Facile synthesis of graphene oxide/palygorskite composites for Pb(II) rapid removal from aqueous solutions

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ABSTRACT

As a kind of earth-abundant and cheap natural clay mineral, palygorskite (Pal) was facilely modified by grafting with graphene oxide (GO) to fabricate GO/Pal composites for rapid removal of Pb(II) from aqueous solutions. The results of characterization confirmed that the GO/Pal composites were successfully grafted between GO sheets and Pal nanorods. The effects of pH, adsorbent dosage, adsorption time, initial Pb(II) concentration and temperature on the adsorption of Pb(II) onto the GO/Pal composites as adsorbents were systematically investigated. The maximum adsorption capacity over 106.6 mg/g was obtained within a short adsorption time of less than 1 h even at 298.15 K. The adsorption of Pb(II) was a fast process that more accurately followed the pseudo-second-order kinetic equation. This process also could be described better with the Langmuir equation model than the Freundlich model. The negative values of $\Delta G^\circ$ and the positive values of $\Delta H^\circ$ and $\Delta S^\circ$ indicated that it was a spontaneous, endothermic and entropy-increasing adsorption process. Compared with pristine Pal and GO powders, such the GO/Pal composites as a cost-efficient and eco-friendly adsorbents could significantly improve the adsorption properties of Pb(II) and would have potential application in the industrial wastewater treatment for rapid removal of Pb(II).

Key words | adsorption, graphene oxide, palygorskite, Pb(II) removal

NOMENCLATURE

Symbols

- $Q_e$ adsorption capacity at equilibrium (mg/g)
- $R_{100}$ Pb(II) removal rate (%)
- $C_0$ initial concentrations (mg/L) of Pb(II) in solution
- $C_e$ equilibrium concentrations (mg/L) of Pb(II) in solution
- $V$ volume of the solution (L)
- $m$ mass of adsorbent (g)
- $Q_t$ adsorption capacity at any time (mg/g)
- $k$ rate constants
- $Q_{e,exp}$ experimental values of the adsorption capacity at equilibrium (mg/g)
- $Q_m$ theoretical maximum values of the saturated adsorption capacity (mg/g)
- $K_L$ Langmuir coefficient (L/mg)
- $K_F$ Freundlich adsorption constant ((mg/g) (L/mg)$^{1/n}$)
- $n$ temperature-dependent dimensionless characteristic coefficient
- $R$ ideal gas constant, 8.314 J/(mol·K)
- $T$ absolute temperature (K)
- $K_d$ partition coefficient (mL/g)

INTRODUCTION

With the acceleration of economic development and urbanization in the world, more and more attention has been given to the water pollution such as potentially toxic heavy metals from aqueous solutions. As a type of non-degradable environmental pollutant, lead and its
compounds increasingly threatens natural ecosystems and humans. A large number of waste residues containing lead have been impregnated into the environment through waste gas or wastewater, resulting in pollution of the water environment even endangering human health (Günay et al. 2007). Especially, industrial wastewaters are considered to be the main source of lead pollution, which has become one of the important human environmental factors (Bhat et al. 2015). Therefore, it is necessary to eliminate lead from wastewater prior to emission into the environment. The current methods for lead removal from aqueous solutions mainly include chemical precipitation, ion exchange, reverse osmosis, adsorption and electrochemical precipitation, etc. (Unlu & Ersoz 2006). Many technologies of wastewater treatment containing lead have been examined, and adsorption is regarded as one of the most promising techniques (Unlu & Ersoz 2006). It is generally preferred for lead removal from aqueous solutions due to its simple operation, high efficiency, compatibility of different adsorbents and cost-effectiveness. However, it is still an important issue to design and synthesize excellent adsorbents with lower cost and higher adsorption performance for lead removal (Chen et al. 2017).

