

Modification of graphene oxide nanosheets for the removal of lead (II) and copper (II) ions from aqueous solutions

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Submitted March 24, 2016; Accepted August 8, 2016

In the present study, the graphene oxide nanosheets (GO) were successfully synthesized from graphite and were modified by HCl and H₂SO₄. The potential of synthesized adsorbents were investigated for the removal of lead (II) and copper (II) ions from aqueous solutions. The synthesized adsorbents were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis. The effect of sorption parameters including pH, contact time and initial concentration on the removal of lead (II) and copper (II) ions onto the GO samples were investigated. The known pseudo-first-order and pseudo-second-order kinetic models were applied to describe the kinetic data of metal ions. The equilibrium data of metal ions were fitted by Freundlich and Langmuir isotherm models. The both copper and lead experimental data were well described using pseudo-second-order kinetic and Langmuir isotherm models. The obtained results indicated that the GO can be consider as an efficient adsorbent for the removal heavy metal ions.

Keywords: Graphene oxide, Adsorption, Kinetic, Isotherm, Lead, Copper

INTRODUCTION

The higher dosages of metal ions have a negative effect on the human health [1]. Lead (II) and copper (II) are the common heavy metals that influence on the nervous system, the reproductive system, the liver and the brain [2, 3]. Lead (II) and copper (II) ions are observed in a variety of industrial wastes. Therefore the removal of lead (II) and copper (II) ions from aqueous systems is necessary. Various techniques including electrochemical separation [4], precipitation [5], membrane filtration [6], ionic exchange [7] solvent extraction [8] and adsorption [9] have been applied to remove the metal ion. Among mentioned techniques, the adsorption process due to its simplicity, easy operational conditions and economical aspects can be considered as an effective method [10]. The physico-chemical properties of any adsorbent can influence on the sorption capacity of metal ions. The various adsorbents including carbon nanotubes, graphene oxide (GO), natural clays, zeolites and polymers have been widely used for metal ions sorption [11-15]. The use of alternative low cost materials is a very important issue in industry applications. Although the researchers used from natural and synthetic polymeric materials such as chitosan, polyvinyl alcohol and polyethylene imine for metal ions sorption; however it is necessary to develop the easily available, inexpensive, and an effective alternative materials for wastewater treatment. GO

(C₅₄H₁₇ + O + (OH)₃ + COOH) is synthesized by oxidization of low-cost graphene-based materials. The chemical functional groups of GO including hydroxyl, epoxide, carboxyl and carbonyl with higher surface area of GO, as well as modified surface properties could be consider as an efficient adsorbent for heavy metal ions removal [16-20]. Also, the removal efficiency of GO can increase remarkably by surface modification of GO with acids. By chemical modification of GO nanosheets, the specific surface area of GO increases and subsequently, the affinity of GO for higher sorption of metal ions increases. In this work, the GO nanosheets were synthesized by Hummers' method. The GO nanosheets were modified by HCl and H₂SO₄ acids to increase the active surfaces of GO nanosheets. The effect of sorption parameters on a batch system for lead adsorption onto the GO and modified GO has been investigated to obtain the optimum conditions for the maximum adsorption of lead (II) and copper (II) ions from aqueous solutions. The nature of the adsorption process with respect to its kinetics and isotherms aspects has been also evaluated.

2. EXPERIMENTAL

2.1 Materials

GO was synthesized via modified Hummers' method [21] from the powder graphite. Briefly, raw graphite and KMnO₄ were mixed in a flask containing 20 mL sulfuric acid and orthophosphoric acid under stirring at 50 °C for 24 h. The prepared mixture was dispersed into the H₂O₂ (30%) and was

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immediately precipitated by centrifuge at 15,000 rpm for 10 min and was washed with HCl, ethanol and deionized water several times. Finally the material was dried at 70 °C for 12 h to obtain the brown GO.

For modification of GO, first 0.1 N HCl, and H2SO4 acid solutions were prepared. Then, the synthesized GO nanosheets were poured into 500-mL flasks containing 250 mL of acid solutions under stirring for 4 h. Finally, the adsorbents were dried in the vacuum oven at 85°C for 2 h. The copper and lead nitrates were purchased from Merck (Germany). Distilled water was used throughout this work.

2.2. Characterization of graphene oxide

The synthesized graphene oxide nanosheets were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis.

