Materials Research Express

PAPER

Preparation of the crosslinked GO/PAA aerogel and its adsorption properties for Pb(II) ions

Qingqing Wang1,2, Liling Lei1,2, Xiyang Kang1,2, Xiqi Su1,2, Fangcao Wang1,2, Cong Wang1,2, Junhong Zhao1 and Zhijun Chen1,2*
1 School of Material and Chemical Engineering, Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, People’s Republic of China
2 Henan Engineering Research Center of Chemical Engineering Separation Process Intensification, People’s Republic of China
E-mail: chenj@zzuli.edu.cn

Keywords: crosslinked, graphene oxide, polyacrylic acid, aerogel, Pb(II), adsorption

Abstract

The graphene oxide(GO)/polyacrylic acid(PAA) was prepared by in situ polymerization in graphene oxide lamellae, and crosslinked graphene oxide/polyacrylic acid complex(CLGO/PAA) was formed by esterification reaction between 1,4-butanediol and carboxylic acid of PAA at same time. The CLGO/PAA aerogel was prepared by freeze drying method. The CLGO/PAA aerogel has good stability and high saturated adsorption capacity for the adsorption of Pb(II) ions in water. The structure and properties of the CLGO/PAA aerogel were characterized by using x-ray diffractometry (XRD), field emission scanning electron microscopy (FESEM), infrared spectroscopy(FT-IR), and atomic absorption spectrometer(AAS), respectively. The results show that the prepared CLGO/PAA aerogel possess elliptical pore structure. In addition, the adsorption properties of the CLGO/PAA aerogel for Pb(II) in water were studied under different pH, different concentrations of Pb(II), contact time and number of adsorbent cycles. The results show that the adsorption amount of Pb(II) could reach to 640 mg g⁻¹ at the initial concentration of Pb(II) was 500 mg l⁻¹, and the adsorption equilibrium could be reached after 60 min. The adsorption amount for Pb(II) was still 143 mg g⁻¹ after 5 times cycle.

1. Introduction

The rapid development of industry has produced a large amount of wastewater. Because wastewater has many negative effects on the environment and human health, the treatment of wastewater has always been a hot topic [1, 2]. In particular, human body’s kidney, nervous system would be damaged by heavy metal Pb(II) [3–6]. There is an urgent need for a method to remove heavy metals from sewage to meet the growing environmental quality requirements [7]. Common methods for treating heavy metal ion pollutants in wastewater include chemical precipitation, extraction, membrane separation, ion exchange, electrochemical and adsorption [8–14]. The adsorption method has gradually entered the researcher’s line of sight because of its simple operation, safety, simple equipment, low cost, wide applicability and possible recyclability of the adsorbents [15]. Common adsorbents include activated carbon, zeolite, carbon nanotubes and chitosan, but these adsorbents are costly, environmentally unfriendly and exhibit low adsorption capacity when adsorbing heavy metal ions [16–18]. Therefore, the development of new adsorbents with higher adsorption capacity has become a research hot spot.

PAA has the characteristics of water solubility, non-toxicity, and good biodegradability. It is often used as a hydrogel or aerogel material. For example, PAA hydrogel prepared by Wiśniewska et al [19] which has a 3D porous network structure and rich functional groups (−OH, COO−), has high adsorption efficiency for metal ions and good biocompatibility. Kong et al [20] prepared GO/PAA hydrogel by graft polymerization, and improved the Cd²⁺ adsorption by adding PAA. Han et al [21] prepared a three-dimensional (3D) dual network GO/PAA hybrid aerogel using a one-pot in situ solution polymerization method. The addition of PAA not only...
acts as a binder, but also provides more multiple active functional groups, high specific surface area, and abundant active sites. The prepared aerogel has excellent adsorption performance for \( \text{Cu}^{2+} \) ions in water.

Graphene oxide (GO) has shown excellent performance in electricity, heat, energy storage and adsorption, which has aroused widespread concern \([22]\). In particular, Graphene oxide (GO) has become one of the important research hotspots in the field of adsorption research due to its large specific surface area. In recent years, some researchers have modified graphene to obtain new adsorbents \([23–25]\). Graphene has a high specific surface area, so it is very suitable as an adsorbent, and GO also has this advantage, but the separation and reuse of GO from the system limits its use \([26]\). However, as adsorbent in water, GO has disadvantages such as poor stability, low hydrophilicity, and low functional group content in water. First, GO is a typical 2D structure material, because of its huge specific surface area, GO sheets are easy to reassemble to form graphite-like structure, which reduces its specific surface area. Second, when soaking in water for long time, GO sheets are easy to disperse in water and difficult to recover. Combining GO with 3D aerogel structure will effectively overcome these shortcomings. Therefore, GO aerogel with 3D structure is becoming one of the research hotspots in the field of adsorption \([27, 28]\). Furthermore, if the cross-linking structure of the GO aerogel does not be formed, its 3D structure should be collapse due to immersed in water for a long time. Therefore, the effective preparation of CLGO aerogel is an important method to apply GO aerogel to water adsorption materials \([29]\).

