A Highly Efficient Adsorbent Based On Starch-Graphene Oxide Architecture For Scavenging Aqueous Pb(II): Isotherms, Kinetics, Thermodynamics And Interaction Mechanism

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**A Highly Efficient Adsorbent Based On Starch-Graphene Oxide
Architecture For Scavenging Aqueous Pb(II): Isotherms, Kinetics,
Thermodynamics And Interaction Mechanism**

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Bangwen Zhang: Project administration, Funding acquisition

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Yanghuan Zhang: Validation

Bo Li: Supervision

Declarations

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Abstract Heavy metal pollution stems from the modern industry is a severe environmental problem. In this work, a highly efficient adsorbent based on starch-graphene oxide architecture (SGO) was fabricated, characterized and employed to scavenge aqueous Pb(II). The scavenging performance was evaluated, and the interaction mechanism between SGO and Pb(II) was elucidated. Results indicate, the starch introduction brought performance enhancement, consequently made SGO outperform both single starch and GO in terms of adsorption efficiency. SGO adsorbs 95.83 % of Pb(II) in 16 min, with adsorption capacity $383.32 \text{ mg}\cdot\text{g}^{-1}$, manifesting some advantages over other analogous adsorbents, such as higher capacity and faster kinetics. The chemical interaction between $\text{Pb}(\text{OH})^+$ and C=O, C-O related groups in SGO supported the adsorption, which was a spontaneous, exothermic and entropy increasing process. The adsorption was well described by the Freundlich, pseudo-second-order model and Intra-particle diffusion models, both intra-particle diffusion and chemical interaction were the rate controlling steps. Based on its high adsorption efficiency, SGO may have promising application in heavy metal scavenging from water.

Keywords Starch-graphene oxide; Pb(II); Scavenging; Adsorption; Interaction mechanism

1. Introduction

The expediting urbanization and industrialization have caused severe environmental issues. Industries including mining, metallurgy, batteries manufacturing, alloys, electroplating [1] discharge excessive amount of heavy metals into aquatic environment, give rise to ever worsening pollution. Heavy metals are related to various toxicological problems such as diarrhea, anaemia, cancer, kidney disease, bone defects, or even mutations in living cells [2]. Among heavy metals, divalent lead Pb(II) is a most hazardous one. Therefore, efficient scavenging Pb(II) from aquatic environment is an issue of both academical interest and technological significance.

Various techniques including chemical precipitation [3], ion exchange [4], membrane extraction [5], electrochemical separation [6], and adsorption [7-13] have

been applied for heavy metal scavenging. In particular, adsorption is recognized as one of the most promising techniques due to its high efficiency, design flexibility, operation easiness, and low cost. As adsorption efficiency is highly dependent on adsorbent quality, exploring high performance adsorbent is urgently needed and eagerly pursued.

Graphene is a novel carbon allotrope bearing single layer carbon atoms with two-dimensional configuration. Owing to its ultra high theoretical specific surface area, good chemical stability and nontoxicity, graphene has promising applications in the field of environmental remediation. Graphene oxide (GO) is an important graphene derivative, which is the precursor of many graphene based materials. GO has the same framework as graphene, and can be fabricated via oxidative exfoliation on natural graphite. Various oxygenous groups including hydroxyl, carbonyl, carboxyl, epoxy are introduced onto aromatic rings during GO fabrication. These oxygenous groups can serve as adsorption sites for both organic and inorganic contaminants. Particularly, GO showed great adsorptive potential towards various heavy metals [15-17].

Except for graphene, bio-adsorbents have received increasing research interests owing to their biodegradability, eco-friendliness, abundant source, and low cost. Various bio-adsorbents such as biochar [7], chitosan [8], cellulose [9], lignin [10], alginate [11], and starch [12] have been employed as adsorbents for wastewater decontamination. Among them, starch has many advantages, such as nontoxicity, biocompatibility, and environmental friendliness. Moreover, abundant hydroxyl groups in starch can act as complexation sites to uptake heavy metals. Thus, a composite based on starch-graphene oxide architecture is expected to fully exploit the adsorption capacity of both starch and graphene to form a high performance adsorbent.

X.F. Ma et al [13] prepared porous starch xanthate (PSX) and porous starch citrate (PSC) for adsorptive removal of aqueous Pb(II). Under optimum condition, PSX and PSC reached maximum adsorption capacities of $109.1 \text{ mg}\cdot\text{g}^{-1}$ and $57.6 \text{ mg}\cdot\text{g}^{-1}$ for Pb(II), respectively, as determined by Langmuir fitting. The adsorption process could

