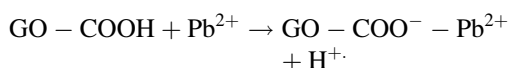
2013; Lee and Yang 2012; Madadrang et al. 2012) have been investigated to remove Pb(II) from aqueous solutions. RGO obtained by vacuum-promoted low-temperature exfoliation was used to adsorb lead ions (Huang et al. 2011). It was interestingly found that the adsorption for Pb(II) was enhanced by heat treatment although the oxygen groups of RGO showed a significant decrease. This was because the adsorption mechanism was mainly attributed to form complex between graphene and the heavy metal ions could occur through Lewis acid–base interaction. The heat treatment at high temperature in a vacuum could eliminate the oxygen-containing groups, leading to increasing in both Lewis basicity and electrostatic attraction. Thus, heat treatment for graphene favored adsorption toward Pb(II). Few-layered GO had the maximum adsorption capacities of Pb(II) calculated from the Langmuir model were about 842, 1,150 and 1,850 mg g$^{-1}$ at 293, 313 and 333 K, respectively, higher than any currently reported (Zhao et al. 2011c). The adsorption mechanism was also mainly attributed to form complex between graphene and metal ions.

Hao et al. (2012) used SiO$_2$/RGO composite to highly selective adsorption of Pb(II). The maximum adsorption capacity of the composite for Pb(II) was 113.6 mg g$^{-1}$, which was much higher than that of bare SiO$_2$ nanoparticles. Electrostatic interaction between Pb(II) and negative surface charge and/or C π electrons of the composite was regarded as the main interactions. Chitosan (CS) is one of the most promising adsorbents for removing heavy metals from wastewater (Babel and Kurniawan 2003). However, its mechanical strength and physical instability are unfavorable (Ngah et al. 2005). Porous CS/GO composite was prepared by a unidirectional freeze-drying method and applied to remove Pb(II) and Cu(II) (He et al. 2011). There was a stronger attraction between Pb(II) and the carboxyl groups on the GO nanosheets than that of Cu(II). This was because Pb(II) has a higher electro negativity and
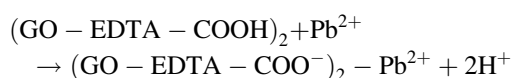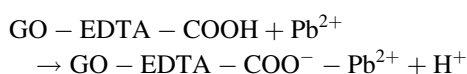
larger ionic radius. In order to separate adsorbents easily, magnetic iron oxide/GO and iron oxide/RGO were used to remove Pb(II) (Yang et al. 2012). The maximum adsorption capacities of Pb(II) adsorption on iron oxide/GO and iron oxide/RGO were 588.24 and 454.55 mg g$^{-1}$. As plenty of oxygen-containing groups on the surface, iron oxide/GO could adsorb Pb(II) efficiency through electrostatic attraction and surface complexation. Fan et al. (2013) used iron oxide/CS/GO to highly selective adsorption of Pb(II) from large volumes of aqueous solutions. The results indicated that Pb(II) adsorption on the composite was strongly dependent on pH. At a lower pH, the amine groups on surface of the composites could be easily protonated, inducing an electrostatic repulsion against Pb(II). Moreover, the protonation of the lone pair electrons of nitrogen hindered the complex formation between the composite surface and Pb(II).

Lee et al. (Lee and Yang 2012) decorated flower-like TiO$_2$ on GO to form composite for the heavy metal ions removal. The capacities of GO and neat TiO$_2$ nanoparticles to remove Zn(II), Cd(II) and Pb(II) were $30.1 \pm 2.5$, $14.9 \pm 1.5$, $35.6 \pm 1.3$ mg g$^{-1}$ and $44.1 \pm 3.2$, $53.2 \pm 1.5$, $53.3 \pm 2.6$ mg g$^{-1}$, respectively. The corresponding capacities of TiO$_2$/GO were $88.9 \pm 3.3$, $72.8 \pm 1.6$ and $65.6 \pm 2.7$ mg g$^{-1}$ for Zn(II), Cd(II) and Pb(II). The results showed that TiO$_2$/GO was a promising candidate adsorbent material for removing heavy metal ions from aqueous solutions beyond the ordinary use of photocatalysts. Since GO-based composites removed Pb(II) through surface complexation, Madadrang et al. (2012) prepared EDTA/GO for Pb(II) removal. Two adsorption processes were suggested: ion exchange and surface complexation. The first adsorption mechanism was an ion exchange reaction between Pb(II) and –COOH or –OH groups:

(1) Pb(II) reacted with –COOH and –OH groups on GO surface to form a complex.

