Fabrication of PVA/GO nanofibers by electrospinning process for the removal of lead (II) and copper (II) ions from aqueous solutions

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Abstract : In the present study, the poly (vinyl alcohol)//graphene oxide Nano sheets (PVA/GO) were successfully synthesized via electrospinning process and its application for the removal of lead (II) and copper (II) ions was investigated in a batch system.The graphiteNano sheets were also modified by HCl and H_2SO_4. The synthesized Nano fibrousadsorbents were characterized usingscanning electron microscopy (SEM),X-ray powder diffraction (XRD), 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 by the Nano fibrous 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 Freundlich and Langmuir isotherm models were used to describe the equilibrium data of metal ions sorption. The both copper and lead experimental data were well described using pseudo-second-order kinetic and Langmuir isotherm models. The obtained results indicated that PVA/GO nanofibers can be considered as an efficient adsorbent for the removal heavy metal ions.

1. INTRODUCTION

The higher dosages of metal ions have a negative effect on the human health such as nervous system, the reproductive system, the liver and the brain[1, 2]. Lead (II) and copper (II) ions are observed in a variety of industrial wastes such as plating, ceramics, glass, mining and battery manufacturing. Therefore the removal of Lead (II) and copper (II) ions from aqueous systems is necessary. Various techniques including electrochemical separation [3,4], precipitation [5], membrane filtration[6], ionic exchange [7] solvent extraction [8-9] and adsorption [9] have been applied to remove metal ion from aqueous systems. The adsorption process due to its simplicity, easy operational conditions and economical aspects is widely preferred as an effective method [10]. Thephysico-chemical properties of any adsorbent can influence on the sorption capacity of metal ions. The nanofibers prepared by electrospinning process due to higher surface area and fine pores shows the high potential for the removal of metal ions from aqueous systems [11-15]. The various materials including carbon nanotubes, graphene oxide (GO), natural clays and zeolites have been added to enhance the metal ions sorption efficiency [16-20]. The use of alternative low cost materials is a very important issue in industry applications.

GO ($C_{54}H_{17}$ + 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 [21-25]. Also, the removal efficiency of GO can increase remarkably by surface modification of GO with acids. By chemical modification of GO Nano sheets, 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 Nano sheets were synthesized by Hummers' method. Then PVA/GO nanofibers were prepared via electrospinning process. The GO Nano sheets were also modified by HCl and H_2SO_4 acids to increase the active surfaces of GO Nano sheets for enhancement in sorption capacity of PVA/GO nanofibers. The effect of sorption parameters in a batch system for lead and copper adsorption onto the PVA/GO and PVA/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. EXPERMENTAL

2.1 Materials

GO was synthetized via modified Hummers' method [26] from the powder graphite. Briefly, raw graphite and $KMnO_4$ 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 H_2O_2 (30%) and was immediately precipitated by a 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 Nano sheets 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 85ᵒC for 2 h.

The copper and lead nitrates were purchased from Merck (Germany). Distilled water was used throughout this work.

2.2. Electrospinning process

The PVA solution (10 wt.%) was prepared by dissolving PVA in water under stirring for 6 h at 30 ˚C. Then, the various concentrations of GO (0, 2, and 5%,

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mass of GO to PVA) were slowly dispersed to the PVA solution at 30 ˚C and stirring was continued for 24 h. The PVA/GO solutions were poured into the plastic syringe. A voltage of 20 kV, tip-collector distance of 14 cm, and feeding rate of 0.5 mL h^{-1} was applied to fabricate the PVA/GO nanofibers.

2.3 Characterization tests

The synthesized nanofibers 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-Kα radiation) with a scanning speed of 0.03˚ (2θ) min^{-1} to confirm the GO Nano sheets structure. The morphology of the nanofibers 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, ThermoJarrel Ash, Model Trace Scan).