As a kind of earth-abundant and cheap natural clay minerals, palygorskite (Pal, also called attapulgite) is a hydrated magnesium aluminum silicate composed of the tetrahedral and octahedral layered structures to form zeolite-like channels with size about 0.58 nm × 0.64 nm (Chen et al. 2011; Li et al. 2015; Liu et al. 2015; Wang et al. 2017). It has a structure consisting of parallel ribbons of 2:1 layers and with the chemical composition of Mg₂Si₆O₂₀(OH)₄(OH₂)₄·4H₂O (Li et al. 2015; Wang et al. 2017). Moreover, Pal exhibits nanorod crystals of about 20–40 nm in diameter and 0.5–5 μm in length. Consequently, it is usually used as an excellent one-dimensional nanometer adsorption material, which has attracted attention for dye wastewater and heavy metal wastewater treatments (Chen et al. 2011; Li et al. 2015; Liu et al. 2015; Wang et al. 2017). Unfortunately, Pal clay has strong hydrogen bonds and electrostatic forces to facilitate the formation of rod-like stacks of crystal aggregates. To improve the adsorption properties, Pal is usually dispersed using additives in coordination with an ultrasonic hydrothermal process and modified with functional groups containing −NH₂ or −COOH and others. For example, Pal/carbon composites as adsorbents were designed and synthesized that had high adsorption capacities for Cr(VI) and dye from aqueous solution (Chen et al. 2011; Liu et al. 2015). Recently, Pal/carboxyl multiwalled carbon nanotubes (MWCNTs) composites were successfully grafting modification, showing good adsorption performance for Cr(VI) in our previous work (Wang et al. 2017). Nonetheless, more works were further done to improve its adsorption capacity and decrease its costs. As a typical 2D nanomaterial with various oxygen-containing groups and great specific surface area, graphene oxide (GO) provides great promise to fabricate adsorbents. Especially, GO with abundant oxygen-containing groups demonstrated high sorption affinity and far more effective than other routinely used sorbents such as bentonite clays and activated carbon even in acidic solutions (Hu et al. 2017; Li et al. 2017; Mojoudi et al. 2019). Thus, GO-based composite had a relatively high adsorption capacity of 59.1 mg/g for Fe(III) at 293 K in our recent investigation (Li et al. 2017). Although such GO adsorbent shows excellent physicochemical properties and adsorбability, it is not yet reasonable for large-scale application due to its cost (Yarı et al. 2015; Hu et al. 2017). Additionally, GO displayed good compatibility with many materials such as carbon and clay, exhibiting great prospects as composite adsorbents for application in wastewater treatment.

Although there are few reports on GO/Pal composites’ characteristics in the literature (Wang et al. 2013; Wang et al. 2019), its promising superior adsorption properties as adsorbent are a possibility that is worthy of evaluation. In this study, as shown in Figure 1, Pal was modified by grafting with GO to fabricate GO/Pal composites for rapid removal of Pb(II) from aqueous solutions. The adsorption kinetic, isotherm and thermodynamic behavior of Pb(II) on the GO/Pal composites as adsorbent were investigated in detail. The evaluation of pH, adsorbent dosage, adsorption time, initial Pb(II) concentration and temperature on the adsorption of Pb(II) were systematically carried out.

**MATERIALS AND METHODS**

**Materials**

Graphite oxide (SE2430) was purchased from the Sixth Element (Changzhou) Materials Technology Co., Ltd and palygorskite powder (JC-TW03, the average size of 7 μm) was provided by Jiangsu Jiuchuan Nanomaterial Technology Co., China. Sodium hexametaphosphate (Na₆O₁₈P₆) was purchased from Aladdin Industrial Corporation (Shanghai, China). Acetic acid, anhydrous sodium acetate, xylenol orange disodium salt, nitric acid, sodium hydroxide, and lead nitrate were obtained from Tianjin Fuchen Chemical Reagent Factory, China. All chemical reagents were of
analytical grade and without further purification prior to use. Home-made deionized water was used in all experiments.

