Improving the selectivity of magnetic graphene oxide through amino modification

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ABSTRACT

Fabricating efficient materials for environmental purposes is a priority and the subject of much attention nowadays. The objectives of this study are to adopt an amino modification approach to improve the selective removal capacity of magnetic graphene oxide (MGO) for Cu(II) ions, and explore how it performs in single and binary systems by taking Cd(II) as a comparison. After grafting the amino groups, the final material exhibited promoted capacities for Cu(II) and Cd(II), and a more apparent selective adsorption process can be observed. The maximum equilibrium adsorbances of amino modified MGO were 578.1 mg g\(^{-1}\) for Cu(II) and 184.7 mg g\(^{-1}\) for Cd(II) under our experimental conditions, compared with 319.1 mg g\(^{-1}\) and 161.2 mg g\(^{-1}\) of MGO for Cu(II) and Cd(II), respectively. Characterization results and experiment data confirmed that the introduction of N species contributed to the enhancement. This may pave the way for better understanding of the underlying mechanism, and provide inspiration for syntheszing new adsorbents.

Key words | Cd(II), covalent bonding method, Cu(II), magnetic graphene oxide, selective ion adsorption, solvothermal method

INTRODUCTION

Industrial, domestic and agricultural activities heavily affect water, which all life depends on, through generating massive waste. Among the various contaminants, heavy metals warrant special attention because of their toxic effect on humans and the environment, even at very dilute concentrations (Muhammad Ekramul Mahmud et al. 2016; Muya et al. 2016). So far membrane filtration (Kanagaraj et al. 2015), chemical precipitation (Cheng 2006), adsorption (Chao & Chang 2012; Liu et al. 2014), ion exchange (Zewail & Yousef 2015), electrochemical methods (Gonzalez et al. 2016), as well as biological treatment technology (Perez et al. 2010) are widely applied to remove such contaminants from water. Although all these methods achieve moderate to efficient removal of heavy metal ions, sorption technology is one of the most effective choices due to the simplicity of design, convenience, low cost, high sorption efficiency, and wide adaptability.

To achieve high sorption capacity, materials of high specific surface area are more favored such as graphene. Since monocrystalline graphitic films a few atoms thick were first obtained in 2004 (Novoselov et al. 2004), graphene has evoked tremendous research interests in numerous fields owing to its remarkable physicochemical properties, and also in environmental remediation (Sun et al. 2011; Zhao et al. 2011; Geng et al. 2012; Li et al. 2012; Lin et al. 2015). The hydrophobicity of pure graphene results in graphene oxide (GO), which has a wide range of functional groups (epoxy, hydroxyl, and carboxyl) and can be easily exfoliated and functionalized, being used more commonly in water purification (He & Gao 2010).

Surface modification is an essential step in engineering materials to adjust their properties, extend their applications and improve their performances (Shen et al. 2016). Great effort has been devoted to the surface modification of GO-based materials to increase their purifying qualities. Nevertheless, the question of how to improve the selectivity and specificity of these adsorbents still necessitates further investigation.

In this study, two kinds of magnetic graphene oxide (MGO) were synthesized through different principles, the one-pot solvothermal method and the covalent bonding method, so that MGOs with and without amino functionalization were
obtained. Cu(II) and Cd(II) ions were taken as model ions to explore the selective adsorption behavior of the above-mentioned two materials after optimizing adsorption conditions. The results described here may provide some enlightenment for fabricating efficient adsorbents for a particular contaminant.

**EXPERIMENTAL SECTION**

**Materials and methods**

Graphite of 325 meshes was purchased from Qingdao Meilikun graphite products factory. Sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), potassium permanganate (KMnO₄), iron(III) chloride hexahydrate (FeCl₃·6H₂O), sodium acetate anhydrous (NaAc), hydrogen peroxide (H₂O₂), tetraethyl orthosilicate (TEOS), N-hydroxysuccinimide (NHS), 1-ethyl-3-(3-dimethyaminopropyl) carbodiimide (EDC), (3-aminopropyl) triethoxysilane (APTES), and other chemical reagents were purchased from Aladdin Chemical Reagent Corporation without any further treatment. Deionized water (DW) was produced by the Milli-Q system.