be well described by the pseudo-second-order model and the Langmuir model. H. Hosseinzadeh [14] prepared starch-graft-poly(acrylamide)/graphene oxide/hydroxyapatite nanocomposite hydrogel via free radical graft copolymerization. The as prepared hydrogel exhibited a feasible, spontaneous and endothermic adsorption for malachite green (MG) dye from aqueous solution, with a maximum adsorption capacity of $297 \text{ mg}\cdot\text{g}^{-1}$. Z.A. Wang et al [15] prepared a soluble starch-functionalized graphene oxide composite (GO-starch) via esterification reaction. The as prepared composite exhibited maximum uptake capacity $43.20 \text{ mg}\cdot\text{g}^{-1}$ for aqueous Cd(II) under optimum condition. The adsorption was endothermic, feasible and spontaneous, which can be well described by the pseudo-second-order model and the Langmuir model. J. Teng et al [16] prepared a porous 3D graphene oxide-starch composite via hydrothermal treating. The as prepared composite showed adsorption capacities of $108.68 \text{ mg}\cdot\text{g}^{-1}$, $32.12 \text{ mg}\cdot\text{g}^{-1}$, $46.28 \text{ mg}\cdot\text{g}^{-1}$, $41.76 \text{ mg}\cdot\text{g}^{-1}$ and $38.168 \text{ mg}\cdot\text{g}^{-1}$ for aqueous Pb(II), Cu(II), Cd(II), Yb(III) and Nd(III), respectively. K.C. Lai et al [17] prepared a xanthan biopolymer integrated 3D hierarchical graphene oxide/titanium dioxide composite using an ice-templating technique. The as prepared composite exhibited maximum adsorption capacity $132.18 \text{ mg}\cdot\text{g}^{-1}$ to $199.22 \text{ mg}\cdot\text{g}^{-1}$ in the temperature range $30\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ for aqueous Pb(II).

In spite of the above research achievements, the adsorption performance of starch-graphene oxide architecture on aqueous Pb(II) is yet to be comprehensively evaluated based on the consideration of the various adsorption parameters, and the interaction mechanism is yet to be revealed at an atomic level. Herein, a starch-graphene oxide composite was fabricated, characterized, and employed as an adsorbent to scavenge aqueous Pb(II) with high efficiency. The scavenging performance was evaluated, and the interaction mechanism was clarified.

2. Experiments and methods

2.1. Materials

Natural flake graphite, KMnO_4 , H_2SO_4 (98 wt%), H_2O_2 (30 wt%), HCl (37.5 wt%), starch ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), $\text{Pb}(\text{NO}_3)_2$, NaOH, EtOH, deionized water. All chemicals are analytically pure.

2.2. Preparation of SGO

GO was synthesized via oxidizing natural flake graphite according to a modified Hummers method [18]. SGO was fabricated via following procedure. Firstly, GO colloidal ($2.3 \text{ mg}\cdot\text{mL}^{-1}$, 100 mL) was ultrasonicated for 30 min for adequate dispersion. Afterwards, fine powder of 0.0766 g water soluble starch ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) was dissolved in 4.5 mL 100 °C deionized water to obtain a starch solution. The as obtained starch solution was added into the GO colloidal, which was ultrasonicated for another 30 min to obtain a homogeneous dispersion. The as-obtained dispersion was transferred into a Teflon-lined stainless steel autoclave and subject to hydrothermal disposal at 180 °C for 10 h. Finally, the product was rinsed with deionized water and EtOH repeatedly and vacuum dried at 60 °C to obtain SGO.

The fabrication process of SGO was illustrated in Scheme 1.

2.3. Characterization methods

The morphology of the samples were observed using transmission electron microscope (TEM; JEOL JEM-2100, Japan). Sample phase was identified by X-ray diffraction (X'Pert PRO, Cu-Ka). The functional groups of the samples were analyzed using Fourier transformation infrared spectroscopy (Bruker IFS66V), Ultraviolet-Visible light spectroscopy (UV-Vis; HITACHI, U-3900, Japan), and Raman spectra (RS; XploRA PLUS, France). The mass content of functional groups in the sample was determined by TG-DTA (NETZSCH STA449C) analyses. The BJH pore distribution and the BET specific surface area of the sample were determined based on the N_2 adsorption-desorption tests conducted on a specific surface and pore size analyzer (Micromeritics; ASAP 2020 V3.04 G). The *pH* of the sample hydrosol was monitored by a *pH* meter (Shanghai Leici Co. Ltd; PHS-3E) for zeta potential measurements using a micro electrophoresis meter (Shanghai Zhongchen Co. Ltd; China) under varying *pH*. The surface elements of the samples before and after Pb(II) adsorption were analyzed using X-ray photoelectron spectra (XPS; Kratos Axis Supra, Al-Ka radiation).

2.4. Batch adsorptions

Pb(II) solutions with a series of target concentrations ($100\text{-}1000 \text{ mg}\cdot\text{L}^{-1}$) were

obtained by dissolving the exact amount of $\text{Pb}(\text{NO}_3)_2$ in deionized water. For batch adsorptions, 20 mL of the $\text{Pb}(\text{II})$ solution was put into a conical flask. The pH of $\text{Pb}(\text{II})$ solution was adjusted to target value (2-12) using 0.1 M HCl or NaOH under the supervision of a pH meter. A certain dosage (200-700 $\text{mg}\cdot\text{L}^{-1}$) of SGO was added into the flask, which was then shaken in a shaker under a preset temperature (10-35 $^\circ\text{C}$). A certain duration of contact time (2-20 min) was completed for $\text{Pb}(\text{II})$ adsorption. Finally, SGO was immediately recovered via vacuum filtration to obtain a clear filtrate. The $\text{Pb}(\text{II})$ adsorbed sample was collected for XPS analysis. The residue concentration of $\text{Pb}(\text{II})$ in the filtrate was measured by atomic absorption spectrophotometer (PerkinElmer A800, USA).