**Preparation of GO/Pal composites**

Palygorskite powders were dispersed in 0.6 g/L Na₆P₆O₁₈ aqueous solution, followed by ultrasonic hydrothermal method for 20–30 min to get a 0.8 g/L uniform dispersion (Wang et al. 2019). Simultaneously, graphite oxide was also dispersed with ultrasomics into water for 30 min to exfoliate a 0.4 g/L homogeneous yellow dispersion. Then, the two dispersions were mixed with the ratio of GO/Pal as 1:4 (mass ratio) and vigorously stirred for 3 h to ensure GO sheet layers intercalated by Pal nanorods and thus forming GO/Pal composites. Finally, the resulting mixtures were washed with deionized water several times, followed by being dried at 323.15 K for 24 h and used as adsorbents for the following adsorption testing and characterization.

**Batch adsorption experiments**

A stock Pb(II) solution of 1,000 mg/L was prepared and further diluted to the required Pb(II) concentrations before use. The batch adsorption experiments were conducted in 50 mL conical flasks with a certain amount of GO/Pal adsorbents and 20 mL of Pb(II) solutions and then equilibrated in a thermostatic water bath oscillator. The pH of the Pb(II) solution was adjusted with 0.1 mol/L HNO₃ and NaOH. After adsorption equilibrium, the adsorbent was separated from solution by centrifugation at 8,000 rpm (CR21GIII, Hitachi, Japan) and the Pb(II) concentration in the solution was measured with the xylene orange spectrophotometric method using a UV-vis spectrophotometer (Lambda35, Perkin Elmer, America) at a wavelength of 570 nm. The adsorption capacity (Qₑ, mg/g) and the removal rate (R%) of the adsorbent for Pb(II) solution were calculated according to the following equations:

\[
Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)
\]

\[
R\% = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)
\]

**Characterization**

Fourier-transform infrared spectra (FTIR, Nicolet 6700, Thermo, USA) were conducted with the KBr tablet method in transmittance mode with 4 cm⁻¹ resolution in the wavenumber range of 4,000–400 cm⁻¹. X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV X-ray diffractometer with Cu Kα source (λ = 0.15418 nm, 40 kV, 20 mA) from 5° to 40°. The surface morphology of these
samples was observed by field emission scanning electron microscope (FESEM, SU-8020, Hitachi, Japan).

RESULTS AND DISCUSSION

Characterization of GO/Pal composites

As shown in Figure 2(a), the GO usually displayed a characteristic reflection at \(2\theta = 10.3^\circ\), while Pal had a series of distinctive reflections at \(2\theta = 8.4^\circ, 13.6^\circ, 16.3^\circ, 19.7^\circ, 26.6^\circ\) and \(35.1^\circ\) (Wang et al. 2011). However, once GO sheets were intercalated by Pal nanorods to form GO/Pal composite, the intensity of GO reflection (\(2\theta = 10.3^\circ\)) and Pal characteristic reflections (for example, \(2\theta = 8.4^\circ\)) were significantly weakened without disappearance (Wang et al. 2017). It is also indicated that the Pal’s ribbon-layer structure composed of continuous tetrahedron sheets and discontinuous octahedron sheets was contorted, and the ordered arrangement of the overall lattice structure was partially damaged (Mu & Wang 2016). Moreover, the diffraction intensity of other reflections displayed no obvious change, suggesting that the silicon-oxygen tetrahedron chains of Pal had not been degenerated (Mu & Wang 2016). It is also consistent with the FTIR results as shown in Figure 2(b). The absorption bands of Pal powder at 1,654 cm\(^{-1}\), 3,430–3,550 cm\(^{-1}\) were ascribed to the H – O – H bending band modes of the zeolitic, adsorbed and crystal water molecules, and those bands at 1,031 cm\(^{-1}\) and 987 cm\(^{-1}\) were attributed to the stretching bands of Si – OH (or Si – O – Si) and Al – OH, respectively (Li et al. 2016). After modification with GO, the intensity of the modified Pal bands at 1,654 cm\(^{-1}\) and 1,031 cm\(^{-1}\) showed more strongly than those of pristine Pal, which was attributed to the amalgamation of the GO band at 1,724 cm\(^{-1}\) (C = O stretching band of carbonyl and carboxyl groups) and 1,621 cm\(^{-1}\) (–OH groups of adsorbed water) with the Pal band at 1,654 cm\(^{-1}\), and the esterification reaction occurred between GO (C – O stretching band at 1,063 cm\(^{-1}\)) and Pal (Si – OH at 1,031 cm\(^{-1}\)). In addition, the surface morphology of the Pal powders before and after the modification with GO was contrastively observed by FESEM. As depicted in Figure 2(c), the dimensions of Pal nanorods were mainly roughly 20 nm in diameter and 0.4–1 \(\mu\)m in length, and the rod-like morphology closely stacked together. GO sheets were 2D platelet-like and stacked in several layers (Figure 2(d)). By sonicating and vigorously stirring in aqueous solution, the rod-like Pal

