Graphene Oxides Cross-linked with Hyperbranched Polyethylenimines: Preparation, Characterization and Their Potential as Recyclable and Highly Efficient Adsorption Materials for Lead(II) Ions

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Abstract: Three GO-HPEI gels were prepared by a cross-linking reaction of graphene oxide (GO) with hyperbranched polyethylenimines (HPEIs) with different molecular weight. The GO-HPEI gels are different from the most reported GO-based materials and have superior adsorption performance because that these gels have more adsorption sites over using the common cross-linking agent (especially double-functionality or tri-functionality monomer). The morphology and structure of the GO-HPEI gels were characterized by FTIR, XRD, SEM, TGA and elemental analyses. The adsorption property of Pb(II) onto GO-HPEI gels and the factors that influence the adsorption, such as the Pb(II) concentration, contact time and pH value, were investigated. The GO-HPEI gel exhibited an adsorption capacity as high as 438.6 mg g⁻¹ for Pb(II) ions, and its insolubility in water makes the separation from wastewater easy. Adsorption experiments demonstrated that the amino groups and the cross-link density affect the adsorption capacity. In the Pb(II) adsorption process, the adsorption kinetic and equilibrium data were well simulated with the pseudo-second-order and Langmuir isotherm models. The adsorption capacity of the GO-HPEI gel for Pb²⁺ only exhibited a slight decrease after eight cycles of adsorption/desorption, indicating its good stability. Therefore, the GO-HPEI gels could serve as promising adsorbents for potential application in the removal of Pb(II) from wastewater.

Keywords: Graphene oxide, Hyperbranched polyethylenimine, Cross-link, Adsorption capacity.

1. Introduction

Lead(II) ions in water are of great concern due to their toxicity, non-biodegradability and accumulation in organisms or the food chain[1, 2]. With the rapid development of industries, the water pollution caused by Pb^{2+} contamination has become a serious issue. Long-term drinking of lead polluted water will cause serious disorders, such as kidney disease, anaemia and mental retardation. Due to their high toxicity, the elimination of Pb^{2+} from aqueous solution is crucial for the environmental pollution cleanup. Therefore, the efficient removal of Pb^{2+} from wastewater is very important and urgent. To date, several technologies and methods for Pb^{2+} removal from wastewater have been developed including solvent extraction, ion-exchange, membrane separation, reverse osmosis and adsorption[3-5]. Adsorption is one of the most promising and widely used approaches due to high efficiencies and economic feasibility [2, 6, 7]. A number of materials, such as activated carbon[8], zeolite[9], clay[10], kaolinite[11], microorganisms[12], manganese oxides[13] and carbon nanotubes[14, 15], have been successfully employed to adsorb Pb^{2+} . However, the low removal efficiencies or low adsorption capacities of these adsorbents limit the engineering application. Therefore, it is necessary to develop new and more efficient materials for adsorption.

Carbon materials are significantly and heavily used for the removal of Pb^{2+} as an engineering adsorbent[16, 17]. Graphene oxide (GO), which is a new material in the carbon family, has attracted much attention for the adsorption treatment of lead-containing wastewater due to its huge surface area and a large number of functional groups[18]. Several researchers have applied GO or GO based materials for Pb^{2+} adsorption[19-26]. However, the adsorption capacities are less than satisfactory. For example, Islam has reported Pb^{2+} adsorption using GO immobilized by polystyrene with an adsorption capacity of 227.92 mg g⁻¹[19]. A nanocomposite LS-GO-PANI

was prepared via in situ polymerization, and this nanocomposite exhibited an adsorption capacity of 216.4 mg g⁻¹ for Pb²⁺[20]. Gui synthesized a magnesium silicate/reduced GO nanocomposite with a high adsorption efficiency for Pb²⁺[21]. Recently, an aminosilanized GO was prepared for the selective adsorption of Pb²⁺, and the maximum adsorption capacity was determined to be 96 mg g⁻¹[22]. Polyamidoamine dendrimer (PAMAM) modified GO can be easily prepared and has a high adsorption capacity[27-29]. In comparison to linear polymers with amino groups, the metal ion binding capacity of PAMAM was much larger due to the presence of the EDA core[30]. GO-PAMAM were prepared via the “grafting-from”[31] or “grafting to”[29] method, and the GO-PAMAM 2.0 total adsorption capacity for Fe³⁺, Cr³⁺, Zn²⁺, Pb²⁺ and Cu²⁺ reached 1.007 mmol g⁻¹.

Apparently, functionalization of GO is essential for improving its adsorption capacity[32-35], especially by the dendritic polymers, such as PAMAMs. However, most reported GO and GO based materials cannot be directly applied as adsorbents because they are water soluble[25, 36] and small in size[23]. Assuming that adsorption occurs, the GO or GO based materials may be difficult to separate from the solution after the adsorption process using traditional separation methods due to its hydrophilic property. Therefore, the industrial application cost of GO or GO based composite materials will increase. In addition, the treated water may be re-polluted.