The adsorbent dosage D ($\text{mg}\cdot\text{L}^{-1}$), adsorption percent R_i (%) and adsorption quantity Q_i ($\text{mg}\cdot\text{g}^{-1}$) were determined by the Eqs. (1)-(3):

$$D = \frac{m}{V} \quad (1)$$

$$R_i = \frac{C_0 - C_i}{C_0} \times 100\% \quad (2)$$

$$Q_i = \frac{(C_0 - C_i)V}{m} \quad (3)$$

Where $i = 0, e$, and t indicate the start, equilibrium and t moment, respectively. C_i ($\text{mg}\cdot\text{L}^{-1}$), V (mL), and m (g) denotes the concentration, volume of $\text{Pb}(\text{II})$ solution, and the mass of adsorbent, respectively. All experiments were conducted in duplicate with mutual difference lower than 5%, and the mean values were presented.

Cyclic adsorption: The $\text{Pb}(\text{II})$ loaded adsorbent was put into 20 mL deionized water, whose pH was adjusted to 2. Then the suspension was shaken for 30 min. Subsequently, the regenerated adsorbent was recovered and used for the next cycle of adsorption. Five consecutive cycles were fulfilled with a same procedure.

3. Adsorption fittings, interaction mechanism

The Langmuir, Freundlich, Temkin and D-R models were used to identify the adsorption type. The pseudo-first-order (PFO), pseudo-second-order (PSO), intra-particle diffusion (IPD), liquid film diffusion (LFD), and Bangham models were used to investigate the adsorption kinetics. The Van't Hoff equation was used to

determine the thermodynamic parameters. The interaction mechanism between adsorbate and adsorbent was elucidated based on comprehensive analyses on the adsorption experiment, adsorption fitting, and the XPS spectra of the adsorbate loaded and unloaded adsorbent.

4. Quantitative evolution of aqueous Pb(II) species with pH

The following reaction was analyzed in terms of equilibrium thermodynamics to quantitatively determine the evolution of aqueous Pb(II) species with pH :

$$\beta_i = \frac{C_{Pb(OH)_i^{2-i}}}{C_{Pb^{2+}} \cdot C_{OH^-}^i} \quad (4)$$

$$C_{Pb(OH)_i^{2-i}} = \beta_i \cdot C_{Pb^{2+}} \cdot C_{OH^-}^i \quad (5)$$

Where $i = 0, 1, 2, 3$. β_i is the stability constant of the i grade complex $Pb(OH)_i^{2-i}$, obviously, $\beta_0 = 1$. C_{OH^-} , $C_{Pb(OH)_i^{2-i}}$ denote the molar concentrations of OH^- , $Pb(OH)_i^{2-i}$, respectively.

Eq. (5) yields Eq. (6), which is used to determine C_t , the total concentration of the overall Pb(II) species:

$$C_t = C_{Pb^{2+}} \sum_{i=0}^n \beta_i \cdot C_{OH^-}^i \quad (6)$$

Eq. (6) yields Eq. (7), which is used to determine X_i , the molar fraction of i grade species:

$$X_i = \frac{C_{Pb(OH)_i^{2-i}}}{C_t} = \frac{\beta_i \cdot C_{OH^-}^i}{\sum_{i=0}^n \beta_i \cdot C_{OH^-}^i} \quad (7)$$

Where $0 \leq X_i \leq 1$, $\sum_{i=0}^n X_i = 1$.

Considering $C_{OH^-} = 10^{pH-14}$, Eq. (7) becomes:

$$X_i = \frac{\beta_i \cdot 10^{i(pH-14)}}{\sum_{i=0}^n \beta_i \cdot 10^{i(pH-14)}} \quad (8)$$

X_i at varying pH is thus determined by Eq. (8) to sketch Fig. 1. As Fig. 1 exhibits, when $pH < 8$, the dominant Pb(II) species is Pb^{2+} , when $8 < pH < 10$, is $Pb(OH)^+$, when $10 < pH < 11$, is $Pb(OH)_2$, when $pH > 11$, is $Pb(OH)_3^-$, respectively.

5. Results and discussions

5.1. Characterization of SGO

Fig. 2 shows the XRD patterns of GO and SGO. For GO, the peak at 11.27° is the (001) reflection of graphene oxide [19]. For SGO, no (001) reflection of graphene oxide appeared. Instead, two peaks appeared at 24.76° , 43.40° , which are assigned to the (002), (100) reflections of graphene, respectively [20]. These suggested that, GO was reduced during SGO fabrication. As reported by X.M. Feng et al [21], GO can be reduced under pure hydrothermal condition without the presence of reducing agent.

Fig. 3 shows the TEM images of GO (a) and SGO (b). In Fig. 3 (a), the sheets and edges of graphene are clearly viewable, displaying typical lamellar morphology. In Fig. 3 (b), the edge and outline of the graphene sheets are still clear. The black areas in the image are the starch grafted onto graphene surface. Moreover, nearly transparent sheets indicate that the graphene is rather thin.