\[\text{Figure 2} \quad \text{(a) XRD patterns, (b) FTIR spectra and FESEM images of (c) Pal, (d) GO, and (e) GO/Pal composites.}\]
nanorods would be intimately incorporated with random location into or on the surface of GO platelets to form GO/ Pal composites as shown in Figure 2(e). The above results of characterization precisely demonstrated that the GO/Pal composites were successfully modified with the GO sheets and Pal nanorods (Wang et al. 2017; Wang et al. 2019).

Effect of pH

The pH in the aqueous solution is an important factor to influence the adsorption process, due to possibly changing the surface charge of adsorbent and the ionization behavior between adsorbent and metal ions. As shown in Figure 3(a), the Pb(II) species distribution with pH in an aqueous solution was simulated with Visual MINTEQ 3.1 software. The Pb$^{2+}$ cation of Pb(II) species predominantly existed over 97.8% within a pH range from 1.0 to 6.0, and then its concentration immediately decreased with increasing pH values at pH > 6.0 in the aqueous solution due to its precipitation (Faur-Brasquet et al. 2002). At pH > 6.0, the Pb(II) species formed lead hydroxide species or precipitate with hydroxide anions. A number of other lead species such as Pb$_4$(OH)$_6$$^{4+}$, Pb$_4$(OH)$_4$$^{4+}$, PbOH$^+$, Pb$_2$OH$_3$$^{3+}$, Pb(OH)$_2$(aq) and Pb(OH)$_3$ in the solution remained in the pH range of 5.0–12.0 (Faur-Brasquet et al. 2002). Therefore, to optimize the pH in the suspensions, the batch adsorption experiments were conducted in the initial pH range from 2.0 to 6.0 to acquire maximum Pb(II) removal efficiency. As shown in Figure 3(b), as the pH increased, both adsorption capacity and removal rate of Pb(II) onto GO/Pal composites sharply increased with increasing pH values from 2.0 up to 5.0 and then nearly became constant after pH > 5.0. Moreover, the point of zero charge (pH$_{pzc}$) of GO/Pal composite was determined as around 5.4 (Figure S1, Srivastava et al. 2006). Thus, Pb$^{2+}$ cations more favorably adsorbed on the negatively charged surface of GO/Pal composite in the pH > pH$_{pzc}$ due to strong electrostatic interactions and resulted in high removal efficiency, which was some slight deviation from experimental results in Figure 3(b). When the pH is higher than 6, the precipitation of Pb(II) species will affect adsorption performance. As discussed above from Figure 2(b), the adsorbent surface was rich in abundant –OH, C = O, –COOH and other groups, and thus the surface was prone to a protonation or deprotonation process in the aqueous solution with different pH. Under a strong acid condition, the number of proton adsorption sites on the adsorbent surface increased, which might result from competitive interaction with protons and electrostatic repulsion between protons and Pb(II) ions for the active adsorption sites of the solid surface leading to a decrease in metal ion uptake (Chen et al. 2017). Therefore, Pb$^{2+}$ cation adsorption was suppressed in the lower pH ranges. Meanwhile, the adsorption performance increased gradually with increasing pH up to 5.0, which was related to the availability of more negatively charged surfaces (more active –Si – O$, –COO$ groups) and the rising electrostatic attraction between Pb(II) metal ions and solid surface sites (Mu & Wang 2016). Therefore, unless otherwise stated, pH 5.0 was selected as the optimum pH for the following other experiments.