Therefore, the introduction of cross-linking with dendritic polymers could be more beneficial for enhancing the feasibility of GO based materials. Based on the specific spheroid-like shape, compact structure and multi-functionality, dendritic polymers (i.e., the dendrimers and hyperbranched polymers) have attracted tremendous interest, and these polymers are the most attractive compounds for the design of new structures and molecules[37, 38]. Unfortunately, the synthesis of dendrimers is a time-consuming and expensive process. Unlike dendrimers,

hyperbranched polymers, which can be economically and easily prepared in one step, have gained increasing attention[38-42], especially in industrial applications. Commercially available hyperbranched polyethylenimine (HPEI) with a large number of primary and secondary amine groups has been widely used for encapsulation or adsorption of guest molecules[43, 44]. In addition, the number of the functional groups reacted as crosslink points will be reduced after the crosslinking reaction, which implies that the adsorption sites of these materials will be reduced. Differently and significantly, these gels have more adsorption sites over using the common cross-linking agent (especially double-functionality or tri-functionality monomer). Therefore, the objective of this work is to synthesize graphene oxide-hyperbranched polyethylenimine gels (GO-HPEI gels) that are recyclable and may possess a high adsorption capacity and be directly applied. These GO-HPEI gels could take full advantage of the characteristics of the specific physical, chemical and surface properties of GO including the specific spheroid-like shape, large number of amino groups of HPEIs, good stability and recyclability of the gels. Therefore, the GO-HPEI gel may have the potential to be a cost-effective adsorbent for the removal of Pb^{2+} from wastewater.

2. Materials and methods

2.1 Materials

Hyperbranched polyethylenimines (HPEI) ($M_n=1800$, 1×10^4 and 7.5×10^5 g/mol, namely HPEI1.8K, HPEI10K and HPEI750K, 99%) were obtained from Aldrich. Lead nitrate, sodium nitrate, potassium permanganate, concentrated sulfuric acid, hydrogen peroxide and other common chemicals were all obtained from Tianjin Chemical Reagent Co. Graphite was obtained from Pingdu Graphite Co.

2.2 Apparatus and instruments

The FTIR spectra of the GO and GO-HPEI gels were recorded on a MAGNA550 FTIR spectrometer (Thermo Nicolet). The X-ray powder diffraction spectra were recorded on a D/max2500VPC X-ray diffractometer (RigakuD). A model JSF5600LV scanning electron microscope (JEOL) was used to characterize the surfaces of the adsorbents. A thermogravimetric analysis apparatus (NETZSCHSTA409PC) was employed under a nitrogen atmosphere. Elemental analysis was performed on an Elementar VarioEL III instrument from Germany. The Pb^{2+} concentrations were determined by an atomic adsorption spectrophotometer (GBC-932).

2.3 Preparation of GO

The preparation of graphite oxide was performed using graphite powder oxidation according to the modified Hummer's method.[45]. Briefly, 5 g of graphite powder and 2.5 g of NaNO_3 were sequentially added into cold 115 mL 98% H_2SO_4 under the condition of ice bath, followed by slow addition of 15 g KMnO_4 at the temperature below 20 °C. Subsequently, the reaction was continued for 30 min at 35 °C, followed by slow addition of 230 mL distilled water under stirring. The reaction was continued for 0.5 h at 98 °C. Then, 30% H_2O_2 was added until the color of the mixture changed to brilliant yellow and there was no gas being produced. The resulting mixture was filtered and washed 3 times with distilled water, and then GO keeping its original structure can be prepared by using freeze-drying technology.

2.4 Preparation of the GO-HPEI gel

Based on HPEI1.8K, HPEI10K and HPEI750K, the GO cross-linked with the three HPEIs are referred to as the GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels. The synthesis of GO-HPEI gel was exemplified for GO-HPEI10K. Scheme 1 shows the preparation of the GO-HPEI gel was carried out in two steps as followed:

Scheme 1 Preparation of GO and GO-HPEI gels.

Step 1: General procedure for the acyl chlorination of GO

The carboxyl group of GO reacts with oxalyl chloride to produce GO-COCl. 0.5 g of GO was added to 15 mL chloroform, further treated by a sonication for about 1h. 20 mL oxalyl chloride, two drops of dimethylformamide as catalyst were added to the above solution and were stirred at room temperature for 12 h. Finally, the reaction temperature was raised to 35 °C for 6 h to finalize the reaction. The chloroform and unreacted oxalyl chloride were removed under vacuum and the residue was washed with chloroform until free from oxalyl chloride.

Step 2: General procedure for the crosslinking reaction of GO

The mixture of HPEI10K (0.5 g) and triethyl amine (1.0 g) in 10 mL of chloroform was slowly added to the above product GO-COCl dispersed in 10 mL chloroform with stirring for 12 h at

25 °C. Finally, the reaction temperature was raised to 35 °C for 5 h to finalize the reaction. After centrifugation, the solid was washed with 1 M potassium carbonate aqueous solution 3 times, then, it was washed with distilled water until giving neutral solution. The product/water system was freeze-dried for 48 h under vacuum to obtain GO-HPEI10K gel.

2.5 Batch adsorption experiments

The adsorption behaviour of GO and GO-HPEI gels were tested including Pb^{2+} concentrations varying from 5 to 300 mg L⁻¹, pH values varying from 1.8 to 5.8, contact time, adsorption kinetics and adsorption isotherms. At predetermined time intervals, the concentrations of the pollutant solutions were measured. All of the adsorption experiments were performed in triplicate. The adsorption capacity (q_t) and adsorption efficiency (A_d) were calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

$$A_d = \frac{C_0 - C_t}{C_0} \quad (2)$$

where C_0 and C_t are the concentrations of Pb^{2+} at the initial and given times, respectively, W is the weight of the dry adsorbents and V is the volume of the solution. It is noted that q_t is the adsorption capacity at a given time, and given a sufficient adsorption time, q_t becomes the equilibrium capacity (q_e).