In order to improve the stability of the prepared GO aerogel and increase its adsorption amount for \( \text{Pb}^{2+} \), the \textit{in situ} polymerization of acrylic acid was initiated between the layer of GO to form CLGO/PAA, and the PAA chains were crosslinked through the action between the –OH in butanediol molecules and –COOH in PAA chains to form a stable crosslinked structure of CLGO/PAA. The CLGO/PAA aerogel structure is prepared as shown in figure 1. The GO/PAA hydrogel was formed by hydrothermal reaction between GO and AA, 1,4-butanediol at 90 °C for 12 h under the initiator of potassium persulfate. Then, the GO/PAA aerogel was formed by freeze-drying the GO/PAA hydrogel, and the GO/PAA aerogel was used for the adsorption of \( \text{Pb}^{2+} \). The crosslinked PAA in the resulted CLGO/PAA aerogel not only stabilizes the structure of GO but also makes the disorder of GO increase and the content of –COOH increase, with the introduction of PAA. The increased carboxyl group improves the hydrophilicity of GO/PAA aerogel and provides more coordination sites for adsorption of \( \text{Pb}^{2+} \) \([21]\). The results have showed that the CLGO/PAA aerogel surface contains a large number of carboxyl functional groups. When the pH of water is alkaline or weak alkaline, the carboxyl group is negatively charged and adsorbs heavy metal ions through the charge attraction between the carboxyl group and metal ions. At the same time, oxygen on the carboxyl group can form a coordination bond with the empty d orbit in the heavy metal, which also increases the adsorption of heavy metal ions in water \([30]\). The prepared aerogel has potential application value in wastewater treatment and soil remediation.
2. Experimental section

2.1. Materials
The graphite was purchased from Sinopharm Chemical Reagent Co., Ltd NaOH, KMnO₄, H₂SO₄, and HCl were purchased from Yantai Shuangshuang Chemical Co., Ltd K₂S₂O₈, Pb(NO₃)₂, 1,4-butanediol, and anhydrous ethanol were purchased from Tianjin Sailboat Chemical Reagent Co., Ltd. Acrylic acid was purchased from Tianjin Guangfu Fine Chemical Research Institute. The resistivity of water used is 18 MΩ cm⁻¹. All chemicals are analytical grade and used directly without purification.

2.2. Synthesis of GO
First, 69 g of concentrated H₂SO₄ (98%) was added to a three-necked flask. After 15 min of ice bath, 2.0 g of milled graphite powder was slowly added in batches. After continuing to ice bath for 30 min, 8.0 g of KMnO₄ powder was added in batches. Then, the three-necked flask was transferred to 35 °C water bath and stirred. In the process, the solution thickened and the color changed from black to dark green. After stirring for 12 h, the flask was removed from the water bath, and 276 ml of H₂O was added. (Divided into 6 portions of 46 ml), the color of the solution changed from dark green to dark brown. The three-necked flask was returned to the 35 °C water bath to continue stirring. After 2 h, 25 ml of H₂O₂ (30%) was slowly added to the flask. After stirring for 15 min, the dispersion turned golden brown. The crude product was obtained after centrifugation at 8000 rpm and washed three times with 5% HCl and dried at 60 °C for 12 h to obtain GO.

2.3. Synthesis of CLGO/PAA aerogel
0.06 g of the GO was added to 10 ml of H₂O and dispersed uniformly in water after ultrasound treatment for 40 min. Then, 0.5 ml of acrylic acid, 0.01 g of K₂S₂O₈ and 0.8 ml of 1,4-butanediol (VₐC₄H₁₀O₂: V₉H₂O = 1:5) were added to the GO dispersion liquid, respectively. The dispersion liquid was treated by ultrasound for 10 min to disperse evenly. The dispersed liquid was transferred into the autoclave. After 12 h of reaction at 90 °C, the solution was cooled to room temperature, then frozen for 12 h at −20 °C to form water crystalline, which were transferred into freeze dryer and dried for 24 h to produce the CLGO/PAA aerogel.