Fig. 4 shows the FTIR spectra of GO and SGO. In the FTIR spectrum of SGO, the peaks O-H (3399 cm^{-1}), C=C (1636 cm^{-1}), C-OH (1400 cm^{-1}), C-O (1047 cm^{-1}) [22] confirms the existence of graphene oxide, while the peak C-H (2923 cm^{-1}) [23] supports the existence of starch. Further observation concludes two differences between GO and SGO: (1) The intensity of O-H, C=C, and C-O peaks of SGO is remarkably lower than that of GO, (2) The O-H peak of SGO (3399 cm^{-1}) is notably red shifted compared to that of GO (3425 cm^{-1}). These differences imply that, the oxygenous groups in GO were involved in a fairly strong chemical interaction with starch to form SGO.

For aromatic compounds, the π - π^* peak signifies the transition of conjugated electrons from the bonding orbital towards the anti bonding orbital, while the n - π^* peak signifies the transition of lone pair electrons in the hetero atoms (O, N, S, etc) towards the anti bonding orbital. Generally, factors enhancing system polarity make π - π^* peak red shift and n - π^* peak blue shift. On the contrary, factors weakening

system polarity make π - π^* peak blue shift and n - π^* peak red shift. Fig. 5 shows the UV-Vis spectra of GO and SGO. Clearly, there are two differences between them: (1) Difference in peak attribution. GO exhibited π - π^* , n - π^* peak at 240 nm, 296 nm, respectively, while SGO exhibited only π - π^* peak at 212 nm. (2) Difference in peak position. The π - π^* peak of SGO (212 nm) notably blue shifted compared to that of GO (240 nm). The disappearance of n - π^* peak, as well as the blue shift of π - π^* peak suggests, GO was reduced during SGO preparation. Reduction removed those polar oxygenous groups bonded to carbon atoms, resulting in the weakening of graphene polarity.

Fig. 6 shows the Raman spectra of GO and SGO, which display the characteristic D band and G band signifying the sp^3 and sp^2 carbon, respectively. Careful inspection designates three differences between the two spectra: (1) Difference in band position, reflecting the difference in the species of functional groups in GO and SGO. (2) Difference in band intensity, reflecting the difference in the quantity of functional groups in GO and SGO. (3) Difference in intensity ratio I_D/I_G . The lower I_D/I_G of SGO (1.12) compared to that of GO (1.39) implies GO reduction during SGO preparation that increased the ratio of sp^2 carbon. During SGO fabrication, some original oxygenous groups in GO were removed (GO reduction), meanwhile, some hydroxyl groups were introduced by starch. This conclusion is in line with that derived from FTIR, UV-Vis spectra.

Fig. 7 shows the TG-DTA curves of SGO. The curves were divided into four consecutive regions as highlighted by different background colors. The slight weight loss of 1.00 % at $T < 100$ °C is due to the evaporation of the surface moisture. The weight loss of 9.60 % at 100 °C $< T < 389$ °C is ascribed to the decomposition of the oxygenous groups [24]. The sharp DTA peak and drastic weight loss of 80.67 % occurred in the subsequent temperature range 389 °C $< T < 611$ °C reflect the bulk pyrolysis of the carbon skeleton [24]. Finally, the DTA value returned to zero, and the residue weight percent stabilized when $T > 611$ °C.

Fig. 8 shows the N_2 adsorption-desorption isotherms and pore size distribution curve (inset) of SGO. The adsorption isotherm exhibited a dramatic increase of

adsorption quantity under low relative pressure (P/P_0) and quantity limit at high relative pressure. On these grounds, the isotherms and hysteresis loop are identified as type IV and H4, respectively, reflecting narrow slit shaped mesopores. The BET surface area and BJH pore volume were $406.52 \text{ m}^2\cdot\text{g}^{-1}$ and $0.1513 \text{ cm}^3\cdot\text{g}^{-1}$, respectively. The average pore size was 3.4 nm, indicating mesoporous feature.

The pH_{pzc} (point of zero charge) is the pH under which the surface charge of colloidal particles reaches zero. When $pH < pH_{pzc}$, the prevalent H^+ is massively adsorbed onto the particle surface to make zeta potential positive. On the contrary, when $pH > pH_{pzc}$, the prevalent OH^- is massively adsorbed onto the particle surface to make zeta potential negative, respectively. Fig. 9 shows, the zeta potential of SGO hydrosol decreased with increasing pH , and reached zero at $pH = 4.5$, indicating that pH_{pzc} of SGO is 4.5.

5.2. Adsorption performance

Performance control

Control assays were conducted to quantitatively evaluate the contribution of the single GO and starch to the adsorption performance of SGO composite. In control assays, all adsorption factors were designed identical for starch, GO and SGO. Fig. 10 exhibits, the adsorption percent/quantity were 79.28 %/ $317.12 \text{ mg}\cdot\text{g}^{-1}$, 92.54 %/ $370.16 \text{ mg}\cdot\text{g}^{-1}$, and 95.83 %/ $383.32 \text{ mg}\cdot\text{g}^{-1}$ for starch, GO and SGO, respectively. SGO outperforms both GO and SGO. The performance improvement owing to starch introduction was mainly due to two reasons: (1) The starch molecules attached onto graphene served as steric hindrance to inhibit the re-stacking and agglomeration of graphene sheets (enhancement of inside). (2) The abundant hydroxyl and ether groups in starch augmented the adsorption sites (introduction from outside).