**Preparation of graphite oxide**

Graphite oxide with abundant oxygen-containing groups was prepared using the improved method through oxidation of graphite flake (Marcano et al. 2010). In a 9:1 mixture of H₂SO₄ and H₃PO₄, with the presence of KMnO₄, graphite was oxidized to graphite oxide. After washing in succession with 1 mol L⁻¹ HCl, water, ethanol, and centrifuging, the dark brown product was dried for further use.

**Synthesis of MGO**

MGO without amino functionalization (termed MGO) was synthesized according to a previously described one-pot solvothermal method (Zhou et al. 2010). Simultaneously, amino functionalized MGO (amino-MGO) was fabricated following He’s method (He et al. 2010). Fe₃O₄ particles were coated with silica and functionalized by APTES in sequence, and finally attached onto the GO sheets. All intermediates and final materials were washed with DW and ethanol and dried overnight.

**Adsorption experiments**

Both MGO and amino-MGO were evaluated for their capacity in Cu(II) and Cd(II) removal from water. Batch adsorption experiments were carried out in 50 mL glass bottles and the working volume was maintained as 20 mL. The target pollutant was spiked into this solution to get the required concentration within the range of 1–150 μg mL⁻¹. Then 2 mg of adsorbent was weighed and added to 20 mL of solution to obtain a homogenous adsorbent dispersion. In all the experiments, solutions were shaken at 150 rpm at room temperature. The samples were collected at predetermined time intervals and analyzed for residual ions. Solid-liquid separation was achieved using a magnet because of the introduction of Fe₃O₄. Ion concentrations present in solution were determined using a flame atomic absorption spectrometer (FAAS, ContrAA®700). The equilibrium uptake (Qₑ) was obtained according to the following equation:

\[ Qₑ = \frac{(C₀ - Cₑ)V}{M} \]

where \( Qₑ \) (mg g⁻¹) represents the adsorption capacity, \( C₀ \) (mg L⁻¹) and \( Cₑ \) (mg L⁻¹) are the initial and residual concentrations of ions, \( V \) (L) is the volume of the metal ion solution, and \( M \) (g) is the mass of adsorbent.

**RESULTS AND DISCUSSION**

**Characterization**

Figure 1 shows the transmission electron microscopy (TEM) images of MGO (Figure 1(a)) and amino-MGO (Figure 1(b)) in the same magnification, depicting that the magnetic nanoparticles have grown on the GO sheet, with the particle size of Fe₃O₄ being about 200 nm. Few-layered GOs are formed, although the TEM image does not estimate the layer numbers of the GO nanosheets exactly. GO in the bottom is translucent, with several wrinkles. Magnetic nanoparticles are attached onto the GO sheets, especially where the characteristic wrinkles are present. Because where the wrinkles lie, there are abundant oxygen-containing groups that have reactivity (Huang et al. 2017). The differences are clear between the Fe₃O₄ particles of those two materials. It is obvious that Fe₃O₄ particles on the amino-MGO are wrapped with a layer of material. This should be attributed to the surface coating process by silica.

In Fourier transform infrared spectrometer (FT-IR spectra, Figure 2), the peak at 570 cm⁻¹ is the vibration of Fe-O, which is in agreement with the characteristic peak for Fe₃O₄ (Bruce & Sen 2005; Zhang et al. 2007). And the peak at 1,211 cm⁻¹ is the symmetric stretching of the epoxy groups (Zhang et al. 2007).
Carboxyl groups arise at 1,665 cm$^{-1}$, and C-OH vibrates at 3,420 cm$^{-1}$ and 1,080 cm$^{-1}$. The covalent reaction consumed the -COOH groups, so a strong peak at 1,625 cm$^{-1}$ of C=O can be seen in amino-MGO (Acik et al. 2015). The silica shell is identified by the appearance of the Si-O-Si asymmetric stretching mode observed at 1,100 cm$^{-1}$ as usual (Guo et al. 2015). Two new characteristic peaks at 1,398 cm$^{-1}$ and 1,290 cm$^{-1}$ correspond with C-N stretching and C-N bending, and -CH$_2$- at 2,930 cm$^{-1}$ also appears after the amidation reaction (Ma et al. 2009) (see Figure S1 in the Supplementary Information, available with the online version of this paper).