2.4. Characterization methods
The prepared samples were characterized by field emission scanning electron microscopy (SEM, JSM-7001F), wide-range powder x-ray diffraction (XRD, AXS D8 x-ray diffraction spectrometer, Bruker, Germany) with a Cu Kα target at scan rate of 0.04° s⁻¹ in region of 2θ from 5° to 80°, IR absorption spectra in the range of 400–4000 cm⁻¹ (Nicolet, Impact 410) with KBr pellets, 5 mg of sample in 500 mg of KBr, and atomic absorption spectrometer (CorotrAA 700), respectively.

2.5. Absorption experiments
The adsorption kinetics study: 1 mg of adsorbent was added to 10 ml of 500 mg l⁻¹ Pb(II) solution, oscillated at 25 °C in water bath thermostat, and after a certain time interval, the Pb(II) concentration was measured using atomic absorption spectrometer (CorotrAA 700). The effect of the initial concentration of Pb(II) on the adsorption performance: 2 mg of adsorbent was added to the Pb(II) solution (150–1000 mg l⁻¹) with different initial concentration, and oscillated for 4 h at 25 °C in a water bath thermostat. The effect of initial pH on the adsorption properties was carried out at a concentration of 500 mg l⁻¹ at 25 °C in pH range of 3.0–7.0 (adjusted by 0.1 M HCl and NaOH solution). In addition, the regenerability of the aerogel was investigated: 1.8 mg of adsorbent was added to 10 ml, 500 mg l⁻¹ Pb(II) solution, shaken at 25 °C for 2 h in a water bath thermostat, desorbed with 5% HNO₃ after each adsorption, cyclic adsorption and measuring the amount of adsorption per time. The adsorption amount was calculated according to equation (1):

\[
Q = \frac{(C_0 - C_t)V}{m}
\]  

Where Q (mg g⁻¹) is adsorption amount, C₀ (mg l⁻¹) is the initial concentration of adsorbed solution, Cᵣ (mg l⁻¹) is equilibrium concentration of solution after adsorption t time, V (L) is the volume of adsorbed solution, m (g) is the mass of adsorbent.

3. Results and discussion

3.1. Characterization of the CLGO/PAA aerogel
In figure 2(a) is an optical photograph of the CLGO/PAA aerogel on the petal of the flower. The petal can support the aerogel body, indicating that the density of aerogel material is very low. Figures 2(b) and (c) are SEM
images of the side cross section of the CLGO/PAA aerogel, showing that the CLGO/PAA aerogel has a porous structure. Figure 2(d) is the SEM image of GO, the GO has a layered structure and different degrees of wrinkles. The presence of these wrinkles reduces the surface energy of the GO, thereby increasing its stability. Figures 2(e) and (f) are SEM images of CLGO/PAA aerogels of different magnifications. After the addition of acrylic acid, interconnected pleated elliptical porous network structures are formed. Compared with GO, CLGO/PAA aerogel has more pore structure and larger specific surface area, which is more favorable for adsorption.

From figure 3, the curve (b) shows that the diffraction peak $2\theta = 11.64^\circ$ on the (001) crystal plane is the characteristic peak of GO, indicating that GO is synthesized [31–33]. Curve (a) shows that the addition of PAA causes the peak to evolve into a broad peak, because the random arrangement of PAA increases the disorder of the material, and the original ordered arrangement of the layers is disturbed. It has been proven that acrylic has been successfully added to GO.

The FT-IR spectra of the PAA, GO and CLGO/PAA aerogel were shown in figure 4. In the infrared spectrum of GO (curve b). The characteristic peak of 3385 cm$^{-1}$ is corresponds (corresponding) to the $\text{–OH}$ stretching vibration peak. The characteristic peak of 1725 cm$^{-1}$ is due to the $\text{C=O}$ stretching vibration peak, the stretching vibration peak of $\text{C=C}$ at 1620 cm$^{-1}$, the stretching vibration absorption peak of $\text{C–O–C}$ at 1040 cm$^{-1}$, and the
characteristic absorption peak of epoxy group on GO at 878 cm$^{-1}$ [34]. Infrared spectrum of PAA (curve a) and CLGO/PAA aerogel (curve c), the infrared absorption peak is relatively wide at around 3442 cm$^{-1}$ and 3426 cm$^{-1}$, which is the stretching vibration peak of $\text{–OH}$, indicating that there is a hydrogen bond between GO and PAA [35]. The peak at 1739 cm$^{-1}$ and 1744 cm$^{-1}$ is attribute to a stretching vibration peak of C=O [36], the peak at 1396 cm$^{-1}$ is a stretching vibration peak of C–OH [37], and the peak at 1025 cm$^{-1}$ and 1000 cm$^{-1}$ is a stretching vibration peak of C–O. 800 cm$^{-1}$ is the out-of-plane deformation vibration of methylene, which proves the existence of long carbon chain of PAA. The results show that the structure of the CLGO/PAA aerogel is consistent with results of the IR spectra.