Effect of pH

pH is a primary influential factor on adsorption, whose influence is exerted on nothing else but adsorbate, adsorbent, and adsorption media. To be specific: (1) pH affect the adsorbate species distribution (Fig. 1), (2) pH affect the adsorbent surface charge (Fig. 9), (3) pH affect the ionization equilibrium of water, the adsorption

media. Fig. 11 shows, adsorption increased noticeably within the pH range of 2 ~ 10 to reach its maximum at $pH = 10$, then decreased. This trend can be interpreted based on Fig. 1 and Fig. 9. When $pH < 4.5$, the cases of adsorbate, adsorbent, and adsorption media are: the dominant Pb(II) species is Pb^{2+} , SGO has positive charge, H^+ concentration is higher than that of OH^- . As a result, the electrostatic repulsion between the positive Pb^{2+} and SGO, as well as the competitive adsorption of H^+ with Pb^{2+} lead to low adsorption efficiency. Yet, when pH exceed 4.5, the surface charge of SGO converts from positive to negative, accordingly, the electrostatic interaction between Pb(II) and SGO converts from repulsion to attraction, resulting in a significant increase of adsorption efficiency. However, when pH exceed 10, $Pb(OH)_2$ appears as the dominant Pb(II) species, who precipitate to decrease the adsorption efficiency. Hence, the maximum adsorption efficiency appeared at $pH = 10$, which was marked as $pH_{opt} = 10$ in Fig. 11.

Effect of contact time

Contact time is an important parameter closely related with adsorption efficiency. Fig. 12 shows a rapid adsorption process, which equilibrated at 16 min (marked as $t_e = 16$ min in Fig. 12), the adsorption percent and quantity were 95.83 % and $383.32 \text{ mg}\cdot\text{L}^{-1}$, respectively. At the beginning, the abundant Pb(II) and vacant adsorption sites on SGO surface facilitate adsorption both thermodynamically and dynamically. However, with the proceeding of adsorption, less and less free Pb(II) and vacant adsorption sites were left, leading to the gradual establishment of adsorption equilibrium.

Effect of adsorbent and adsorbate concentration

The adsorbent and adsorbate concentration in the adsorption system is also important. The optimum adsorbent concentration, or adsorbent dosage which is capable of harnessing the target adsorbate with a wide concentration range not only determines the adsorption cost, but also examines the adsorbent adaptability. Fig. 13 exhibits batch adsorptions with a varying adsorbent dosage on a fixed adsorbate concentration. While Fig. 14 exhibits batch adsorptions with a varying adsorbate concentration by a fixed adsorbent dosage. Clearly, adsorption percent and quantity

increased and decreased with increasing adsorbent dosage, while decreased and increased with increasing adsorbate concentration, respectively. On the one hand, increasing adsorbents consume more adsorbates, making adsorption percent increase. On the other hand, increasing adsorbents may lead to agglomeration, making adsorption quantity decrease. Similarly, on the one hand, increasing adsorbates make those excessive ones have no vacant adsorption sites to be accommodated, making adsorption percent decrease. On the other hand, increasing adsorbates occupy most of the adsorption sites, making adsorption quantity increase. For Pb(II) with initial concentration $200 \text{ mg}\cdot\text{L}^{-1}$, the optimum SGO dosage is $500 \text{ mg}\cdot\text{L}^{-1}$, marked as $D_{opt} = 500 \text{ mg}\cdot\text{L}^{-1}$ in Fig. 13. Fig. 14 displays, SGO with dosage $500 \text{ mg}\cdot\text{L}^{-1}$ kept adsorption percent over 92.5 % on Pb(II) with initial concentration $100\sim1000 \text{ mg}\cdot\text{L}^{-1}$, demonstrating good adaptability to concentration fluctuation.

Effect of temperature

The effect of temperature on adsorption efficiency was examined. Fig. 15 shows, as temperature rose from 10°C to 35°C , adsorption percent and quantity were decreased by 1.07 % and $4.28 \text{ mg}\cdot\text{g}^{-1}$, respectively. The temperature effect was adverse, implying that adsorption is exothermic. This adverse effect can be understood from the dynamic aspect. Increasing temperature induces more fierce Brownian movement, leading to the breakage of the adsorbent-adsorbate interaction to hinder adsorption.

Recycling efficiency

Recycling efficiency of adsorbent is also important when it is considered for pilot or industrial scale application. Fig. 16 shows, the adsorption percent and quantity were 65.97 % and $263.87 \text{ mg}\cdot\text{g}^{-1}$ in the third cycle, while 47.42 % and $189.69 \text{ mg}\cdot\text{g}^{-1}$ in the fifth cycle, respectively. Efficiency deterioration is due to two losses. (1) Adsorbent (matter) loss. Fine and hydrophilic adsorbent particles are difficult to recover. (2) Affinity (energy) loss. Adsorption sites with high affinity are difficult to regenerate.