2.6 Recycling of the GO-HPEI gel

To measure the adsorption capacities of the regenerated GO-HPEI gels, 10 mg of the GO-HPEI1.8K gel was added to 100 mL of a Pb^{2+} solution. After adsorption, this Pb^{2+} adsorbed GO-HPEI gel was added to a 10 mL nitric acid solution at a pH of 1 for desorption. The gel was removed from the acid solution after the Pb^{2+} were completely desorbed from the GO-HPEI1.8K gel, and the gel was washed with water and dried in a vacuum. Then, the adsorption/desorption

of the regenerated GO-HPEI1.8K gel was repeated to investigate the recyclability of the GO-HPEI1.8K gel.

2.7 Pb²⁺ adsorption in real wastewater samples.

To evaluate the practicality of this gel, 5-35 mg of the GO-HPEI1.8K gel was added to 100 mL of a Pb²⁺ wastewater (46.5 mg L⁻¹, Yantai Jin Chao Yu Ke Storage Battery Co., Ltd). The adsorption capacity (q_e) and adsorption efficiency (A_d) were calculated according to the equation (1) and (2), respectively.

3. Results and discussion

3.1 Characterization of the GO and GO-HPEI gel

Fig. 1 FTIR spectra of GO and GO-HPEI gels.

The FTIR pattern of GO is shown in Fig. 1 and reveals the presence of oxygen-containing functional groups. The peaks at 1115, 1403 and 1630 cm⁻¹ correspond to C-O-C stretching, C-OH stretching and C-C stretching modes, respectively, of the sp² carbon skeletal network, and the peaks located at 1734 and 3430 cm⁻¹ correspond to C=O stretching vibrations of the -COOH groups and O-H stretching vibration, respectively[46]. In comparison to GO, the GO-HPEI gel exhibits new bands at 1650-1659 cm⁻¹[6] along with the disappearance of the carboxyl absorption peak that was located 1734 cm⁻¹, which was due to the characteristic C=O stretching bond frequency of the amide groups[47], indicating the successful transformation of the amine groups of HPEI into amide groups. The new absorptions between 2840 and 2950 cm⁻¹ are characteristic of the C-H stretching bond frequency of HPEI ethylene groups. In the FTIR spectrum of the GO-HPEI gel, most of the bands that correspond to the GO powder are significantly less intense (1403, 1115 cm⁻¹) or even disappear (1734 and 1631 cm⁻¹), which

suggests the formation of an intertwined network in the GO-HPEI gels via amide covalent bonding of the carboxyl groups in the GO with the amine groups in HPEI. These results confirm that the GO-HPEI gels were successfully prepared by cross-linking HPEI with GO.

Fig. 2 XRD patterns of GO and GO-HPEI gels.

The XRD pattern of graphite (Fig. 2a) contains a diffraction peak at $2\theta = 26.18^\circ$ ($d = 0.34$ nm) [46] corresponding to the normal graphite spacing (002) of the graphite plane, which disappeared in the prepared graphene oxide. For the GO (Fig. 2b), the broad and relatively weak diffraction peak at $2\theta = 11.1^\circ$ and an interlayer spacing of 0.7964 nm corresponding to the typical diffraction peak of GO are due to the (002) plane. During the oxidation process, the interlayer spacing increases from 0.34 to 0.7964 nm when the graphite is modified to graphene oxide, which may be due to the creation of oxygen-containing functional groups on the GO surfaces. This result is consistent with those from previous studies[29]. For the GO-HPEI gels (Fig. 2c, 2d and 2e), broad and weak peaks located at a 2θ value of 21.6 – 22° in the XRD pattern were observed and correspond to the amorphous feature of the cross-linked polymer matrix. The GO-HPEI gels exhibit similar XRD patterns regardless of the different molecular weight of

HPEI. It is important to note that there is no visible GO characteristic peak in the XRD patterns of the GO-HPEI gels, indicating the long-range disorder or full exfoliation of GO in the GO-HPEI gel matrix due to the uniform dispersion of GO within HPEI[48].

Fig. 3 SEM of GO and GO-HPEI gels

The SEM images of the GO and GO-HPEI gel are shown in Fig. 3. Based on the SEM images in Fig. 3a, GO has a sheet-like structure with a smooth surface and wrinkled edge. After GO was cross-linked with HPEI to form the GO-HPEI gels, it becomes porous, wrinkled and folded (Fig. 3b-d)[49]. The GO-HPEI gels exhibit a much rougher surface, which indicates that the various molecular weight HPEI and the GO layers were cross-linked forming porous and intertwined networks. Therefore, the surfaces of the GO-HPEI gels are very rough. The difference between

GO and GO-HPEI gel can also be observed from the digital photographs (Fig. S1). It is obvious that GO has a sheet-like structure and GO-HPEI gels are macroscopical materials with certain shapes. Moreover, TEM is an effect tool for the morphologic characterization of materials, the images of TEM of GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels (Fig. S2b, 2c and 2d) show distinctly that GO-HPEI gels are composed of graphene oxide (Fig. S2a) with some crumples, indicating that the GO-HPEI gels were synthesized successfully. After adsorption of lead, EDX spectrum (Fig. S2f) along with TEM (Fig. S2e) indicates the presence of lead.