3.2. Comparing the adsorptive properties of the CLGO/PAA aerogel for Pb (II) with the other adsorbents

Table 1 is the comparison of the adsorption properties of different adsorbents for Pb (II) in the literature. The data show that the CLGO/PAA aerogel has better adsorption capacity. In order to acquire the optimal adsorption conditions of CLGO/PAA aerogel for Pb (II), the effects of adsorption kinetics, adsorption time, initial concentration of Pb (II), pH and number of cycles on adsorption performance were examined.

3.3. Stability of CLGO/PAA aerogel in water

After a certain amount of CLGO/PAA aerogel was immersed in water for 54 h, the leaching solution was taken to determine the infrared spectrum, and deionized water (DW) was used as a reference. Figure 5 shows the infrared spectrum of DW and CLGO/PAA leachate. The results showed that the leaching solution did not contain organic functional groups, indicating that the aerogel had good stability in water.

3.4. Adsorption studies of CLGO/PAA aerogel for Pb (II)

When Pb(II) is adsorbed by GO/PAA aerogel material, the unique porous structure of the aerogel material facilitates the diffusion of Pb(II), and the large specific surface area can provide more active binding sites [44, 45]. In the initial stage of adsorption, the Pb(II) solution was formed into a liquid film on the surface of the adsorbent, which provided a driving force for the migration of Pb(II) to the porous surface. As the concentration...
increased, the diffusion of Pb\(^{II}\) was accelerated. At this time, the adsorption rate was mainly affected by surface adsorption and internal diffusion \[21, 46, 47\]. However, the action of GO/PAA aerogel to adsorb Pb\(^{II}\) is mainly electrostatic interaction \[21, 48\]. The addition of PAA increases the carboxyl groups on the surface of the adsorbent. As the pH value increases, the protonation of the carboxyl groups is enhanced, therefore the adsorption capacity of Pb\(^{II}\) is enhanced, which in turn adsorbs more Pb\(^{II}\) \[47, 48\].

The adsorption kinetics of CLGO/PAA aerogel for Pb\(^{II}\) was analyzed by kinetic model. The pseudo-first-order kinetic and pseudo-second-order kinetic \[49–51\] can be calculated according to equations (2) and (3), respectively.

\[
\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

where \(q_e\) (mg g\(^{-1}\)) is the adsorption amount after adsorption equilibrium, \(q_t\) (mg g\(^{-1}\)) is the adsorption amount at the time of adsorption \(t\), \(k_1\) (min\(^{-1}\)) is the quasi-first-order kinetic constant and \(k_2\) (g/(mg-min)) is the quasi-second-order kinetic constant.

From the fitting results in figure 6 and table 2, it is known that the correlation coefficient \(R^2\) (0.957) of the pseudo-second-order kinetic model is closer to 1 than the pseudo-first-order kinetic model. In addition, the theoretical adsorption amount obtained by fitting the pseudo-second-order kinetic model (649.35 mg g\(^{-1}\)) is close to the experimental value (532 mg g\(^{-1}\)), from which it can be inferred that the adsorption of CLGO/PAA aerogel for Pb\(^{II}\) is more in line with the pseudo-second-order kinetics.

In figure 7(a), when the concentration of Pb\(^{II}\) is lower than 500 mg l\(^{-1}\), a large number of active substances are in the primary stage, and the adsorption rate is mainly controlled by surface adsorption \[21\]. With the increase of concentration, a concentration gradient appeared on the surface and inside of the adsorbent, which provided the necessary driving force for the migration of Pb\(^{II}\) to the porous, and accelerated the diffusion of Pb\(^{II}\) into the adsorbent \[47\]. At this time, the adsorption amount increases with the concentration of Pb\(^{II}\).