$$GO - COOH + Pb^{2+} \rightarrow GO - COO^- - Pb^{2+} + H^{+\cdot}$$

$$(GO - COOH)_2 + Pb^{2+} \rightarrow (GO - COO^-)_2 - Pb^{2+} + 2H^+$$

$$GO - OH + Pb^{2+} \rightarrow GO - O^- - Pb^{2+} + H^+$$

$$(GO - OH)_2 + Pb^{2+} \rightarrow (GO - O^-)_2 - Pb^{2+} + 2H^+$$

(2) Pb(II) might also react with –COOH groups of EDTA to form a complex with EDTA groups.

$$GO - EDTA - COOH + Pb^{2+} \rightarrow GO - EDTA - COO^- - Pb^{2+} + H^+$$

$$(GO - EDTA - COOH)_2 + Pb^{2+} \rightarrow (GO - EDTA - COO^-)_2 - Pb^{2+} + 2H^+$$

### 3.2.2 Adsorption of Hg(II)

Materials functionalized with sulfur, nitrogen, and oxygen have been shown high binding affinity to mercury (Cai and Jia 2010; Zhu et al. 2009b). Conducting polymers incorporating these functional groups had been used for water treatment but their surface area was not large (Wang et al. 2009). In view of this, a novel polypyrrole/RGO composite was prepared to selective highly adsorption of Hg(II) (Chandra and Kim 2011). The maximum adsorption capacities were about 400 and 980 mg g$^{-1}$ for polypyrrole and the polypyrrole/RGO composite. The enhanced adsorption capacity of the composite originated from the increasing adsorption sites for Hg(II) in the presence of graphene sheets. The highly selective adsorption resulted from nitrogen provided by polypyrrole with the lone pair of electrons which coordinated with Hg(II) and formed a stable complex. The adsorption rate of Hg(II) on the polypyrrole/RGO composite was very fast and completed within 20 min, while in the case of polypyrrole it was not completed even after 3 h.

In order to separate adsorbents easily, many investigations focused on decorating the magnetic nanoparticles on graphene and utilizing magnetic separation approach. Sreeprasad et al. (2011) developed a new methodology which immobilized RGO-based composites on river sand using CS as the binder. The obtained materials were found to be efficient adsorbent candidates for removal Hg(II) for field application. The RGO-based composites, such as MnO$_2$/RGO and Ag/RGO, could be formed through a redox-like reaction between RGO and the metal precursors KMnO$_4$ and AgNO$_3$. Fig. 8 shows the TEM micrographs of the Ag/RGO composite.

### 3.2.3 Adsorption of Cu(II)

GO is often used to remove copper from aqueous solutions. For example, Yang et al. (2010) found that the GO nanosheets could be aggregated by Cu(II) in aqueous solution with a huge Cu(II) absorption capacity. The absorption capacity was much higher than that of CNTs and around 10-fold of that of AC (measured under the same conditions), ranking it among the most effective absorbents for the Cu(II) removal. Cu(II) could induce the folding and aggregation of GO, in which coordination between Cu(II) and oxygen atoms on GO was regarded as the primary driving force. After adsorption process finished, the adsorbents could be easy separated due to the aggregation of GO sheets to form the precipitates. (Mi et al. 2012); (Wu et al. 2013a) also applied GO for the removal Cu(II) from aqueous solutions. However, they thought that the adsorption mechanism mainly attributed to ion-exchange

**Fig. 8** TEM images of Ag/
RGO showing well dispersed
Ag nanoparticles over a RGO
sheet "Reprinted from Journal
of Hazardous Materials, 186,
2011, 921-923, Reduced
graphene oxide-metal/metal
oxide composites: Facile
synthesis and application in
water purification, Sreeprasad,
T.S., Maliyekkal, S.M., Lisha,
K.P., Pradeep, T.J., Copyright
(2011), with permission from
Elsevier"
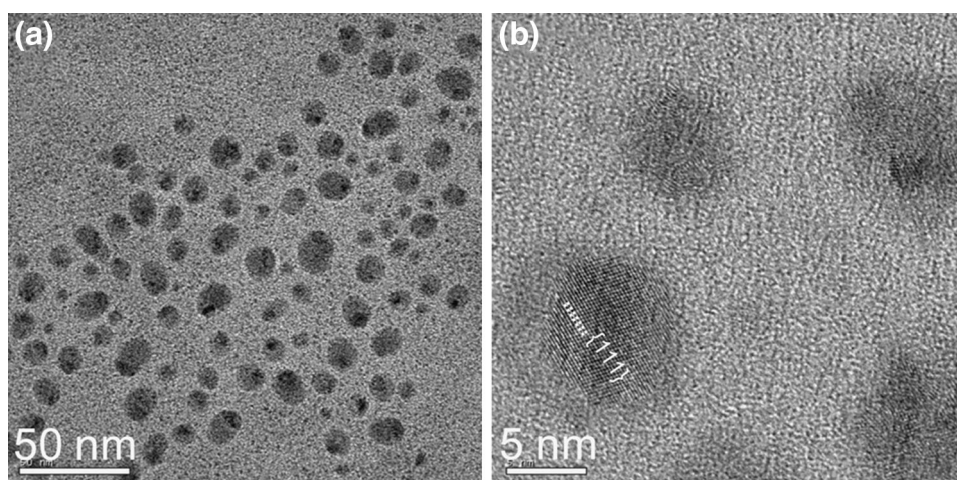