As shown in Table S1, the BET surface area of GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K estimated from Barret-Joyner-Halenda (BJH) analysis of the isotherms were determined to be 77.82, 61.57 and 50.65 m²/g, respectively. Also, the average of the pore size distributions (Table S1) of the three kinds of GO-HPEI gels were 85.13, 91.65 and 84.72 nm, respectively. The value of the pore radius indicates that GO-HPEI gel was a macroporous material.

Fig. 4 TGA curves of graphite powder, GO and GO-HPEI gels under a nitrogen atmosphere.

The thermal properties of GO and GO-HPEI gels were investigated using TGA, and the results are shown in Fig. 4. The initial weight loss for GO below 100 °C was due to the evaporation of the adsorbed water, and the maximum weight loss temperature was approximately 200 °C, which corresponded to the decomposition of labile oxygen containing groups on the GO[48, 50]. As the temperature increased further, the GO exhibited a gradual weight loss. The final weight loss (53.8%) indicates that the prepared GO is deeply oxidized and contains numerous oxygen containing groups. In comparison to GO, the GO-HPEI gel becomes more thermally stable and increases the tiptop temperature of pyrolysis, which corresponds to the cross-linked GO and HPEI network. The maximum weight loss temperature was higher than 200°C, and the GO-HPEI gels exhibit a gradual weight loss, suggesting that the GO-HPEI gels exhibit better thermal stability. The final weight loss for the GO-HPEI750K, GO-HPEI10K and GO-HPEI1.8K gels are 39.05%, 48.88%and 50.06%, respectively, which were confirmed by the elemental analyses (Table 1).

Table 1

Elemental analyses of GO and GO-HPEI gels

sample	C%	N%	H%
GO	45.06	0.01	1.94
GO-HPEI1.8K	49.09	17.93	4.12
GO-HPEI10K	50.25	18.51	4.44
GO-HPEI750K	59.98	20.16	4.83

To understand the cross-link density of the reaction between GO and HPEI, we analysed the elemental composition of GO and GO-HPEI gels using elemental analyses. As shown in Table 1, the carbon content (%) was 45.06, 49.09, 50.25 and 59.98 for GO, GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K, respectively, and these results are similar to the corresponding TGA results

(46.2, 49.94, 51.12 and 60.95, respectively). Based on the nitrogen content of the GO-HPEI gels, the weight of nitrogen in the GO-HPEI gels are all approximately 18~20%. This result indicates that the HPEI1.8K, HPEI10K, HPEI750K weights are nearly the same in the GO-HPEI gels because HPEI1.8K, HPEI10K and HPEI750K are hyperbranched polymers resulting from the cationic ring-opening polymerization of aziridine. Therefore, the molar ratio of HPEI1.8K, HPEI10K and HPEI750K in the GO-HPEI gels is approximately 3706:689:1. The cross-linking density follows the trend $\text{GO-HPEI1.8K} < \text{GO-HPEI10K} < \text{GO-HPEI750K}$, which explains the trend in the thermal stability of the GO-HPEI gels (i.e., $\text{GO-HPEI750K} > \text{GO-HPEI10K} > \text{GO-HPEI1.8K}$), as shown in Fig. 4. In addition, hyperbranched polyethylenimine contains primary, secondary and tertiary amine functional groups. The molar ratios of the primary, secondary and tertiary amine groups of HPEI1.8K, HPEI10K and HPEI750K are 37:35:28, 33:40:27[51] and 25:50:25[52], respectively. The primary amine groups and the cross-linking density have an important effect on the adsorption. We deduced the adsorption capacity may be that $\text{GO-HPEI1.8K} > \text{GO-HPEI10K} > \text{GO-HPEI750K}$, which is based on the ratio of primary amines in GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K (approximately 37:33:25) as well as the cross-linking density ($\text{GO-HPEI1.8K} < \text{GO-HPEI10K} < \text{GO-HPEI750K}$).

3.2 Adsorption of Pb^{2+} on GO and GO-HPEI gels

Fig. 5 q_e and A_d of GO and GO-HPEI gels for Pb^{2+} . (The adsorbent concentration was fixed at 0.1 g L⁻¹ with an initial pH value of 5.5 at 25 °C).

The Pb^{2+} uptake abilities of GO and GO-HPEI gels were examined simply by soaking them in 100 mL of a solution containing Pb^{2+} for a sufficiently long time. As shown in Fig. 5, GO-HPEI1.8K exhibited the highest adsorption capacity and adsorption efficiency, which were as high as 421.86 mg g⁻¹ and 99.9%, respectively, and the highest adsorption capacities of GO, GO-HPEI10K and GO-HPEI750K gels are 85.1, 355.4 and 312.6 mg g⁻¹, respectively. The GO-HPEI gels exhibits an enhanced adsorption capacity for Pb^{2+} compared to that of GO due to the existence of a large amount of primary, secondary and tertiary amine groups on the GO-HPEI gels. In addition, the compact and spheroidal topology of HPEI was favourable for encapsulating Pb^{2+} . As shown in Fig. 5, the gels with the lower molecular weight HPEI exhibit much higher adsorption capacities than the gels with the higher molecular weight HPEI. This result may be due to higher cross-linking density of the gel with the higher molecular weight HPEI, resulting in a more compact gel.