The XRD pattern was recorded at 25 °C on a Philips instrument (X'pert diffractometer using Cu-K α radiation) with a scanning speed of 0.03° (2 θ) min⁻¹ to confirm the GO nanosheets structure. The morphology of the synthesized GO was determined using SEM (MV2300) after gold coating. The specific surface area of GO samples was estimated using Brunauer–Emmett–Teller (BET) method. The final concentration of heavy metal ions in the adsorption medium was determined using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model Trace Scan).

2.3 Adsorption experiments

The Pb (II) and Cu (II) ions sorption efficiencies onto the GO samples were carried out as functions of pH (2-7), contact time (0-180 min), initial concentration (10-500 mg L⁻¹) and temperature (25-45 °C) in a batch system. The adsorbent dosage was constant during experiments (1 g L⁻¹). The sorption capacity of metal ions was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{1000M} \quad (1)$$

where C₀ and C_e (mg/L) are the initial and equilibrium metal ion concentrations, respectively; V is the liquid volume (mL) and M is the weight of dried used adsorbent (g). The kinetic and isotherm parameters were obtained by nonlinear regression using MATLAB software.

3. RESULTS AND DISCUSSION

3.1 Characterization of GO nanosheets

The SEM image of synthesized GO nanosheets is shown in Fig.1. As shown, the homogeneous nanosheets with the film thickness of about 30 nm was produced. The XRD spectra of graphite and GO are shown in Fig. 2. The results confirmed that the oxygen functional groups have penetrated into the graphite interlayers [19].

The S_{BET}, pore volume and average pore diameter of synthesized GO nanosheets and modified GO are listed in Table 1. As shown, the GO nanosheets modified with HCl had a maximum surface area and pore diameter. The results indicated that the modification of GO with HCl produced the voids in the GO structure which resulted in the increasing of S_{BET}, pore volume and pore diameter of modified GO samples.

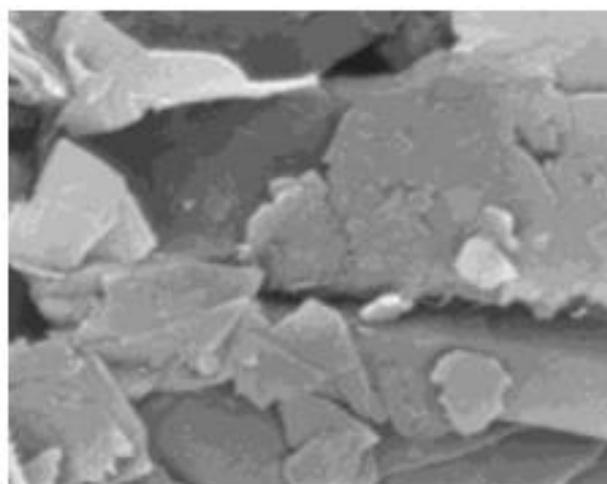


Fig.1. SEM image and thickness distribution of GO nanosheets.

Table 1. Physical properties of synthesized GO nanosheets

Sample	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
GO	437.9	0.761	6.32
GO modified HCl	490.3	0.887	7.90
GO modified H ₂ SO ₄	480.7	0.812	7.12