In the initial stage of adsorption, Pb\(^{II}\) liquid film is first formed on the surface of the adsorbent. The liquid film is positively charged. As the concentration of Pb\(^{II}\) increases, the concentration of Pb\(^{II}\) on the liquid film also increases. There is electrostatic repulsion between the membrane and the positively charged Pb\(^{II}\) in the solution \[46\]. Therefore, when the concentration of Pb\(^{II}\) is more than 500 mg l\(^{-1}\), the adsorption amount

---

**Table 2.** The fitted results of the adsorption kinetics of CLGO/PAA aerogel for Pb\(^{II}\).

| Pb\(^{II}\) Conc. (mg l\(^{-1}\)) | Qe(exp) (mg g\(^{-1}\)) | Qe(cal) | \(K_1\) (1 min\(^{-1}\)) | \(R^2\) | Qe(cal) | \(K_2\) (g/(mg-min)) \(\times 10^{-4}\) | \(R^2\) |
|---------------------------------|------------------------|----------|------------------------|----------|----------|----------------------------|----------|
| 500                             | 532                    | 15.197   | 0.0337                 | 0.722    | 649.35   | 0.363                        | 0.957    |

---

**Figure 5.** Infrared spectra of DW (Deionized water) and CLGO/PAA leachate.
decreases with the increase of Pb(II) concentration. When the concentration of Pb(II) is 500 mg l\(^{-1}\), the maximum adsorption capacity of the aerogel is 640 mg g\(^{-1}\).

In Figure 7(b), it can be seen that the effect of adsorption time on the amount of adsorption. At the beginning of adsorption, the CLGO/PAA aerogel has a large number of active adsorption sites, the adsorption rate is fast, and the adsorption amount increases with time. At this time, a large number of active substances are in the primary stage, and the adsorption rate is mainly controlled by surface adsorption \[21\]. When the adsorption reaches a certain time, the active sites on the adsorbent decrease, and a concentration gradient will exist on the surface and inside of the adsorbent, which will promote the diffusion of Pb(II) into the adsorbent \[48\]. At this time, the adsorption rate is determined by the internal diffusion of the adsorbent. The Pb(II) on the
adsorbent will also generate a repulsive force to the Pb(II) in the aqueous solution, further, increasing the difficulty of adsorption of Pb(II) in the aqueous solution, and causing the adsorption rate slow. The adsorption procedure reached to the equilibrium in 60 min. The adsorption rate increased with the contact time before 60 min, then became slow after 60 min. In addition, under the same adsorption time, the adsorption capacity of GO/PAA aerogel is higher than GO, indicating that the adsorption performance of GO/PAA aerogel material is better than GO when adsorbing Pb(II).

Figure 7(c) is the effect of pH on the amount of adsorption. When the pH below 6, the adsorption amount increases with the increase of pH. When the pH is greater than 6, the adsorption amount decreases with the increase of pH, and the adsorption amount reaches the maximum when pH = 6. When the pH is low, a large amount of $\text{H}^{+}$ is present in the solution, and at the same time, the oxygen-containing groups are protonated, resulting in a positively charged GO/PAA surface [45, 46]. There is a repulsive force between the adsorbent and Pb(II). Besides, excessive $\text{H}^{+}$ will occupy the limited adsorption sites of Pb(II), which is not conducive to the adsorption of Pb(II). As the pH value increases, more negatively charged adsorption sites are formed on the GO/PAA surface, and the competition between $\text{H}^{+}$ and metal ions weakens. Strong electrostatic attraction between Pb(II) and anionic groups on the surface of GO/PAA enhances the adsorption capacity of the adsorbent [21, 44, 48]. When the pH is greater than 6, Pb(II) will be hydrolyzed, and the hydrolyzed product will adhere to the surface of the adsorbent, which will affect the performance of the adsorbent, resulting in the decrease of adsorption amount.

Figure 7(d) shows the effect of the number of cycles on the amount of adsorption. After the CLGO/PAA aerogel cycling 5 times, the adsorption amount is 143 mg g$^{-1}$. The high recyclability of GO/PAA aerogel may be attributed to its stable skeleton structure [45]. Such recycle use not only improves the utilization of the adsorbent, but also demonstrates the value of the material for recycling.