Effect of adsorbent dosage

The effect of adsorbent dosage on the Pb(II) adsorption was studied by adding various amounts of GO/Pal composites into the solution containing 20 mL of 50 mg/L Pb(II)
solution at pH 5.0. As described in Figure 4, the Pb(II) removal rate increased from 13.5% to 63.3% as the adsorbent dosage increased in the range from 5 to 25 mg, and then held almost constant as the adsorbent dosage was above 25 mg. This could be attributed to the unsaturated adsorption sites during the adsorption process thus eventually increasing with growing adsorbent amounts (Chen et al. 2017). However, the adsorption capacity decreased when the adsorbent dosage was over 10 mg. It might be related that excess adsorbent was accumulated and then the active site was covered resulting in a decrease in the adsorption capacity. Therefore, 10 mg GO/Pal composite (i.e. 0.5 g/L adsorbent/solution) was selected for further experiments.

Effect of initial Pb(II) concentrations

The adsorption of Pb(II) onto the GO/Pal composite was investigated by varying the initial Pb(II) concentration from 10 to 100 mg/L, which is the common concentration range of industrial effluent. Meanwhile, the limits for maximum permissible concentrations in drinking water and wastewater in China are 0.05 and 1 mg/L, respectively. As shown in Figure 5, the percentage of Pb(II) removal decreased from 100% to 50.3% with the increasing initial concentration due to the fixed adsorbent dosage in this work. This might have contributed to the lower availability of adsorption sites at the higher Pb(II) dose. The Pb\(^{2+}\) cation with higher concentration required more active adsorption sites on the adsorbent for rapid removal. The gradual increase of Pb\(^{2+}\) cation concentration gradually saturated these active adsorption sites (Badawi et al. 2017). The increase of Pb(II) concentration would accelerate their diffusion from the solution to the adsorbent surface and would provide the increased driving force to overcome the resistance to the mass transfer of Pb\(^{2+}\) between the aqueous phase and solid phase. Thus, the adsorption uptake of Pb(II) (or equilibrium adsorption capacity) was significantly enhanced by an increase in initial concentration due to the increasing driving force of the concentration gradient with the increasing initial Pb\(^{2+}\) concentration (Badawi et al. 2017). Therefore, as shown in Figure 5, the adsorption capacity increased from 21.0 for 10 mg/L of Pb(II) initial concentration to 101.5 mg/g for a 100 mg/L concentration. The following sorption isotherms (Figure 7) also presented this similar trend.

Adsorption kinetics

To evaluate the removal effectiveness of GO/Pal composite, the effect of contact time on the Pb(II) adsorption properties is presented in Figure 6. The adsorption rate of the initial stage was very fast and the adsorption equilibrium could be reached within 60 min (\(Q_e\) about 60 mg/g), indicating that the molecules’ adsorption was on the external surface of the particles and the adsorption of the GO/Pal composite for Pb(II) was a rapid process. Moreover, nearly 100% of Pb(II) could be removed within 60 min. Following this phase a slow process occurred, which was possibly because after the adsorption on the exterior surface reached the saturation point, the metal ions diffused into the pores and then were adsorbed by the interior surface of the adsorbent. In order to further explore the adsorption kinetics of Pb(II) on GO/Pal composite, two kinetic models including the pseudo-first-order (Equation (3)) and pseudo-second-order...
(Equation (4)) kinetic models were introduced as follows (Ho & McKay 1999; Azizian 2004; Ho 2006):