5.3. Adsorption isotherms, kinetics, thermodynamics

The Langmuir model describes monolayer adsorption on the adsorbent surface with homogeneous affinity, assuming no interactions exist among adsorbates [25].

$$Q_e = Q_{max} K_L C_e / (1 + K_L C_e)$$

Where Q_{max} ($\text{mg} \cdot \text{g}^{-1}$) denotes the adsorption quantity corresponding to monolayer coverage on the adsorbent surface, K_L ($\text{L} \cdot \text{mg}^{-1}$) is the Langmuir constant related to the adsorption heat. The adsorption feature is characterized based on the separation or equilibrium factor R_L which is defined as $R_L = 1 / (1 + C_0 K_L)$. Specifically, $0 < R_L < 1$ indicates favorable adsorption, $R_L > 1$ indicates unfavorable adsorption, $R_L = 0$ indicates irreversible adsorption, and $R_L = 1$ indicates linear adsorption.

The Freundlich model describes adsorption on the adsorbent surface with heterogeneous affinities [26].

$$Q_e = K_F C_e^{1/n}$$

Where K_F and n are the Freundlich constants related to the adsorption capacity and intensity, respectively. The n parameter characterizes adsorption type: $n < 1$ indicates chemical adsorption, while $n > 1$ indicates physical adsorption, respectively.

The Temkin model assumes that adsorption is supported by chemical interaction, which decreases linearly with adsorption coverage [27].

$$Q_e = (RT/A_T)(\ln B_T + \ln C_e)$$

Where R ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) is the gas constant, T (K) is the absolute temperature. A_T ($\text{J} \cdot \text{mol}^{-1}$) and B_T ($\text{L} \cdot \text{g}^{-1}$) are Temkin constants associated with the adsorption heat and the maximum binding energy, respectively.

The D-R model is used to distinguish the adsorption type using the mean free energy of adsorption E ($\text{kJ} \cdot \text{mol}^{-1}$): $E < 8 \text{ kJ} \cdot \text{mol}^{-1}$ indicates physical adsorption, while $8 < E < 16 \text{ kJ} \cdot \text{mol}^{-1}$ indicates chemical adsorption [28].

$$\ln Q_e = \ln Q_{max} - \beta \varepsilon^2 \quad \varepsilon = RT \ln [1 + (1/C_e)] \quad E = (2\beta)^{-0.5}$$

Where Q_{max} is the theoretical maximum adsorption capacity, ε is the Polanyi potential, β ($\text{mol}^2 \cdot \text{J}^{-2}$) is a constant related to E .

The pseudo-first-order (PFO) model assumes that the adsorption rate is proportional to the quantity of vacant sites [29].

$$\ln(Q_e - Q_i) = \ln Q_e - k_l t$$

Where k_l (min^{-1}) is the PFO rate constant.

The pseudo-second-order (PSO) model assumes that the adsorption rate is

proportional to the square of the quantity of vacant sites, and chemisorption, or chemical interaction is the rate-controlling step [30].

$$t/Q_t = [1/(k_2 Q_e^2)] + (t/Q_e)$$

Where k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the PSO rate constant.

The intra-particle diffusion (IPD) model developed by Weber and Morris [31] is used to check whether intra-particle diffusion is a rate-controlling step.

$$Q_t = k_{id} t^{0.5} + C$$

Where k_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$) is the IPD rate constant, C ($\text{mg} \cdot \text{g}^{-1}$) is a constant reflecting the boundary layer thickness.

The liquid film diffusion (LFD) model is used to examine whether liquid film diffusion is the sole rate-controlling step [32].

$$\ln[1 - (Q_t/Q_e)] = -k_{fd} t$$

Where k_{fd} is the LFD rate constant.

The Bangham model is used to examine whether pore diffusion is the sole rate-controlling step [33].

$$\log\{\log[C_0/(C_0 - Q_t \cdot m)]\} = \log(k_0 m / 2.303 V) + \alpha \log t$$

Where m (g) is the adsorbent mass, V (L) is the volume of the adsorbate solution, k_0 and α are constants.

The thermodynamic parameters are calculated based on the Van 't Hoff equation:

$$\ln K^\ominus = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

$$K^\ominus = \frac{Q_e}{C_e}$$

Where $K^\ominus$ ($\text{L} \cdot \text{g}^{-1}$), ΔG ($\text{kJ} \cdot \text{mol}^{-1}$), ΔH ($\text{kJ} \cdot \text{mol}^{-1}$), and ΔS ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) are the equilibrium constant, free energy change, enthalpy change, and entropy change of adsorption.

The meanings of Q_i , C_i ($i = 0, e, t$) in all the above equations are consistent with the definition given in 2.4.

Fig. 17, 18, and 19 shows the fitting curves of the isotherm models, kinetic models, and Van't Hoff equation, respectively. The fitting and calculation results were listed in

Table 1.