4. Conclusions

In this study, we initiated the in situ polymerization of acrylic acid in GO to prepare CLGO/PAA aerogel and used it to remove Pb(II) from water. Through characterization and adsorption experiments, we found that the addition of PAA increased the pore structure of the adsorbent and provided more adsorption sites for adsorption. The adsorption amount of Pb(II) (500 mg l$^{-1}$) can reach to 640 mg g$^{-1}$, the adsorption equilibrium is reached in 60 min, and the adsorption effect is best when pH = 6. The addition of 1,4-butanediol achieved the recycling of the aerogel material. The experiment showed that the adsorption amount of Pb(II) was up to 143 mg g$^{-1}$ after 5 times cycle. This method provides a novel method which can efficient and renewable adsorption heavy metal ion in from wastewater.

Acknowledgments

This work was supported by grants from the National Natural Science Foundation of China (Nos. 21401170, 21271160, 91022111, 21371092), and Henan Province Science and Technology Major Project (No. 181100310300).

ORCID iDs

Zhijun Chen @ https://orcid.org/0000-0002-8274-8252

References

[1] Bi J T, Huang X, Wang J K, Wang T, Wu H, Yang L Y, Huang F F, Ji C and Chen X H 2019 Oil-phase cyclic magnetic adsorption to synthesize Fe$_3$O$_4@$TiO$_2$-nanotube composites for simultaneous removal of Pb(II) and Rhodamine B Chem. Eng. J. 366 50–61
[2] Fu F L and Wang Q 2011 Removal of heavy metal ions from wastewaters: a review J. Environ. Manage. 92 807–18
[3] Yu J, Zhao S K, Chen P, Zhu G T, Jiang X T and Di S Y 2019 Adsorption behavior and mechanism of Pb(II) on a novel and effective porphyrin-based magnetic nanocomposite Appl. Surf. Sci. 484 124–34
[4] Tan Y Q, Chen M and Hao Y M 2012 High efficient removal of Pb(II) by amino-functionalized Fe$_3$O$_4$ magnetic nano-particles Chem. Eng. J. 191 104–11
[5] Liang X X, Ouyang X K, Wang S Y, Yang I Y, Huang F F, Ji C and Chen X H 2019 Efficient adsorption of Pb(II) from aqueous solutions using aminopropyltriethoxysilane-modified magnetic attapulgite@chitosan (APTS-Fe$_3$O$_4$/APT@CS) composite hydrogel beads Int. J. Biol. Macromol. 137 741–50
[6] Kwaansa-Anshs E E, Knuurah M, Nti S O and Opoku F 2019 Adsorption of heavy metals (Cu, Mn, Fe and Ni) from surface water using oroychromis niloticus scales Pollution. 5 115–22
[7] Wu D, Wang Y G, Li Y, Wei Q, Hu L H, Yan T, Feng R, Yan J G and Du B 2019 Phosphorylated chitosan/CoFe$_2$O$_4$ composite for the efficient removal of Pb(II) and Cd(II) from aqueous solution: adsorption performance and mechanism studies J. Mol. Liq. 277 181–8
[8] Bhathini K K, Meena M S, Ghoshal A K and Saha P 2015 Supported liquid membrane based removal of lead(II) and cadmium(II) from mixed feed: conversion to solid waste by precipitation J. Hazard. Mater. 299 504–12

[9] Alyuz B and Veil S 2009 Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins J. Hazard. Mater. 167 482–8

[10] Hamza M F, Wei Y Z, Mira H I, Abdel-Rahman A A-H and Guibal E 2019 Synthesis and adsorption characteristics of grafter hydrazinyl amine magnetic-chitosan for Ni(II) and Pb(II) recovery Chem. Eng. J. 362 310–24

[11] Chu Y T, Khan M A, Wang F Y, Xie M Z, Wu I L and Zhu S D 2019 Kinetics and equilibrium isotherms of adsorption of Pb(II) and Cu(II) onto raw and arginine-modified montmorillonite Adv. Powder Technol. 30 1067–76

[12] Fan C Z, Li K L, Lin X Y, Ying D W, Wang Y L and Jia J P 2017 Comparative and competitive adsorption of Pb(II) and Cu(II) using tetrathylenglyptamine modified chitosan/CoFe2O4 particles J. Hazard. Mater. 326 211–20

[13] Tan Y, Wang K L, Yan Q, Zhang S F, Li Z J and Yi Y 2019 Synthesis of amino-functionalized waste wood flour adsorbent for high-capacity Pb(II) adsorption Rsc. Adv. 9 10475–84

[14] Huang M J, Shang Y S, Yang G L, Liu B X and Yang B 2019 Facile synthesis of hollow mesoporous MgO spheres via spray-drying with improved adsorption capacity for Pb(II) and Cd(II) Environ. Sci. Pollut. R 26 18825–33