The magnetic properties of MGO and amino-MGO (Figure 3(a)) are characterized using a vibrating sample magnetometer (VSM) at room temperature. S-like magnetization hysteresis loops indicate that the saturation magnetization value is 59.99 emu g$^{-1}$ for MGO and 38.18 emu g$^{-1}$ for amino-MGO. Surface modification of Fe$_3$O$_4$ with silica and APTES decreases the dosage of magnetic particles in amino-MGO, leading to a lower saturation magnetization value than for MGO. But both of them could be efficiently separated from aqueous solution with a magnet (see insert in Figure 3(a)).

Temperature-mass curves convey the content of the organic functional groups of the sample. The TGA curves (Figure 3(b)) shows light weight loss before 120 °C, which is the evaporation of water because of residual solvent or moisture absorption during storage. Then MGO exhibits two steps of mass loss. Removing labile oxygen-containing groups on the surface of the composite as CO, CO$_2$, and H$_2$O vapors causes 6.76% loss from 120 to 350 °C (Yao et al. 2015a). Another 19.83% loss from 350 to 625 °C should be assigned to carbon oxidation of aromatic rings (Yao et al. 2015b). Although amino-MGO has the same tendency, it is divided into three stages. Except for 6.72% weight degradation of oxygenated functional groups from 120 to 250 °C and 10.13% loss of carbon skeleton from 410 to 655 °C, thermal decomposition of aminopropyl groups grafted to the silica surface generates a mass loss of 2.40% between 250 °C and 410 °C is also observed (Wang et al. 2010). The remaining components exhibit good thermal stability, and weights remain at 73.34% for MGO and 78.58% for amino-MGO. The residues consist of Fe$_3$O$_4$ particles and a SiO$_2$ layer coated on them for amino-MGO, while there are only Fe$_3$O$_4$ particles left for MGO.

Surface charge properties under different pH conditions measured by Malvern Zetasizer Nano ZS are shown in Figure 4. The solution pH affects the degree of deprotonation and the speciation of the surface functional groups. In
the range of pH 2.0–7.0, MGO is always negative and becomes more negative when the pH turns neutral. The increase in pH results in more -COOH and –OH deprotonating and changing into -COO⁻ and -O⁻. As for amino-MGO, the low pH value protonates –NH₂ to –NH₃⁺ and oxygen-containing groups exist as -COOH and -OH, so leading to a positive surface potential. But it also turns to a negative charged surface as the pH rises. The absence of amino groups causes a more negative surface potential for MGO than amino-MGO under all pH conditions.

Effect of pH

One of the most important parameters for the adsorption of metal ions is the pH of the solution (Anandkumar & Mandal 2011). Considering the hydrolysis of heavy metals, Cd(II) solutions of pH 2.0 to 7.0 and Cu(II) solutions of pH 2.0 to 5.5, adjusted with chlorhydric acid and sodium hydroxide, were prepared. Ion concentrations were kept at 50 μg mL⁻¹. After shaking for 6 h, the remaining ions were accurately detected. With the increase in pH, the equilibrium capacity always kept increasing (Figure 5). Agreeing with the zeta potential results, the surface charge is more negative at high pH and the electrostatic interactions between the metal ions and GO nanosheets become stronger, and thereby result in an increase in metal ion sorption (Zhao et al. 2011). Moreover, amino-MGO exhibited a larger capacity than MGO in all pH conditions for both ions. Considering the difference in surface groups on GO and amino-MGO, this should be attributed to the amino groups modified on the surface. Previous studies also confirmed that N species can lead to an increase in adsorption capacity (Yuan et al. 2013; Liu et al. 2014; Wang et al. 2014). Moreover, the deprotonation of –NH₃⁺ enhanced the chelation between –NH₂ and metal ions, which was more observable for Cu(II) (Figure 5(b)).