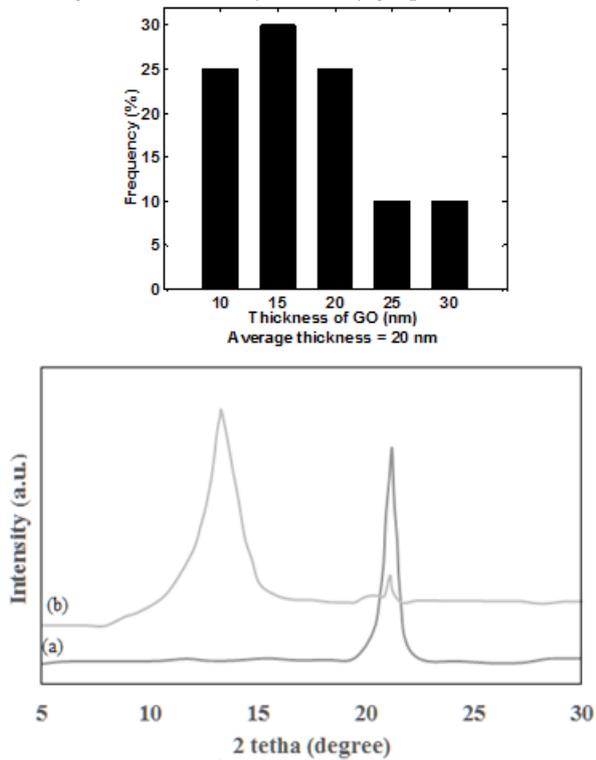


Fig.2. XRD patterns of (a) graphite and (b) synthesized GO nanosheets

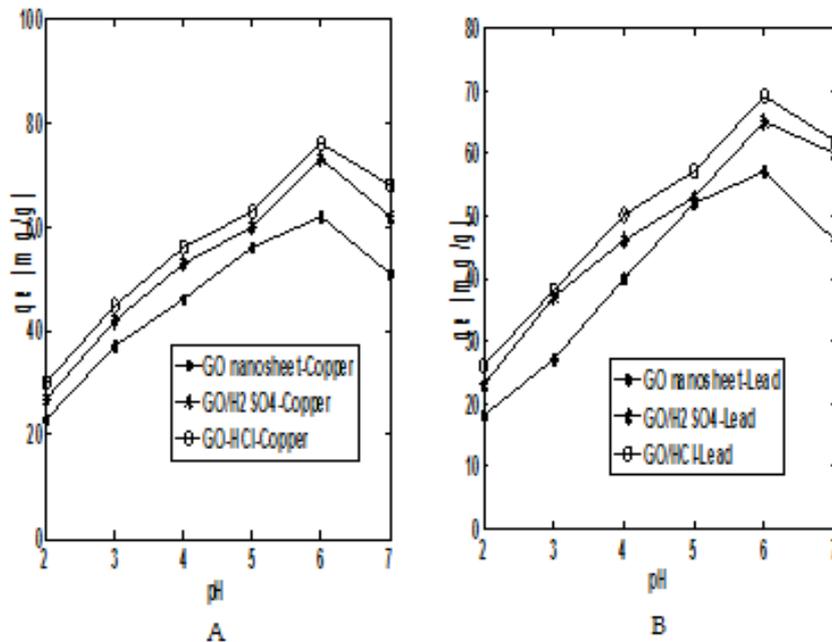


Fig.3. Effect of pH on the removal of (a) Cu (II) and (b) Pb (II) ions using synthesized GO adsorbents.

3.2. Effect of pH on the lead and copper sorption

The effect of pH on the lead and copper sorption using synthesized GO and modified GO at initial concentrations of 50 mg L⁻¹ for Pb (II) and Cu (II) ions, adsorbent dosage of 1 g L⁻¹, contact time of 3 h and temperature of 25 °C in the range of 2-7 is illustrated in Fig.3. As shown, the sorption capacities of GO adsorbents reached the maximum values at pH of 6 for both metal ions. At lower pH values, the

competition of hydrogen ion with metal ions for chelating with available sites of GO adsorbents led to decrease the adsorption capacities of metal ions. At pH above 6, the formation of hydroxylated complexes of metal ions resulted in decreasing adsorption capacities of lead and copper ions by the GO samples. Therefore, the pH of 6 was selected as an optimum value for lead and copper sorption onto the GO adsorbents.

3.3 Effect of contact time on the lead and copper sorption and kinetic models

The effect of contact time on the copper and lead sorption using synthesized GO is illustrated in Fig.4. As shown, more than 90% of total adsorption of lead and copper sorption occurred within the first 1 hour. After 2 hours, almost all of the internal and external active sites are saturated and the system reached the sorption equilibrium.

Known kinetic models including pseudo-first-order and pseudo-second-order models were used to describe the adsorption kinetics of metal ions using GO adsorbents. The kinetic equations are expressed as follows [22, 23]:

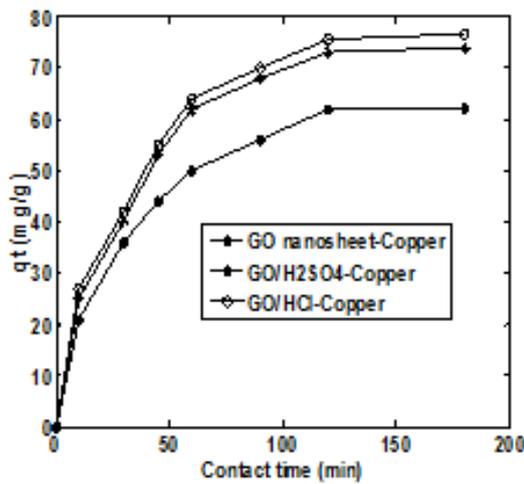
$$\text{Pseudo-first-order: } q_t = q_e (1 - \exp(-k_1 t)) \quad (2)$$

$$\text{Pseudo-second-order } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