2.4 Adsorption experiments

The Pb (II) and Cu (II) ions sorption efficiencies onto the PVA/GO nanofibroussamples 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:

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

where C_0 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 images of PVA/GO nanofibersare shown in Fig.1. As shown, by increasing GO up to 2%, the fiber diameter was decreased. By increasing GO content, the fiber diameter was increased. Therefore, the PVA/GO 2% nanofibrous adsorbent is selected for further experiments.The XRD spectra of PVA/graphite and PVA/GO are shown in Fig. 2. The results confirmed that the oxygen functional groups have penetrated into the graphite interlayers [24].
The S$_{BET}$, pore volume and average pore diameter of PVA/ GO nanofibers and PVA/modified GO nanofibers are listed in Table 1. As shown, the PVA/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 in nanofibers. Therefore, the PVA/GO modified with HCl nanofiber was selected for further experiments.
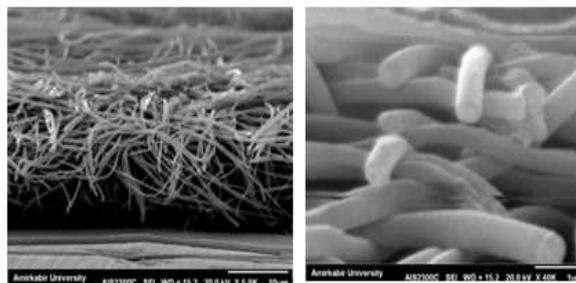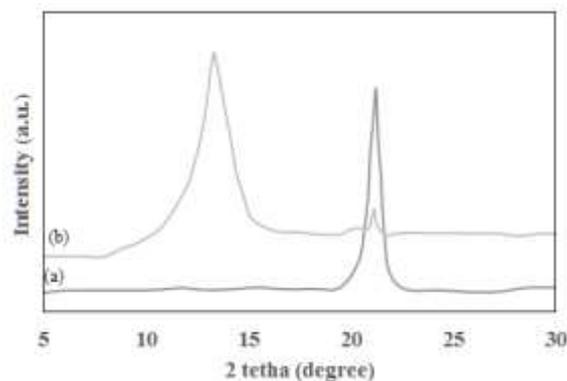

Figure 1. SEM image of PVA/GO2% nanofibers

Figure 2. XRD patterns of (a) PVA/graphite and (b) PVA/GO nanofibers

Sample	SBET (m²g⁻¹)	Pore volume (cm³ g⁻¹)	Average pore diameter (nm)
PVA/GO	238.9	0.711	4.32
GO modified HCl	290.3	0.802	5.90
GO modified H₂SO₄	280.7	0.789	5.12

Table 1 . Physical properties of synthesized PVA/GO nanofibers

3.2 Effect of pH on the lead and copper sorption

The effect of pH on the lead and copper sorption using selected PVA/M-GO$_{HCl}$nanofibers in initial concentrations of 100 mg L^{-1} for Pb (II) and Cu (II) ions, adsorbent dosage of 0.5 g L^{-1}, contact time of 60min and temperature of 25 ˚C in the range of 2-7 is illustrated in Fig.3. As shown, the sorption capacities of PVA/M-GO$_{HCl}$nanofibers adsorbent 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 nanofibrous 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 nanofibrous samples. Therefore, the pH of 6 was selected as an optimum value for lead and copper sorption onto the Nano fibrous adsorbent.
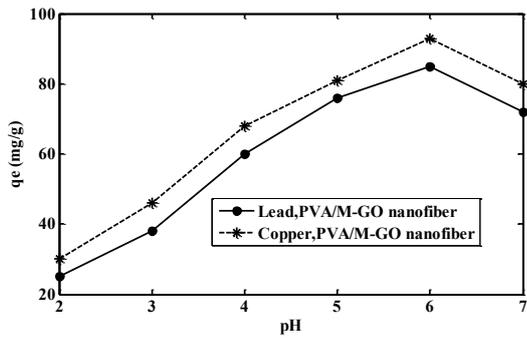
Figure 3. Effect of pH on the removal of Cu (II) and Pb (II) ions using synthesized nanofibrous adsorbent

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]:

Pseudo-first-order $\quad q_t = q_e \left(1 - \exp(-k_1 t)\right)$ (2)

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

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

Adsorbent	Metal ions	Pseudo-first-order			Pseudo-second-order		
		q_{eq} (mg/g)	k_1 (min^{-1})	R^2	q_{eq} (mg/g)	k_2 (g/mg.min)	R^2
PVA/M-GO$_{HCl}$	Cu (II)	91.84	0.0490	0.971	99.89	0.0005324	**0.995**
	Pb (II)	82.04	0.0465	0.975	92.55	0.0004632	**0.991**