rather than surface complexation, which could be identified
from the decrease of pH value after adsorption.

### 3.2.4 Adsorption of Ni(II) and Co(II)

$MnO_2$ with different polymorphic phases (α, β, γ, λ, and δ-
type) has attracted much attention because of its particular
physical and chemical properties (Khan et al. 2005).
However, it is difficult to be applied independently due to
its easy conglomeration and poor dispersion. Ren et al.
(2011b) prepared δ-$MnO_2$/RGO composite as adsorbent for
the removal of Ni(II) from wastewater. The adsorption
capacity of Ni(II) for the composite was 1.5 and 15 times
higher than that for δ-$MnO_2$ and RGO, which mainly came
from the $MnO_2$ nanoparticles grown on the surface of RGO
generating more effective adsorption sites. Liu et al.
(2011a) synthesized magnetic $Fe_3O_4$/GO composite for the
removal of Co(II) from aqueous solutions. They also
observe that the adsorption capacity of Co(II) for the
composite was higher than that of Co(II) on $Fe_3O_4$, which
was attributed to the high adsorption ability of Co(II) on
GO. The adsorption mechanism of Co(II) was inner-sphere
surface complexation at low pH values, whereas the
removal of Co(II) was accomplished by simultaneous
precipitation and inner-sphere surface complexation at high
pH values. The adsorbent could be separated and recovered
by magnetic separation.

Excepting for the adsorption for the removal of heavy
metal ions mentioned above, graphene and its composites
are also applied for the recovery of noble metals from
aqueous solutions. For example, GO (Liu et al. 2013) and
CS/GO (Liu et al. 2012a) have been reported to adsorb
Au(III), Pd(II) and Pt(IV) from aqueous solutions. Both
GO and its composite demonstrated an excellent adsorption
capacity for noble metals.

### 3.3 Adsorption isotherms, kinetics and thermodynamics

The Langmuir, Freundlich and Temkin isotherm equations
are used to interpret the adsorption experimental data.
Among them, the Langmuir model supposes that uptake of
ions occurs on a homogenous surface by monolayer
adsorption with homogeneous binding sites, equivalent
adsorption energies, and no interaction between adsorbed
species. The Freundlich isotherm assumes heterogeneous
adsorption due to the diversity of the adsorption sites or the
diverse nature of the ions adsorbed. The Temkin isotherm
considers the effects of the heat of adsorption that
decreases linearly with coverage of the adsorbate and
adsorbent interactions. From the reported experimental
data (Mi et al. 2012; Huang et al. 2011; Zhao et al. 2011c;
Hao et al. 2012; Deng et al. 2010; Wu et al. 2011c; Fan
et al. 2013; Liu et al. 2011a; Wu et al. 2013b; Madadrang
et al. 2012), almost all the adsorption isotherms for
graphene and its based composites could be used the
Langmuir model to descript. This implied that a monolayer
adsorption and a homogenous distribution of adsorption
sites.

The adsorption kinetics describes the solute uptake rate
governing the contact time of the adsorption reaction is one
of the important characteristics that define the efficiency of
adsorption. The adsorption kinetic data are usually ana-
lyzed in terms of pseudo-first-order, pseudo-second-order
and intraparticle diffusion kinetic equations. Almost all the
adsorption kinetics for graphene and its based composites
followed the pseudo-second-order kinetics (Mi et al. 2012;
Hao et al. 2012; Zhu et al. 2012; Chandra et al. 2010; Deng
et al. 2010; Debabrata and Kaushik 2012; Sheng et al.
2012; Fan et al. 2013; Wu et al. 2013b), which based on the
assumption that the rate-limiting step might be chemical
adsorption and the adsorption behavior might involve

valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Chen et al. 2008).