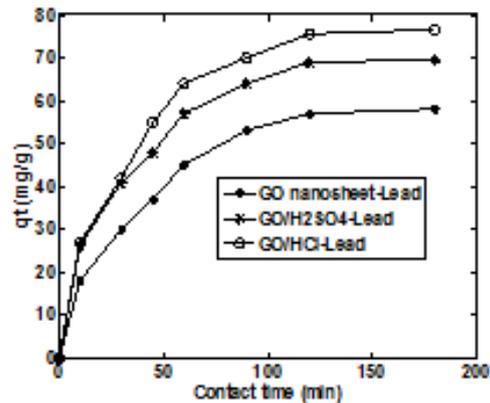
where q_t and q_e (mg g^{-1}) are the adsorption capacities of metal ions at time t and equilibrium time, respectively. The quantities k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The results are presented in Table 2. The results showed that the adsorption kinetics data of metal ions onto the synthesized GO adsorbents were well fitted by the pseudo-second-order kinetic model ($R^2 > 0.991$).

Table 2. Kinetic parameters of Cu (II) and Pb (II) ions sorption using synthesized GO nanosheet.

Adsorbent	Metal ions	Pseudo-first-order		R^2	Pseudo-second-order		R^2
		q_{eq} (mg/g)	k_1 (min^{-1})		q_{eq} (mg/g)	k_2 ($\text{g/mg}\cdot\text{min}$)	
GO nanosheets	Cu (II)	61.84	0.0290	0.986	73.83	0.0004695	0.995
	Pb (II)	59.04	0.0245	0.985	72.55	0.0003632	0.991
GO/H ₂ SO ₄	Cu (II)	74.22	0.0295	0.987	89.10	0.0003763	0.994
	Pb (II)	68.91	0.0309	0.983	86.80	0.0004649	0.993
GO/HCl	Cu (II)	76.33	0.0299	0.984	90.97	0.0003866	0.991
	Pb (II)	75.31	0.0315	0.985	89.67	0.0003923	0.991



(a)



(b)

Fig.4. Effect of contact time on the removal of (a) Cu (II) and (b) Pb (II) ions using synthesized GO nanosheets.

3.4 Effect of initial concentration and isotherm models

The influence of initial concentration of lead and copper on the adsorption capacity of GO samples at three different temperatures (298, 308 and 318K) is

The known Freundlich and Langmuir isotherm models were used to describe the equilibrium data of lead and copper ions sorption onto the GO samples.

shown in Fig. 5. As shown, the metal ions sorption capacity was increased by increasing the temperature which indicated that the adsorption process onto the GO adsorbents was favorable at higher temperatures.

The isotherm equations are expressed as follows [24, 25]:

Freundlich isotherm model

$$q_e = k_F C_e^{\frac{1}{n}} \quad (6)$$

$$q_e = q_m \frac{bC_e}{1+bC_e} \quad (7)$$

Langmuir isotherm model

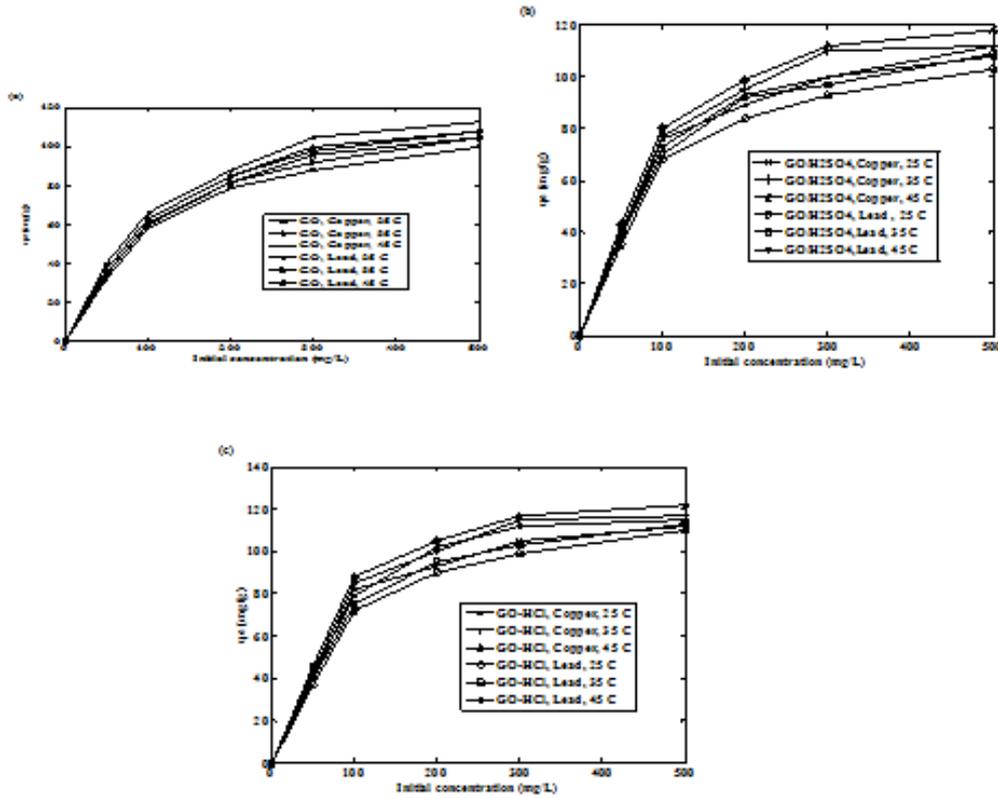


Fig.5. Effect of initial concentration on the copper and lead sorption at different temperatures using (a) GO, (b) GO/H₂SO₄, (c) GO/HCl.

Table 3. Isotherm parameters of metal ions sorption onto the GO samples.

Adsorbent	Metal	T(°C)	Freundlich isotherm			Langmuir isotherm		
			K _F (mg/g)	n	R ²	q _{max} (mg/g)	K _L (L/mg)	R ²
GO	Cu (II)	25	13.04	3.563	0.934	120.1	0.02551	0.983
		35	17.04	3.762	0.940	122.0	0.03226	0.982
		45	20.90	4.026	0.944	126.5	0.04036	0.982
	Pb (II)	25	12.22	3.554	0.911	112.6	0.02618	0.985
		35	13.34	3.639	0.917	113.3	0.02933	0.987
		45	15.06	3.802	0.916	115.5	0.03380	0.985
GO/H ₂ SO ₄	Cu (II)	25	13.6	3.457	0.938	124.7	0.03192	0.986
		35	18.8	3.594	0.921	128.3	0.03563	0.980
		45	21.5	3.707	0.922	135.7	0.03723	0.985
	Pb (II)	25	13.4	3.462	0.938	118.6	0.02642	0.991
		35	14.42	3.573	0.942	121.7	0.02966	0.991
		45	16.8	3.781	0.944	125.1	0.03592	0.990
GO/HCl	Cu (II)	25	13.9	3.417	0.918	127.7	0.03352	0.987
		35	19.8	3.514	0.921	130.3	0.03893	0.983
		45	23.5	3.727	0.928	138.7	0.03923	0.982
	Pb (II)	25	13.98	3.492	0.928	120.6	0.02842	0.993
		35	14.82	3.873	0.932	126.7	0.03255	0.990
		45	18.8	3.981	0.924	129.1	0.03954	0.986

The quantity q_m is the maximum value of metal ion adsorption per unit weight of membrane that is related to the monolayer adsorption capacity and b is

related to the enthalpy of adsorption. The parameters of isotherm models were calculated by nonlinear regression of q_e versus C_e using MATLAB software.

The results are summarized in Table 3. By comparing the correlation coefficients, it was found that the equilibrium data was best described by Langmuir isotherm model ($R^2 > 0.98$) compared with Freundlich ($R^2 > 0.91$) isotherm model. This behavior indicated the monolayer reaction of lead and copper ions using GO samples where k_F (mg g⁻¹) and n are Freundlich parameters related to the sorption capacity and intensity of the sorbent, respectively. The quantities q_{max} (mg g⁻¹) and b (mg⁻¹) are the Langmuir model constants.

4. CONCLUSION

In the present study, GO/H₂SO₄ and GO/ HCl were successfully synthesized from graphite and their application for the removal of lead and copper from aqueous solution were investigated. The experimental results in batch system indicated the maximum sorption of lead and copper ions onto the GO samples was obtained at equilibrium time of 120 min and temperature of 45°C. Isotherm studies revealed that Langmuir model was well described the equilibrium data of lead and copper compared with Freundlich isotherm model. Kinetics studies of both lead and copper sorption followed by pseudo-second order model. The obtained results revealed the modified GO with HCl had a high potential for heavy metal removing compared with pure GO and GO/H₂SO₄ adsorbents.

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