Table 1 shows, among the four isotherm models, the Langmuir model and the Freundlich model yielded considerable high R^2 of 0.9853 and 0.9994, respectively. The latter is higher than the former. Yet the former is also rather satisfactory. Moreover, parameters indicative of the adsorption type are: $R_L < 1$, $n < 1$. These fitting results demonstrate: (1) The affinity of the adsorbent surface is more heterogeneous rather than homogeneous. (2) Adsorption is favorable and chemical. However, neither D-R nor Temkin fitting were satisfactory enough.

Among the four kinetic models, the PSO model gave the highest R^2 of 0.9999. Moreover, adsorption capacity as determined by the PSO model were $384.62 \text{ mg}\cdot\text{g}^{-1}$, which is consistent well with the experimental value $383.32 \text{ mg}\cdot\text{g}^{-1}$ (Fig. 12). These suggest that the adsorption rate is controlled by chemical interaction between adsorbent and adsorbate [30]. The IPD model also yielded rather satisfactory fitting: $R^2 = 0.9953$, implying that intra-particle diffusion was also involved as a rate-controlling step [31]. However, none of the PFO, LFD and Bangham models gave satisfactory fitting, implying that neither liquid film diffusion nor pore diffusion was the rate controlling step. The above analyses made us reach a conclusion: the adsorption rate was controlled by both intra-particle diffusion and chemical interaction.

The thermodynamic parameters $\Delta G < 0$, $\Delta H < 0$, $\Delta S > 0$ indicated that the adsorption were spontaneous, exothermic and entropy increasing, respectively. The relatively high negative ΔH and the positive ΔS gave two implications: (1) Adsorption was mainly driven by strong chemical interaction between adsorbent and adsorbate, as supported by the Freundlich and PSO model. (2) The system randomness increased during adsorption.

5.4. Interaction mechanism

The XPS spectra of the adsorbent before (SGO) and after (SGO-Pb) adsorption were compared to elucidate the interaction mechanism between adsorbent and adsorbate. Fig. 20 shows the survey spectra of GO, SGO and SGO-Pb. The O1s and C1s signals come from oxygen and carbon, the intrinsic elements of graphene oxide

and starch. For SGO-Pb, the new at 138.4-143.3 eV is Pb4f signal [34], which came from the adsorbed Pb(II). The inset under the violet arrow is the high resolution Pb4f spectrum. Fig. 21 displays the O1s spectra of SGO and SGO-Pb. There are three discrepancies between them. (1) Discrepancy in peak position. After Pb(II) adsorption, two sub peaks at 532.4 eV and 530.8 eV shifted to 532.2 eV and 530.7 eV respectively. (2) Discrepancy in peak shape. Before Pb(II) adsorption, the major and minor sub peak was the one at the higher and lower binding energy, while after Pb(II) adsorption, the major and minor sub peak became the one at the lower and higher binding energy, respectively. (3) Discrepancy in peak intensity. The overall peak intensity increased notably after Pb(II) adsorption. The adsorption was conducted at the optimum *pH* of 10 (Fig. 11), the *pH* under which Pb(OH)⁺ is the dominant Pb(II) species (Fig. 1). Evidently, the adsorption of oxygen containing Pb(OH)⁺ by SGO increased the O1s peak intensity. In conclusion, the changes in O1s peak position, shape and intensity caused by adsorption demonstrated that the chemical interaction between Pb(OH)⁺ and the oxygenous groups in SGO supported the adsorption. This conclusion coincides with that drawn from both Freundlich and PSO fittings. Fig. 22 compares the C1s spectra of SGO and SGO-Pb. Three discrepancies exist likewise. (1) Discrepancy in peak position. Before Pb(II) adsorption, the sub peaks C=O, C-O and C-C were at 286.60 eV, 284.44 eV and 283.76 eV, respectively. After Pb(II) adsorption, the sub peak C=O vanished, while C-O and C-C shifted to 284.34 eV and 283.65 eV, respectively. (2) Discrepancy in peak shape. Before Pb(II) adsorption, the ratios of the sub peaks C=O, C-O and C-C were 11.99 %, 36.70 % and 51.31 %, respectively. After Pb(II) adsorption, these ratios become 0, 43.72 % and 56.28 %, respectively, implying the participation of C=O, C-O related groups in adsorption. (3) Discrepancy in peak intensity. The overall peak intensity decreased obviously after Pb(II) adsorption. This is due to the waning and waxing effect: the O1s signal wax, makes C1s signal wane. Consequently, the changes in C1s peak position, shape and intensity caused by adsorption suggested that the chemical interaction between Pb(OH)⁺ and C=O, C-O related oxygenous groups in SGO supported the adsorption. This conclusion supports that of O1s spectra, Freundlich and PSO fittings.

5.5. Performance evaluation

The adsorption performance of SGO on aqueous Pb(II) was further estimated via comparing with some analogous adsorbents reported in literature [35-42], as listed in Table 2. Clearly, SGO has some advantages as relatively higher capacity and faster adsorption kinetics.