3.3 Effect of contact time on the adsorption of Pb^{2+} for GO and GO-HPEI gels

Fig. 6 Effect of contact time on q_t for Pb^{2+} adsorption on GO and GO-HPEI gels. (The concentrations of Pb^{2+} and adsorbents are maintained at 100 mg L^{-1} and 0.1 g L^{-1} , respectively, with an initial pH value of 5.5 at 25°C).

The adsorption process of GO and GO-HPEI gels was studied, and the results are shown in Fig. 6. The adsorption capacity increases rapidly at the beginning as the adsorption time increased. When the adsorption time was 4 h, the adsorption capacities of the GO, GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels reach 61.2, 213.3, 198.4 and 192.6 mg g^{-1} , respectively. The GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gel adsorption capacity reach 229.4, 221.7 and 212.4 mg g^{-1} , respectively, which was 99.25, 98.2 and 98.6%, respectively, of the maximum during the first 8 h of the adsorption. However, the GO adsorption capacity only reaches 70.6 mg g^{-1} , indicating that the GO-HPEI gel exhibits excellent absorption property compared with GO. Therefore, the GO-HPEI gels are a promising adsorbent for removing Pb^{2+} from wastewater, and the adsorption behaviours of the GO-HPEI gels were systematically investigated, as discussed below.

3.4 Effect of the initial pH on the adsorption of Pb^{2+} by the GO-HPEI gels

Fig. 7 Effect of the initial pH value on the adsorption of Pb^{2+} at a concentration of 100 mg L^{-1} with a GO-HPEI gel concentration of 0.1 g L^{-1} at 25°C .

The adsorption of Pb^{2+} on the GO-HPEI gels was investigated at different initial pH values. The solution pH was ranged from 1.8 to 5.8 because lead ions exist as Pb^{2+} in this pH range, and a small portion of $\text{Pb}(\text{OH})^+$ ions will be formed when the pH approaches 6.0[1, 53]. As shown in Fig.7, the Pb^{2+} adsorption capacity of the GO-HPEI gels increases from 30-60 to 260-290 mg g^{-1} as the pH value increased from 1.8 to 5.8. The adsorption capacity increased slowly at a pH of less than 4 and sharply at a pH of 4~6. The surface charge of the GO-HPEI gel is positive at a high H^+ concentration, and the Pb^{2+} adsorption onto the GO-HPEI gels is primarily dominated by the competitive adsorption between the protons and Pb^{2+} , which means that the species of GO-HPEI gel surface groups are $-\text{COOH}$ and $-\text{OH}$. Then, it is not conducive to the adsorption at high H^+ concentration [20]. However, an increase in the pH leads to neutralization of the positive charge on the surface, which should increase the adsorption of Pb^{2+} . With an initial pH value of

5.8, the adsorption capacity of the GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels for Pb^{2+} reached a maximum value of 286.6, 278.7 and 260.5 mg g^{-1} , respectively. This phenomenon is due to a change in the ionization state of the hydroxyl, carboxyl and amino functional groups [54]. The partial surface $-\text{COOH}$ and $-\text{OH}$ groups in the GO-HPEI gel are converted to $-\text{COO}^-$ and $-\text{O}^-$ as the pH of the solution increased. The electrostatic interactions of $-\text{COO}^-$, $-\text{O}^-$ and Pb^{2+} are favourable for adsorption. In addition, the protonation degree of the amino groups decreased as the pH value increased, and the chelating ability of these primary and secondary amino groups for Pb^{2+} was enhanced. However, when the pH was near or higher than 7.0, the adsorption results may be inaccurate due to the appearance of $\text{Pb}(\text{OH})_2$ precipitation[20]. In general, the initial pH of the Pb^{2+} solution is fixed at 5.0 to 6.0, and this pH range is similar to that for application to Pb^{2+} removal from industrial wastewater. Based on these results, the pH value for the adsorption was fixed at approximately 5.8 in following studies.

3.5 Adsorption kinetics

To investigate the adsorption process, pseudo-first-order[20, 55] and pseudo-second-order kinetic model[56-58] as well as intraparticle diffusion were used to fit the kinetics data.

The pseudo-first-order kinetic model can be expressed in a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where k_1 (1/min) is the rate constant and q_e and q_t (mg g^{-1}) are the amounts of Pb^{2+} adsorbed by the adsorbent at equilibrium and at any time t (min), respectively.

The pseudo-second-order kinetic model can be expressed in a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is a constant.

In general, the Δq (%) value is a main factor for comparing the validity of the kinetic

model[59]. If the data from a model and the experimental data are close, the Δq (%) value will be lower.

Table 2

Parameters for the two kinetic models for Pb(II) ion adsorption onto GO-HPEI gels.