[15] Xiong C, Wang S X, Sun W T and Li Y 2019 Selective adsorption of Pb(II) from aqueous solution using nanosilica functionalized with diethanolamine: equilibrium, kinetic and thermodynamic Microchem. J. 146 270–8

[16] Wang Y G, Shi L, Gao L, Wei Q, Cui L M, Hu L H, Yan L G and Du B 2015 The removal of lead ions from aqueous solution by using magnetic hydroxpropyl chitosan/oxidized multiwalled carbon nanotubes composite J. Colloid. Interf. Sci. 451 7–14

[17] Li X H, Liu Y M, Zhang J L, Zhao M Q and Zhu K H 2019 Study on the adsorption behavior of glutaric acid modified Pb(II) imprinted chitosan-based composite membrane to Pb(II) in aqueous solution Mater. Lett. 251 172–5

[18] Huang X, Wei D, Zhang X W, Fan D W, Sun X, Du B and Wei Q 2019 Synthesis of amino-functionalized magnetic acicular granular sludge-biochar for Pb(II) removal: adsorption performance and mechanism studies Sci. Total Environ. 685 681–9

[19] Wiśniewska M, Fijalkowska G, Ostolska I, Franus W, Nosalt-Wiercińska A, Tomaszewska B, Goscińska J and Wójcik G 2018 Investigations of the possibility of lithium extraction from geothermal water using natural and synthetic zeolites applying poly(acrylic acid) J. Clean. Prod. 195 821–30

[20] Kong W J, Yue Q Y, Li Q and Gao B Y 2019 Adsorption of Cd2+ on GO/PAA hydrogel and preliminary recycle to GO/PAA-Cds as efficient photocatalyst Sci. Total Environ. 668 1165–74

[21] Han Q Q, Li W X, Zhou Z Y, Fang Z, Xu Z W and Qian X M 2018 Self-assembled three-dimensional double network graphene oxide/polyacrylic acid hybrid aerogel for removal of Cu2+ from aqueous solution Environ. Sci. Pollut. R. 25 34438–47

[22] Park S and Ruffo R S 2009 Chemical methods for the production of graphenes Nat. Nanotechnol. 4 217

[23] Cui L M, Wang Y G, Hu L H, Gao L, Du B and Wei Q 2015 Mechanism of Pb(II) and methylene blue adsorption onto magnetic carbonate hydroxyapatite/graphene oxide RSC. Adv. 5 9759–70

[24] Wang L, Hu D, Kong X K, Liu J G, Li X H, Zhou Z, Zhao H G and Zhou C H 2018 Anionic polyelectrolyte Poly(–glutamic acid)–functionalized magnetite Fe3O4–GO–(o–MWCNTs) hybrid nanocomposite for high-efficiency removal of Cd(II), Cu(II) and Ni(II) heavy metal ions Chem. Eng. J. 346 38–49

[25] Abhishek R, Sharma P P, Vikrant Y, Hariom G and Vaibhav K 2019 Synthesis and characterization of different metal oxide and GO composites for removal of toxic metal ions Sep. Sci. Technol. 54 426–33

[26] Kaur N, Kaur M and Singh D 2019 Fabrication of mesoporous nanocomposite of graphene oxide with magnesium ferrite for efficient sequestration of Ni(II) and Pb(II) ions: adsorption, thermodynamic and kinetic studies Environ. Pollut. 253 111–9

[27] Subrati A, Mondal S, Ali M, Alhindhi A, Ghazi R, Abdalla A, Reinthal D and Alhashass S 2017 Developing hydrophobic graphene foam for oil spill cleanup Ind. Eng. Chem. Res. 56 6945–51

[28] Li J, Zhao S, Zeng X, Huang W, Gong Z, Zhang G, Sun R and Wong C P 2016 Highly stretchable and sensitive strain sensor based on facilely prepared three-dimensional graphene foam composite ACS. Appl Mater Inter 8 18934–61

[29] Dong X, Wang X, Wang L, Song H, Zhang H, Huang W and Chen P 2012 3D graphene foam as an efficient and recoverable adsorbent for Cd(II) and Pb(II) removal from aqueous solution J. Hazard. Mater. 381 120914

[30] Zhang J, Xie X, Li J, Meng X G and Gao H 2019 Characteristics and mechanism of Pb(II) adsorption/desorption on GO/rGO under sulfide-reducing conditions J. Ind. Eng. Chem. 73 233–40