6. Conclusion

A highly efficient adsorbent based on starch-graphene oxide architecture (SGO) was fabricated, characterized and employed to scavenge aqueous Pb(II). The interaction mechanism between SGO and Pb(II) was analyzed. Adsorption assays indicated, SGO outperforms both single starch and GO in terms of adsorption efficiency. Specifically, SGO adsorbs 95.83% of Pb(II) in 16 min, with adsorption capacity $383.32 \text{ mg}\cdot\text{g}^{-1}$, manifesting some advantages as higher capacity and faster kinetics over other analogous adsorbents. Analysis on interaction mechanism revealed, chemical interaction between $\text{Pb}(\text{OH})^+$ and C=O, C-O related groups in SGO supported the adsorption, intra-particle diffusion and chemical interaction are the rate controlling steps. Based on its efficient adsorption performance, SGO may be a promising adsorbent for heavy metal scavenging from water.

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Figures

Figure 1

Quantitative evolution of aqueous $\text{Pb}(\text{OH})_3^-$ species with pH

Figure 2

XRD patterns of GO and SGO

Figure 3

TEM images of GO (a), SGO (b)

Figure 4

FTIR spectra of GO and SGO

Figure 5

UV-Vis spectra of GO and SGO

Figure 6

Raman spectra of GO and SGO

Figure 7

TG-DTA curves of SGO

Figure 8

N₂ adsorption-desorption isotherms of SGO (inset: Pore size distribution of SGO)

Figure 9

Dependence of zeta potential of SGO hydrosol on pH (pH = 10, t = 20 min, D = 500 mg·L⁻¹, C₀ = 200 mg·L⁻¹, T = 25 °C)

($pH = 10$, $t = 20$ min, $D = 500$ mg·L⁻¹, $C_0 = 200$ mg·L⁻¹, $T = 25$ °C)

Figure 10

Comparison of adsorption performance of starch, GO and SGO on aqueous Pb(II) ($pH = 2-12$, $t = 20$ min, $D = 500$ mg·L⁻¹, $C_0 = 200$ mg·L⁻¹, $T = 25$ °C)

($pH = 2-12$, $t = 20$ min, $D = 500$ mg•L⁻¹, $C_0 = 200$ mg•L⁻¹, $T = 25$ °C)

Figure 11

Effect of pH on the adsorption of Pb(II) by SGO ($pH = 10$, $t = 2-20$ min, $D = 500$ mg•L⁻¹, $C_0 = 200$ mg•L⁻¹, $T = 25$ °C)

($pH = 10$, $t = 2-20 \text{ min}$, $D = 500 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 200 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

Figure 12

Effect of contact time on the adsorption of Pb(II) by SGO ($pH = 10$, $t = 20 \text{ min}$, $D = 200-700 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 200 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

($pH = 10$, $t = 20 \text{ min}$, $D = 200\text{-}700 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 200 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

Figure 13

Effect of SGO dosage on the adsorption of $\text{Pb}(\text{II})$ ($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 100\text{-}1000 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 100-1000 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

Figure 14

Effect of $\text{Pb}(\text{II})$ initial concentration on its adsorption by SGO ($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg} \cdot \text{L}^{-1}$, $C_0 = 100-1000 \text{ mg} \cdot \text{L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$)

($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg}\cdot\text{L}^{-1}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $T = 10\text{-}35^{\circ}\text{C}$)

Figure 15

Effect of temperature on the adsorption of $\text{Pb}(\text{II})$ by SGO ($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg}\cdot\text{L}^{-1}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $T = 25^{\circ}\text{C}$, cycles = 5)

($pH = 10$, $t = 20$ min, $D = 500$ mg·L⁻¹, $C_0 = 200$ mg·L⁻¹, $T = 25$ °C, cycles = 5)

Figure 16

Cyclic adsorption performance of SGO on Pb(II) ($pH = 10$, $t = 20$ min, $D = 200$ - 700 mg·L⁻¹, $C_0 = 200$ ·mg L⁻¹, $T = 25$ °C)

Figure 17

Fitting curves of the adsorption of Pb(II) by SGO based on different isotherm models (a) Langmuir; (b) Freundlich; (c) Temkin; (d) D-R (pH = 10, t = 2-20 min, D = 500 mg·L⁻¹, C₀ = 200 mg·L⁻¹, T = 25 °C)

Figure 18

Fitting curves of the adsorption of Pb(II) by SGO based on different kinetic models (a) Pseudo-first-order, (b) Pseudo-second-order, (c) Intra-particle diffusion, (d) Liquid film diffusion, (e) Bangham (pH = 10, $t = 2-20$ min, $D = 500 \text{ mg}\cdot\text{L}^{-1}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $T = 10-35^\circ\text{C}$)

($pH = 10$, $t = 20 \text{ min}$, $D = 500 \text{ mg}\cdot\text{L}^{-1}$, $C_0 = 200 \text{ mg}\cdot\text{L}^{-1}$, $T = 10\text{-}35 \text{ }^{\circ}\text{C}$)

Figure 19

Fitting curve of $\text{Pb}(\text{II})$ adsorption by SGO based on Van't Hoff equation

Figure 20

XPS Survey spectra of GO, SGO, SGO-Pb (inset: Pb4f spectrum of SGO-Pb)

Figure 21

O1s spectrum of (a) SGO, (b) SGO-Pb

Figure 22

C1s spectrum of (a) SGO, (b) SGO-Pb