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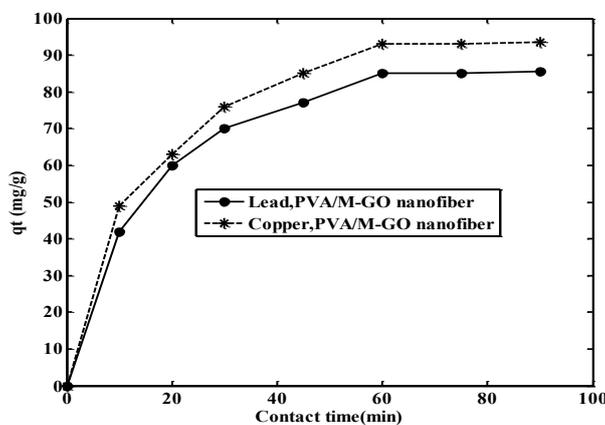

Figure 4. Effect of contact time on the removal of Cu (II) and Pb (II) ions using synthesized nanofibers

3.4 Effect of initial concentration and isotherm models

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

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

The isotherm equations are expressed as follows [29, 30]:

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

Langmuir isotherm model $\quad q = q \dfrac{bC}{1+bC}$ (7)

where k_F (mg g^{-1}) and n are Freundlich parameters related to the sorption capacity and intensity of the sorbent, respectively. q_{max} (mg g^{-1}) and b (mg^{-1}) are the Langmuir model constants.

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 nanofibers.
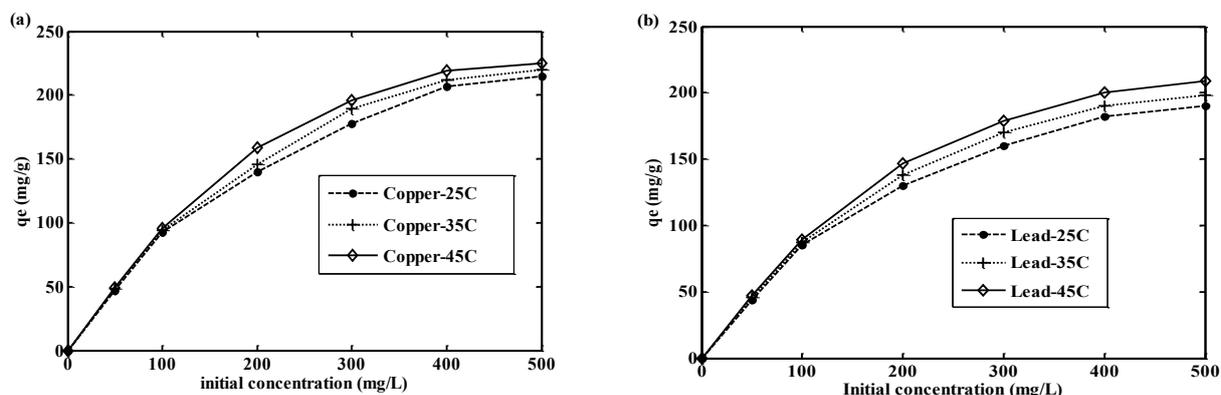

Figure 5. Effect of initial concentration on the (a) copper and (b) lead sorption at different temperatures using nanofibers

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
Nanofiber	Cu (II)	25	23.04	3.563	0.954	220.1	0.06551	0.986
		35	27.04	3.762	0.960	2282.0	0.07226	0.985
		45	30.90	4.026	0.964	236.5	0.08036	0.984
	Pb (II)	25	19.22	3.554	0.958	202.6	0.05618	0.983
		35	23.34	3.639	0.957	213.3	0.05933	0.982
		45	25.06	3.802	0.966	220.5	0.06380	0.981

4. CONSLUSION

In the present study, PVA/GO were successfully synthesized via electrospinning process for the removal of lead and copper from aqueous solution were investigated. The modification of nanofibers indicated that the modification of GO with HCl can be chosen as an appreciate method for increasing surface area and capability of PVA/GO nanofibers. The effect of GO content indicated that the GO 2% was an optimum content for incorporation of GO into the PVA nanofibers. The experimental results in batch system indicated the maximum sorption of lead and copper ions onto the PVA/GO nanofibers were obtained in pH of 6, equilibrium time of 60 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 resulted revealed the PVA/M-GO$_{HCl}$ nanofibers had a high potential for heavy metal ions removal.

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