\[
\ln \left( \frac{Q_e}{Q_t} \right) = \ln \frac{Q_e}{C_0} - k_1 t \quad (3)
\]

\[
t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (4)
\]

where \( Q_t \) and \( Q_e \) are the adsorption capacity (mg/g) at any time \( t \) (min) and at equilibrium, respectively; \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg-min)) are the rate constants calculated based on the data in Figure 6 at different temperatures from the pseudo-first-order and pseudo-second-order adsorption models, respectively. As seen in Table S1, the pseudo-second-order kinetic equation (linear correlation coefficient \( R^2 \) larger than 0.99) was better than the pseudo-first-order model (linear correlation coefficient \( R^2 \) less than 0.94) to describe the Pb(II) adsorption kinetics process. Also, the theoretically calculated \( Q_e \) values from the pseudo-second-order model seemed generally closer to the experimental values (\( Q_{e,exp} \)) compared to those from the pseudo-first-order equation. Therefore, the kinetic modeling of Pb(II) adsorbed by the GO/Pal composite belongs to the pseudo-second-order kinetic model. According to the assumption of the pseudo-second-order model, it means that the adsorption of Pb(II) on GO/Pal adsorbents seems inclined to a chemical adsorption process (Ho 2006).

**Adsorption isotherms**

Figure 7 presents the adsorption isotherms of Pb(II) on GO/Pal composites as the relationship between the adsorption capacity at equilibrium and the equilibrium concentration of Pb(II) in the solution. The adsorption isotherms were attained at an initial Pb(II) concentration range of 10–200 mg/L at temperature ranges of 298.15–318.15 K. As shown in Figure 7, the adsorption capacities rapidly increased with the increasing equilibrium concentration of Pb(II), and then achieved equilibrium at a concentration higher than 100 mg/L, indicating that nearly all of the available adsorption sites on the adsorbent would be saturated at the equilibrium state.

In order to illustrate the adsorption mechanism of Pb(II) on GO/Pal composites, the Langmuir (Langmuir 1918) and Freundlich (Badawi et al. 2017) isotherm models are commonly adopted to analyze the adsorption mechanism of metal ions on the adsorbent surface. The nonlinear forms of the Langmuir (Equation (5)) and Freundlich (Equation (6)) equations are given as follows (Liu et al. 2018):

\[
Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (5)
\]

\[
Q_e = K_F C_e^{1/n} \quad (6)
\]

where \( Q_m \) is the theoretical maximum values of the saturated adsorption capacity calculated from Langmuir fitted lines. The constant \( K_L \) (L/mg) is the Langmuir coefficient, which is related to the adsorption energy. \( K_F \) ((mg/g) (L/mg)\(^{1/n}\)) is the Freundlich adsorption constant and \( n \) is the temperature-dependent dimensionless characteristic coefficient. Specifically, a larger \( K_F \) value suggests a greater adsorption capacity, and a large \( n \) value indicates stronger adsorption strength. The data of Pb(II) equilibrium adsorption from Figure 7 fitted by the Langmuir and Freundlich models are presented in Figure S2 and the calculated parameters at different temperatures are listed in Table S2, respectively. The experimental data for Pb(II) adsorbed
onto GO/Pal composites at different temperatures were fitted with the Langmuir isotherm better than the Freundlich model according to the correlation coefficient ($R^2$) and RMSE (root mean square error) analysis. In addition, the maximum adsorption capacity ($Q_m$) with the Langmuir model increased with increasing temperatures, and those values calculated at temperature ranges of 298.15–318.15 K (109.72, 117.37, 121.55 mg/g, respectively) were very close to those experimental values, as shown in Figure 6 (106.64, 116.26, 119.44 mg/g, respectively). Therefore, the Langmuir isotherm model, rather than the Freundlich model, was better fitted to the Pb(II) adsorption on GO/Pal composites, indicating that the adsorption process exhibited homogeneous adsorption characteristics and a high monolayer adsorption capacity.