Kinetic models	parameters	GO-HPEI1.8K			GO-HPEI10K			GO-HPEI750K		
		50mg/L	100mg/L	200mg/L	50mg/L	100mg/L	200mg/L	50mg/L	100mg/L	200mg/L
Pseudo first-order	$q_e(\text{cal})(\text{mg/g})$	160.69	139.07	219.92	130.89	147.23	303.92	121.03	160.67	182.83
	$k_1(1/\text{min})$	0.0076	0.0094	0.0098	0.0062	0.0074	0.0122	0.0057	0.0085	0.0077
	R^2	0.9854	0.9707	0.9734	0.9792	0.9433	0.9753	0.9594	0.9797	0.9816
	$\Delta q(\%)$	24.88	48.82	42.59	28.04	42.61	2.88	24.34	31.14	29.71
Pseudo second-order	$q_e(\text{cal})(\text{mg/g})$	210.53	235.85	343.64	177.62	232.56	314.47	160.51	232.21	251.26
	$k_2 \times 10^{-5} (\text{g/mg} \cdot \text{min})$	8.97	18.6	12.1	9.10	11.5	9.42	7.847	10.05	8.427
	R^2	0.9990	0.9998	0.9997	0.9994	0.9995	0.9992	0.9994	0.9990	0.9992
	$\Delta q(\%)$	5.38	2.43	2.51	5.68	3.67	1.26	7.67	9.53	5.09
$q_e(\text{exp})$ (mg/g)		201.66	231.26	336.74	169.75	225.79	311.26	151.05	215.44	241.38

The plots of the different kinetic models are shown in Figs.S3, S4 and S5, and the kinetic model parameters were obtained from fitting, and the results are shown in Table 2. The R^2 values of the pseudo-second-order kinetic curves (Figs.S3 b, S4 b and S5 b) exceed 0.999 (0.9990-0.9998), which indicates that the pseudo-second-order kinetic model agrees well with the kinetic data. The R^2 values (0.9433-0.9854) of the pseudo-first-order kinetic curves (Figs.S3 a, S4 a and S5 a) are lower than those for the pseudo-second-order kinetic model, and the pseudo-first-order kinetic model does not provide a good fit to the experimental kinetic data. The q_e values calculated from the pseudo-second-order kinetic model are similar to the experimental q_e , which can further support the good agreement. For example, the calculated q_e values of the GO-HPEI1.8k gels obtained using the pseudo-second-order kinetic model are 210.53, 235.85 and 343.64, which are closer to the experimental q_e values of 201.66, 231.26 and 336.74, respectively.

In addition, based on an analysis of the Δq (%) values for both models, the pseudo-second-order kinetic model exhibits good agreement with the experimentally obtained kinetic data. The consistency also indicates that the adsorption of Pb^{2+} onto the GO-HPEI gels is a process that is primarily controlled by the chemical interaction between Pb^{2+} and the binding sites.

Fig.8 Intraparticle diffusion model for Pb^{2+} adsorption onto the GO-HPEI gels.

To understand the rate-controlling steps that affect the absorption kinetics and the adsorption mechanism, the kinetic results were analysed by the intraparticle diffusion model:

$$q_t = k_{id}t^{1/2} + C \quad (5)$$

where k_{id} (mg g⁻¹ min^{-0.5}) is the intraparticle diffusion coefficient and C is the adsorption constant corresponding to the intercept. The plots of q_t versus $t^{1/2}$ are shown in Fig.8. The first sharper portion of the plot represents the diffusion of Pb^{2+} through the aqueous phase to the GO-HPEI gel surface (external diffusion), and the second portion is due to a gradual adsorption stage, corresponding to the diffusion of Pb^{2+} inside the GO-HPEI gel (intraparticle diffusion)[60, 61].

The intraparticle diffusion parameters and determination coefficients are summarized in Table S2. For the GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels, k_{1id} was higher than k_{2id} , and C_2 was larger than C_1 . These results indicated that the rate of Pb^{2+} adsorption was higher in the beginning due to the large available surface area of the GO-HPEI gels for the adsorption of Pb^{2+} . When the adsorbed material formed a thick layer due to inter-ionic attractions and molecular association, the adsorption capacity of the GO-HPEI gels was nearly saturated, and the adsorption rate depended on the rate at which the Pb^{2+} was transported from the exterior to the interior sites of the GO-HPEI gel. If the plot is linear and passed through the origin, the intraparticle diffusion would be the rate governing step. In this study, none of the plots passed through the origin (Fig.8), which indicated that the intraparticle diffusion was not the only rate-controlling step. Other mechanisms, such as ion-exchange, electric attraction or complexation, may also affect the rate of adsorption[62, 63].

3.6 Adsorption isotherms

Langmuir[64] and Freundlich isotherms[65] are used to describe and understand the mechanism of adsorption. The Langmuir isotherm can be expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_m (mg/g) is the maximum adsorption capacity of the adsorbate per unit mass of adsorbent and K_L (L/mg) is the Langmuir equilibrium constant.

To determine whether the adsorption is favourable, a dimensionless constant separation factor (R_L) can be determined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where C_0 is the initial Pb^{2+} concentration (mg/L). The R_L parameter value can indicate whether the isotherm type is unfavourable ($R_L > 1$), linear ($R_L = 1$), or favourable ($0 < R_L < 1$).

The Freundlich isotherm can be expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (8)$$

where n and K_F are the Freundlich constants for the adsorption intensity and the adsorption capacity, respectively. $n > 1$ indicates favourable adsorption conditions.