The thermodynamics studies showed that the adsorption process for graphene and its based composites was spontaneous, endothermic and feasible (Ren et al. 2011b; Liu et al. 2013, 2012a; Zhao et al. 2011c; Sheng et al. 2012; Fan et al. 2013; Liu et al. 2011a). The parameters such as Gibbs energy ($\Delta G$) value was negative, both enthalpy ($\Delta H$) and entropy ($\Delta S$) were positive. The negative value of $\Delta G$ indicated the spontaneous nature of the adsorption process. The positive value of $\Delta H$ demonstrated the adsorption was endothermic, which had been identified by the fact that the adsorption capacity increased with the temperature increasing. One interpretation for the positive $\Delta H$ might be that metal ion was dissolved well in water and the hydration sheath of metal ion had to be destroyed before its adsorption on the adsorbent. This dehydration process needed energy, and high temperature is beneficial for adsorption. The positive value of $\Delta S$ meant an irregular increase of the randomness at the adsorbent/solution interface during the adsorption process.

### 3.4 Regeneration of adsorbents

Repeated availability is an important factor for an advanced adsorbent. Such adsorbents not only possess higher adsorption capability, but also show better desorption property, which will reduce overall cost for adsorbents (Rodrigues et al. 2010). From this point, the graphene-based adsorbent can be called as an advanced adsorbent. The desorption agents used to regenerate include HCl (Ren et al. 2011b; Madadrang et al. 2012; Wu et al. 2013a), EDTA (Deng et al. 2010) and thiourea-HCl solution (Liu et al. 2012a, 2013). When HCl was used as a desorption agent, the adsorbent surface was completely covered with $H^+$ ions while the coordination spheres of chelated metal ions was disrupted. Thereafter, metal ions could not compete with $H^+$ for ion-exchange sites. As a result, metal ions broke away from the solid surface into the solution. In a typical desorption process, almost all the Pb (92 %) adsorbed on EDTA/GO surface could be removed by HCl within 1 h (Madadrang et al. 2012). As for the efficiency of the graphene-based adsorbent, it is a little decrease with the increasing number of cycle. For example, the adsorption capacity for GO to adsorb Cu(II) could maintain above 95 % of its initial capability after five cycles and above 90 % after ten cycles (Wu et al. 2013a).

## 4 Conclusions and future work

This review presents the adsorption applications of graphene-based nanomaterials in the removal of inorganic pollutants from aqueous solutions. Due to its especial structure, a large amount of adsorption sites such as the oxygen functional groups, C π electrons and the outer surface of the decorated nanoparticles are provided to adsorb pollutants. For the sake of electrostatic interaction, a low pH value is favor to adsorb anionic pollutants, while a high pH value is favor to adsorb cationic pollutants. Anions have been proposed to be adsorbed on adsorbents through specific and/or nonspecific adsorption. However, the adsorption of cations is based on the three adsorption mechanisms such as electrostatic interaction, ion exchange and complex formation. The adsorption isotherms and kinetics can be described by Langmuir and pseudo-second-order model. The adsorption process for graphene-based nanomaterials is spontaneous, endothermic and feasible. The regeneration of adsorbents can be realized with desorption agents such as HCl solution. The adsorption efficiency is a little decrease with the increasing number of cycle.

Much progress has been made over the last few years in adsorption applications of graphene. Though the raw materials used to produce graphene are abundant in nature and they are biodegradable and biocompatible, there are still a lot of challenges to do to enhance graphene adsorption properties in future. The aggregation of graphene nanosheets limits the available adsorption sites for binding with pollutants. To avoid the aggregation, introducing oxygen groups or nanoparticles is a powerful approach. Moreover, those oxygen groups enhancing the dispersion properties of graphene in solutions can greatly increase the interactions between graphene with pollutants, and thereby increase the removal ability of graphene. The introduced nanoparticles uniformly dispersed on graphene has their own adsorption ability and/or catalytic/oxidation (or reduction) effect. After being introduced on graphene, the adsorption capacity or catalytic effect is greatly enhanced. The small size (nanoscale) of graphene makes them to be difficult to separate from aqueous solutions. Ultra centrifugation separation method is efficient to separate graphene. However, high energy consumption is necessary. Membrane filtration method is another efficient technique to separate graphene from aqueous solutions. However, the membrane is easily to be blocked. Compared with centrifugation and filtration methods, the magnetic separation method is considered as a rapid and effective technique for separating nanoparticles from aqueous solutions. The magnetic graphene-based composites are promising materials in environmental pollution management in large scale in real work. More efforts aimed at the development of practical applications of these fascinating materials are required in future.

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