Static adsorption and dynamic adsorption data

Static adsorption tests of MGO and amino-MGO were carried out by increasing the initial concentration of each ion from 1 to 150 μg mL⁻¹ (Figure 6). The pHs of the solutions were 7.0 for Cd(II) and 5.5 for Cu(II). And 6 h was selected as the shaking time to ensure full equilibrium. To gain a better understanding of sorption mechanisms and to quantify the sorption data, the Langmuir and Freundlich models were used to simulate the experimental data.

Figure 3 | (a) Magnetization curves, a and b correspond to MGO and amino-MGO; (b) TGA curves.

Figure 4 | Zeta potential of MGO and amino-MGO.
The linear form of the Langmuir isotherm model is represented as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L},$$

and the linear form of the Freundlich isotherm model can be expressed as:

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$$

where $C_e$ (mg L$^{-1}$) is the equilibrium concentration of metal, $Q_e$ (mg g$^{-1}$) is the amount of metal adsorbed per weight unit of adsorbent at equilibrium, $Q_m$ (mg g$^{-1}$) is the maximum achievable uptake at complete monolayer coverage, $K_L$ (L mg$^{-1}$) is the Langmuir adsorption equilibrium constant that relates to the heat of sorption, $K_F$ (mg g$^{-1}$) is the Freundlich constant representing the adsorption capacity, $n$ (dimensionless) is the adsorption intensity.

The fitted results of the two isotherm models are presented in Table 1. It can be seen that the Langmuir model shows good agreement with the experimental data for all correlation coefficients ($R^2$) greater than 0.97. The fact that the sorption data of MGO and amino-MGO is in accordance with the Langmuir model suggests that monolayer coverage of Cu(II) and Cd(II) on the surfaces is the main sorption mechanism (Li et al. 2012). High surface area and abundant functional groups all contribute to the excellent adsorption properties.

Cd(II) or Cu(II) solution of 150 μg mL$^{-1}$ were used for dynamic adsorption, results are shown in Figure 7. The
equilibrium uptakes of two materials for Cd(II) at pH 7.0 and Cu(II) at pH 5.5 increased with the extension of time from 1 to 120 min. The adsorption processes finished and equilibrium was reached at 40 min. Adsorption kinetics are defined using pseudo-first-order (Equation (4)) and pseudo-second-order (Equation (5)) models, respectively.

\[
\ln\left(\frac{Q_t}{Q_e} - 1\right) = \ln Q_e - k_1 t \\
\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2}
\]

where \(Q_t\) and \(Q_e\) represent the amount of heavy metal ions adsorbed (mg g\(^{-1}\)) at time \(t\) (min) and the equilibrium time (min), \(k_1\) (min\(^{-1}\)) and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) are the equilibrium rate constant for the pseudo-first-order and pseudo-second-order.

The sorption kinetics fitted very well to the pseudo-second-order model, and the obtained kinetic parameters are listed in Table 2. Correlation coefficients (\(R^2\)) are relatively high (>0.994), and the calculated \(Q_e\) values from the model are very close to the experimental ones. These results imply that the overall rate of the adsorption process is controlled by chemisorption rather than mass transfer (Sítko et al. 2013).

To sum all these parameters up, both MGO and amino-MGO exhibited better properties in adsorbing Cu(II) than Cd(II) ions. By comparing the Cd(II) and Cu(II) adsorption behavior of different adsorbents (Table S1, Supplementary Information, available with the online version of this paper), it can be found that our materials were cost-effective and showed practical application potential for water treatment. The amino modification also endows amino-MGO with larger \(Q_m\) and \(Q_e\) values, especially the ones of Cu(II), when compared with MGO. So we speculated that amino-MGO and MGO tend to adsorb Cu(II) rather than Cd(II), even if two kinds of heavy metal ions co-exist.