Table 3

Comparison of the results for two isotherm models for Pb^{2+} adsorption onto GO-HPEI gels.

sample	Langmuir			Freundlich		
	q_m	K_L	R^2	n	K_F	R^2
GO-PEI1.8K	438.61	0.0258	0.9975	4.1322	96.2915	0.9484
GO-HPEI10K	393.43	0.0278	0.9979	4.4015	94.7815	0.9421
GO-PEI750K	336.33	0.0259	0.9982	4.3316	78.5384	0.9351

The Langmuir and Freundlich adsorption isotherms for the GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K gels are shown in Fig. S6. The isotherm parameters are obtained by fitting the adsorption equilibrium data to the isotherm models, and the isotherm constants and correlation coefficients are summarized in Table 3.

The adsorption of Pb^{2+} on the GO-HPEI gels fitted well to the Langmuir isotherm model with a high R^2 (0.9975-0.9982), and the dimensionless constants (R_L) lie within the favourable limit (between 0 and 1), indicating a favourable process. The maximum adsorption capacities of Pb^{2+} on the GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750 gels from triplicate tests were 407 ± 31 , 368 ± 25 and 315 ± 21 mg g⁻¹, respectively. For comparison, the adsorption capacities of Pb^{2+} onto various GO or modified GO materials collected from the references are listed in Table 4[6, 20, 46, 66-71]. The comparative results indicate that the adsorption capacity of the GO-HPEI gels is higher than those previously reported. Although the adsorption capacity of the GO-HPEI gels is

similar to the GO-based nanomaterials, the GO-based nanomaterials exhibit a certain dissolubility in aqueous solution, which must be centrifuged or filtered after the adsorption process. Therefore, their results may be inaccurate. In this study, the GO-HPEI gel size is much larger than that of the nanomaterial and direct precipitation occurred. In this stage, the GO-HPEI gels can be more easily and conveniently used.

Table 4

Maximum adsorption capacity of Pb^{2+} on various graphene oxide-based materials

Adsorbents	q_m (mg/g)	Conditions	References
chitosan/GO	76.9	pH 5.0	[6]
graphene	16.6	pH 6.0	[66]
SiO ₂ /graphene	113.6	298 K, pH 6.0	[67]
GO@SiO ₂	13.6	pH 5.5	[68]
GO@PS	227.9	pH 7.5	[19]
GO	367	298K, pH 6.8	[25]
RGO-EDTA	230	298K, pH 6.8	[25]
GO/TiO ₂	65.6	298K, pH 4.5	[69]
GO-gelatin/chitosan	100	RT, pH 6.0	[70]
LS-GO-PANI	216.4	303 K, pH 5.0	[73]
2- or 3- layered GO nanosheets	400	pH 6.0, T 293 K	[46]
Functionalized graphene GNS ^{PF6}	405.9	pH 5.1, RT	[71]
GO-HPEI1.8K gel	438.6	288K, pH 5.8	This work
GO-HPEI10K gel	393.4	288K, pH 5.8	This work
GO-HPEI750K gel	336.3	288K, pH 5.8	This work

The primary reason for the high absorption capacity of Pb^{2+} by the GO-HPEI gels can be explained as follows. First, the graphene oxide contains a large amount of oxygen-containing functional groups and a huge specific surface area, which contributed to the improved adsorption capacity of Pb^{2+} [20]. Second and more importantly, hyperbranched polyethylenimines contain numerous primary, secondary and tertiary amine functional groups. The nitrogen of the coexisting primary, secondary and tertiary amine functional groups has a strong affinity for Pb^{2+} [20, 72]. Therefore, the GO-HPEI gels can form strong complexes with Pb^{2+} , enhancing the adsorption capacity of Pb^{2+} . In addition, HPEIs consist of terminal, linear and dendritic structures leading to the functional end-groups from the terminal and linear structure of HPEIs being located in the periphery and interior of the spheroid-like materials[51]. Then, HPEI based materials can effectively improve the encapsulation capacity of guest molecules due to their specific spheroid-like shape and multifunctionality. Third, the synergistic effect of the amino and carboxyl groups also plays a key role in the adsorption. After the carboxyl group attaches to Pb^{2+} , the amino group on HPEI can afford another site for the coordination of Pb^{2+} , which makes the GO-HPEI gels more efficient for binding to Pb^{2+} .

The R^2 values of the Freundlich isotherms for the adsorption of Pb^{2+} onto GO-HPEI1.8K, GO-HPEI10K and GO-HPEI750K are 0.9484, 0.9424 and 0.9351, respectively, which suggest that the adsorption of Pb^{2+} on the GO-HPEI gels can be reasonably explained by the Freundlich model. The n values are all greater than 1, which also indicates that the adsorption of Pb^{2+} is favourable at this studied condition [7, 56].

3.6 Effect of Competing Ions.

Fig. 9 Effect of competing ions on the adsorption capacity of GO-HPEI1.8K gel (The concentrations of Co^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} are all maintained at 100 mg L^{-1} with an initial pH value of 5.0 at 25°C).