Furthermore, to evaluate the effect of temperature on the adsorption process of Pb(II) on GO/Pal composites, the adsorption thermodynamic parameters such as Gibbs free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) were calculated with the data in Figure 6 using the following equations:

$$K_d = \frac{(C_0/C_e - 1)V}{m} \tag{7}$$

$$\Delta G^o = -RT \ln K_d = -RT \ln (K_d/C_e) \tag{8}$$

$$\frac{\partial \Delta G^o}{\partial T} = -\Delta S^o \tag{9}$$

$$\Delta H^o = \Delta G^o + T\Delta S^o \tag{10}$$

The thermodynamic parameters were calculated and are listed in Table S3. As seen from Table S3, the values of $\Delta H^o$ and $\Delta S^o$ in the temperature range were positive, indicating that the adsorption of Pb(II) on GO/Pal composites was an endothermic and entropy-increasing process. Meanwhile, the negative values of $\Delta G^o$ suggested that the adsorption process was a spontaneous process and thus improved temperature was conducive to the adsorption process. Generally, if the values of $\Delta H^o$ in the adsorption process are in the range of 40–800 kJ/mol, the adsorption is usually a chemisorption process. Otherwise, values less than 40 kJ/mol belong to a physisorption process. The values of $\Delta G^o$ for the physisorption adsorption process were between 0 and $-20$ kJ/mol, the hybrid process of physisorption together with chemisorption adsorption was within $-20$ to $-80$ kJ/mol, while the chemisorption process was in the range of $-80$ to $-400$ kJ/mol. Therefore, these values of $\Delta H^o$ and $\Delta G^o$ in Table S3 suggested the adsorption of Pb(II) on GO/Pal composites in this work was physisorption together with a chemisorption adsorption process.

Comparison of adsorption performance

The adsorption performance of Pb(II) on the Pal, GO and GO/Pal composites were compared under the same optimized conditions. As demonstrated in Figure 8, GO/Pal composites through modification reaction could effectively improve the Pb(II) adsorption performance from aqueous solutions. In addition, the adsorption properties of GO/Pal composites in this work and other reported results for Pb(II) on different Pal (or GO)-based adsorbents are comparatively listed in Table S4. The higher adsorption capacity of GO/Pal composite for Pb(II) was acceptable, compatible, and comparable with other adsorbents at room temperature within rapid time. Therefore, GO/Pal composites could be a new potential economical sorbent for Pb(II) removal.

CONCLUSIONS

GO/Pal composites with excellent adsorption properties for Pb(II) from aqueous solutions were successfully synthesized by grafting modification between GO sheets and Pal nanorods. The adsorption of Pb(II) on GO/Pal composites achieved adsorption equilibration rapidly within 60 min. The experimental results of bath adsorption were in good agreement with the Langmuir adsorption isothermal model and the kinetics of Pb(II) adsorption obeyed the pseudo-second-order model. The adsorption process was found to be a spontaneous endothermic process from the thermodynamic study. Moreover, compared with pure Pal clay and GO powder, the modification of GO/Pal adsorbent was shown to

![Comparison of adsorption performance](image)

Figure 8 | The adsorption capacities of Pb(II) on the Pal, GO, and GO/Pal composite ($T = 318.15$ K, $m = 10$ mg, $C_0 = 200$ mg/L, $V = 20$ mL, $pH = 5.0$, $t = 12$ h).
enhance the adsorption capacity. As such, the GO/Pal composite is expected to be a new type of highly efficient adsorbent for industrial wastewater containing Pb(II).

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