[31] Qiao K, Guo S L, Zheng Y D, Xu X T, Meng H Y, Peng J, Fang Z Y and Xie X J 2018 Effects of graphene on the structure, properties, electro-response behaviors of GO/PAA composite hydrogels and influence of electro-mechanical coupling on BMSc-differentiation Mat. Sci. Eng. C-Mater. 93 853–63

[32] Dong J, Ozaki D and Nakashima K 1997 Infrared, Raman, and near-infrared spectroscopic evidence for the coexistence of various hydrogen–bond forms in poly(acrylic acid) Macromolecules 30 1111–7

[33] Yu Y, Shu Y and Ye L 2018 In situ crosslinking of poly (vinyl alcohol)/graphene oxide–glutamic acid nano-composite hydrogel as microbial carrier: intercalation structure and its wastewater treatment performance Chem. Eng. J. 336 306–14

[34] Liu D, Ding C, Chi F, Pan N, Wen J, Xiong J and Hu S 2019 Polymer brushes on graphene oxide for efficient adsorption of heavy metal ions from water J. Appl. Polym. Sci. 136 68136

[35] Kaur N, Kaur M and Singh D 2019 Fabrication of mesoporous nanocomposite of graphene oxide with magnesium ferrite for efficient sequestration of Ni(II) and Pb(II) ions: adsorption, thermodynamic and kinetic studies Environ. Pollut. 253 111–9

[36] Bao S, Yang W, Wang Y, Yu Y and Sun Y 2020 One-pot synthesis of magnetic graphene oxide composites as an efficient and recoverable adsorbent for Cd(II) and Pb(II) removal from aqueous solution J. Hazard. Mater. 381 120914

[37] Yao M, Wang Z, Liu Y, Yang G and Chen J 2019 Preparation of dialdehyde cellulose grafted graphene oxide composite and its adsorption behavior for heavy metals from aqueous solution Carbohydr. Polym. 212 345–51

[38] Yu Y, Zhang G and Ye L 2019 Preparation and adsorption mechanism of polyvinyl alcohol/graphene oxide–sodium alginate nanocomposite hydrogel with high Pb(II) adsorption capacity J. Appl. Polym. Sci. 136 67318
[44] Lei Y L, Chen F and Luo Y J 2014 Three-dimensional magnetic GO foam/Fe₃O₄ nanocomposite as an efficient absorbent for Cr (VI) removal J. Mater. Sci. 49 4236–45
[45] Zhang I Y, Zhang W L, Zhou Z Q and Li C M 2016 γ-Fe₂O₃ nanocrystals-anchored macro/meso-porous graphene as a highly efficient adsorbent toward removal of methylene blue J. Colloid Interf. Sci. 476 200–5
[46] Zhao B C, Jiang H. b., Lin Z K, Xua S. f., Xie J and Zhang A P 2019 Preparation of acrylamide/acyric acid cellulose hydrogels for the adsorption of heavy metal ions Carbohyd. Polym. 224 115022
[47] Liu C Y, Liu H Y, Xu A R, Tang K Y, Huang Y and Liu C L 2017 In situ reduced and assembled three-dimensional graphene aerogel for efficient dye removal J. Alloy. Compd. 714 522–9
[48] Chen L, Hao Q Q, Li W X, Zhou Z Y, Zhou F, Xu Z W, Wang Z X and Qian X M 2018 Three-dimensional graphene-based adsorbents in sewage disposal: a review Environ. Sci. Pollut. R 25 25840–61
[49] Kong W J, Li Q, Li X D, Su Y, Yue Q Y, Zhou W Z and Gao B Y 2018 Removal of copper ions from aqueous solutions by adsorption onto wheat straw cellulose-based polymeric composites J. Appl. Polym. Sci. 135 46680
[50] Jia C J, Zhao J H, Lei L L, Kang X Y, Lu R, Chen C T, Li S L, Zhao Y L, Yang Q X and Chen Z J 2019 Novel magnetically separable anhydride functionalized Fe₃O₄@SiO₂@PEI-NTDA nanoparticles as effective adsorbents: synthesis, stability and recyclable adsorption performance for heavy metal ions RSC Adv. 9 9533–45
[51] Lei L L, Yang Q X, Zhao J H, Zhang Y, Jia C Y, Lu R, Nie L M and Chen Z J 2019 Preparation and Adsorption of 2-Nitro-1,3-benzenediol of Fe₃O₄/GO/PPy composite. Chinese J. Inorg. Chem. 35 658–66