To determine the application feasibility of GO-HPEI1.8K gel to Pb^{2+} , the q_s of respective ions adsorbed on GO-HPEI1.8K gel from the mixed solution of Co^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} with the same concentration (100 mg L^{-1}) were measured. As shown in Fig. 9, the adsorption capacities of the GO-HPEI1.8K gel toward Co^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} reach 22.8, 25.3, 29.8, 33.7, 40.8 and 116.2 mg g^{-1} , respectively. It is obvious that the absorption property of GO-HPEI1.8K gel toward Pb^{2+} is higher than that toward other heavy metal ions, meaning a high selectivity toward Pb^{2+} . These are attributed to the relatively stronger complexation between the Pb^{2+} and the carboxyl or amine functional groups on GO-HPEI1.8K gel [29, 67, 74]. All these results suggest that the GO-HPEI gel is a promising adsorbent for removing Pb^{2+} from wastewater containing heavy metal ions.

3.7 Adsorption ability of the regenerated GO-HPEI1.8K gel

Fig. 10 Re-adsorption of Pb^{2+} on the GO-HPEI1.8K gel (The concentration of Pb^{2+} was maintained at 100 mg L^{-1} with an initial pH value of 5.5 at 25°C).

In this study, the recyclability of the GO-HPEI1.8K gel was chosen as the model adsorbent for Pb^{2+} adsorption. The adsorption/desorption experiment of the recycled GO-HPEI gel was investigated by cycling eight times. The results are shown in Fig. 10. It is important to note that the adsorption capacity of the GO-HPEI1.8K gel for Pb^{2+} decreased slightly from 236.9 to 212.5 mg g^{-1} after eight cycles, which indicates the good reusability of the GO-HPEI1.8K gel. The decrease in the adsorption capacity may be primarily due to the decrease in the number of binding sites after each desorption step because a portion of the amide bonds may be hydrolysed during the regeneration in the presence of a strong acid. Overall, the GO-HPEI gels exhibit good recyclability and can be repeatedly used for practical application.

3.8 Column Adsorption.

Batch adsorption study does not give accurate scale up data. Therefore, it is necessary to examine the column adsorption. The effect of sample volume (50-500 mL) for the adsorption of Pb^{2+} (maintained at 50 mg L^{-1}) on the GO-HPEI1.8K gel was investigated. It can be seen from Fig.11, the adsorption of Pb^{2+} is quantitative until a 300 mL of sample volume. In addition, the amount of the adsorbent, flow rate, column height, and diameter of the column also play a pivotal role in the performance of the column. Details related to the dynamic and regeneration adsorption of the GO-HPEI gels will be systematically investigated in our further work.

Fig. 11 Effect of the sample volume on the adsorption of Pb^{2+} on GO-HPEI1.8K gel. Experimental conditions: Column, $20 \times 1 \text{ mm}$; GO-HPEI1.8K gel, 0.1 g ; Flow rate, 0.5 mL min^{-1} ; Pb^{2+} concentration, 50 mg L^{-1} ; Temperature, $22 \text{ }^{\circ}\text{C}$.

3.8 Pb²⁺ adsorption in real wastewater samples.

Fig. 12 q_e and A_d of GO-HPEI1.8K gel for Pb²⁺. (The Pb²⁺ concentration in wastewater was 46.5 mg L⁻¹ with an initial pH value of 5.5 at 25 °C).

To evaluate the practicality of this gel, we applied GO-HPEI1.8K gel in the removal of Pb²⁺ in real wastewater. As shown in Fig. 12, GO-HPEI1.8K exhibited the highest adsorption capacity and adsorption efficiency, which were as high as 230.1 mg g⁻¹ and 99.1%, respectively. These experiments and results demonstrated that GO-HPEI1.8K gel could be used for Pb²⁺ removal in real sample.

4. Conclusions

In the presented study, a new adsorbent (i.e., GO-HPEI gel) has been successfully prepared and characterized. Importantly, the GO-HPEI gels are different from the most reported GO-based materials and have superior adsorption performance for Pb²⁺. The adsorption capacities of the GO-HPEI gels for Pb²⁺ are highly pH dependent. The functional groups and specific spheroid-like shape of the GO-HPEI gel enhanced its adsorption ability for Pb²⁺. The maximum adsorption capacity for Pb²⁺ is as high as 438.6 mg g⁻¹. The adsorption capacity of the GO-HPEI

gel is much higher than most GO-based materials and nanomaterials. The adsorption kinetics and isotherms data indicated that the Pb^{2+} adsorption follows pseudo-second-order kinetic and Langmuir isotherm models. The GO-HPEI1.8K gel exhibits a higher adsorption capacity than the GO-HPEI10K and GO-HPEI750K gels, suggesting that the cross-linking density and primary amine groups have an important effect on adsorption. In addition, the GO-HPEI gels exhibit good stability in aqueous solutions, which is critical factor for their usage and recycling. In addition, the adsorption capacity of the GO-HPEI1.8K gel for Pb^{2+} only decreased slightly from 236.9 to 212.5 mg g^{-1} after eight cycles of adsorption/desorption. To summarize, these results demonstrate that the GO-HPEI gel has great potential as an effective and economical adsorbent for removing Pb^{2+} from wastewater.

Acknowledgements

This work was financially supported by the National Science Foundation of China (21304043, 51403097, 21171085), the Natural Science Foundation of Shandong Province (ZR2012BQ024, 2014ZRB019WZ) and Natural Science Foundation of Ludong University (LY2012003, LY2013010).

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