### Binary adsorption

As contaminated samples rarely contain just one heavy metal, and metals co-exist and compete for binding to different ligands, the above prediction was investigated by batch
experiments. A series of mixed solutions of Cd(II) and Cu(II) of the same concentrations varied from 1 to 150 μg mL⁻¹ were used with the pH adjusted to 5.5. Results are plotted in Figure 8. The equilibrium uptakes of amino-MGO and MGO of Cu(II) steadily increase with the initial concentration (C₀). Whereas, for the Cd(II) ion, Qₑ almost rises linearly along with C₀ in the low concentration range (C₀ < 40 μg mL⁻¹), then comes into a stationary stage, finally decreasing gently at high concentrations (C₀ > 80 μg mL⁻¹). This reveals that competition occurred between two components in the high concentration range. The mechanism can be understood as follows. There are a large number of functional groups on the graphene and the modified oxide nanoparticles for metal ions to combine with at low concentrations. Active sites decrease with increased concentration, and Cu(II) takes priority to adsorb onto the materials, together with nearly no growth of Cd(II). When in high concentrations, the two constituents compete for the limited sites. The adsorbance of Cu(II) ions rises, for Cu(II) owns larger stability constants when coordinating with surface groups (Smith & Martell 1975; Martell & Smith 1977).

From the view point of ion properties, Cu(II) has a smaller ionic radius than Cd(II) (0.72 Å versus 0.97 Å), which makes Cu(II) ions polarize O or N ligands on the sorbent more effectively than the larger Cd(II) ions. In addition, the electronegativity (Pauling) of Cu(II) is 1.90, while it is 1.69 for Cd(II). Predominantly, Cu(II) ions are adsorbed onto the electron-rich surface containing large amounts of oxygen and nitrogen atoms owing to a stronger affinity to the electrons (Kosa et al. 2012). On the other hand, the theory of soft and hard acids and bases (SHAB) (Ayers 1998) can be employed to explain this. The epoxy, hydroxyl, and carboxyl groups on MGO and amino-MGO as well as the additional amino groups on amino-MGO are all divided into hard bases. Following the rule, expressed as hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases, the Cu(II) ion (classified as a borderline acid) is adsorbed in preference to the Cd(II) ion (classified as a soft acid). All mentioned above came out because amino-MGO and MGO adsorbed Cu(II) more efficiently than Cd(II). Meanwhile, the increase in the hard base group can promote the maximum capability of material and enhance its selectivity.

To visualize the selectivity of MGO and amino-MGO for Cd(II) and Cu(II), the distribution coefficient K (mL g⁻¹) and the selection factor (α) are used.
where $Q_e$ (mg g$^{-1}$) is the equilibrium uptake, $C_e$ (mg L$^{-1}$) is the equilibrium concentration of Cu(II) or Cd(II), and $\alpha_{Cu/Cd}$ shows the selectivity for Cu(II) relative to Cd(II).

The values of $\alpha_{Cu/Cd}$ are not investigated because of the slightly competitive effect exhibited between Cd(II) and Cu(II) when the initial concentrations are less than 40 $\mu$g mL$^{-1}$. Figure 9 presents the data of $\alpha_{Cu/Cd}$ from 40 to 150 $\mu$g mL$^{-1}$. All the values of $\alpha_{Cu/Cd}$ are larger than 1, confirming that the Cu(II) has a greater affinity to the active adsorption sites than Cd(II). The curve of amino-MGO always locates over that of MGO, which illustrates that amino-MGO has a stronger selectivity for Cu(II) ions compared with MGO.

**CONCLUSIONS**

In summary, the selectivity of two kinds of graphene adsorbents, amino-MGO and MGO, were explored using Cu(II) and Cd(II) as model ions. TEM, FT-IR, VSM, TGA and Zetasizer Nano ZS were employed to characterize and guarantee the successful synthesis of materials. It is needless to emphasize that excellent adsorption quantities, rapid adsorption rates and an easy magnetic separation make these materials very attractive for water treatment. Both materials prefer to adsorb Cu(II) rather than Cd(II) as a result of the abundant surface groups, which have better affinity to copper ions. After the amidation reaction, the active sites on the surface of amino-MGO increased and endowed amino-MGO with more apparent selectivity for Cu(II) as well as larger adsorbance. Our results may have some implications in the improvement of the selectivity and efficiency of adsorbents by proper modification methods.

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**CONFLICT OF INTEREST**

The authors declare that they have no conflict of interest.

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