



Functionalized Graphene Oxide/Polyacrylonitrile Nanofibrous Composite: Pb²⁺ and Cd²⁺ Cations Adsorption

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ABSTRACT

In this research, graphene oxide (GO) was functionalized by tannic acid to produce GO-TA and fabricate a novel functionalized graphene oxide/ polyacrylonitrile (PAN) nanofibrous as an adsorbent in order to remove two hazardous heavy metals from aqueous solutions. The results showed that the composite adsorbent can properly adsorb Pb²⁺ and Cd²⁺ metal cations, due to having the numerous potential active sites. The optimum conditions for 97.37% of Pb²⁺ and 94.28% of Cd²⁺ ions removal were meanly obtained at pH of 6.3, nanoparticles weight percentage of 4.26 wt.%, metal ions concentration of 35.74 ppm and contact time of 70.5 min. The maximum adsorption capacities for lead and cadmium ions were found at 344.83 and 312.5 mg/g, respectively.

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1. INTRODUCTION

There are a lot of heavy metal ions such as lead and cadmium in the water resources. This causes plenty of problems such as dizziness, emphysema, kidney damage, cancer, neurological diseases and disorders [1]. Various techniques have been used to reduce the heavy metal ions from wastewaters such as electrochemical treatment [2], membrane processes [3], electrodialysis [4] and adsorption [5]. The adsorption process is effective and economical for treating the dilute aqueous solutions [6]. Recently, graphene oxide use in the adsorption process has been encouraged because graphene has a flat monolayer of carbon atoms that have closely been packed together in a two-dimensional lattice where each carbon atom is sp² hybridized and bonded in a honeycomb structure [7]. It has a bunch of functional groups on its surface which makes it as a natural hunter of cations [8]. Manzoor et al. synthesized the crosslinked beads from chitosan and carboxymethyl cellulose using arginine for removal of Pb(II) and Cd(II) ions from a wastewater. They could remove Pb(II) and Cd(II) ions with efficiencies of 95.3 and

93.5%, respectively [9]. In fact, graphene oxide is an unique material for heavy metal ions removal due to having large specific area and abundant functional groups [10]. Furthermore, GO can eliminate several heavy metal ions such as Pb²⁺ and Cd²⁺ ions from aqueous solutions [11]. Üçer et al. [12] used activated carbon in granule form modified with tannic acid for Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions removal from aqueous systems. Pekdemir et al. [13] selected tannic acid for the removal of Cd(II) and Pb(II) ions. The removal of Cd(II) and Pb(II) was investigated as a function of pH ranging from 2.5 to 13.

According to the above background, the current work was conducted to produce a nanofibrous composite as an adsorbent made of PAN as a polymer matrix combined with graphene oxide. It was also functionalized by tannic acid (PAN/GO-TA). Moreover, it was applied for Pb²⁺ and Cd²⁺ ions adsorption from an aqueous solution. Several parameters affects involving solution pH, nanoparticles weight percentage, initial concentration and contact time on the adsorption process. The adsorption process was designed and optimized by Design Expert software.

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2. MATERIALS AND METHODS

2.1. Materials

All chemicals involving natural graphite flakes, tannic acid, N-dimethylformamide (DMF), sulfuric acid, hydrochloric acid, potassium permanganate and hydrogen peroxide (30%) were purchased from Merck supplier. Commercial polyacrylonitrile powder with average molecular weight of 70000 g/mol was obtained from Iran Polyacryl Company. $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ as the sources of lead and cadmium were purchased from Merck supplier.

2.2. Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized from natural graphite powder based on the modified Hummers' method [14]. In brief, graphite powder (3.0 g) was added to concentrated H_2SO_4 (70 cm^3) with stirring in an ice bath, KMnO_4 (9.0 g) was slowly added under vigorous stirring while the temperature of the suspension was maintained below $20 \text{ }^\circ\text{C}$. Then, the reaction set-up was transferred to a $40 \text{ }^\circ\text{C}$ oil bath and vigorously stirred for about 0.5 h. Then, the reaction mixture was stirred for 15 min at $95 \text{ }^\circ\text{C}$ by adding 150 cm^3 of distilled water. Extra 500 cm^3 of distilled water was added, followed by slow addition of 15 cm^3 of H_2O_2 . The solution color changed from dark brown to bright yellow. The mixture was washed with 250 cm^3 of an aqueous solution of HCl (1:10) to remove metal ions. The obtained solid was dried in air and diluted with 600 cm^3 of deionized water to disperse graphite oxide in the solution. The aqueous mixture was centrifuged (Hettich Zentrifugen, Germany) at 4000 rpm and then washed for few hours to obtain graphene oxide in the pure form. This process was repeated several times. The graphene oxide solution was sonicated (SONREX Digite C DT52 H, Bandelin, Germany) for 30 min at room temperature ($\approx 25 \text{ }^\circ\text{C}$). Finally, the mixture was dried at $80 \text{ }^\circ\text{C}$ in an air oven (53 l, model Digital UNB400, Memmert, Germany).

2.3. Functionalizing Graphene Oxide

200 mg of graphene oxide powder was dispersed in 10 cm^3 of deionized water by sonication for 15 min at the room temperature. 50 mg of tannic acid was then added to the aqueous dispersion of graphene oxide and stirred until a homogeneous solution was obtained. The mixture was heated at $90 \text{ }^\circ\text{C}$ for about 8 h (under reflux).

2.4. Preparing Pan/Go-Ta Composite

The composite electrospinning solutions were prepared by adding various amounts (1, 3, 5 and 6 wt.%) of tannic acid for functionalizing graphene oxide (GO-TA) to the 13 wt % PAN/DMF solution. The mixtures were stirred for 24 h at the room temperature.

2.5. Electrospinning Process

The electrospinning setup applied in this work was involving a high voltage power source, cylindrical grounded collector, syringe (as

a polymer reservoir) and nozzle. The voltage of 20 kV applied to the PAN polymer solution and the gap between the nozzle and collector was 11 cm. A syringe pump (TERUMO TC-527) was used to control the flow of the PAN solution with a rate of 0.5 ml/h to the nozzle tip. The nanofibrous PAN/GO-TA composite adsorbents were collected on the cylindrical grounded collector. Figure 1 shows the electrospinning setup used in this research.

3. CHARACTERIZATION PROCESS

GO, GO-TA and PAN/GO-TA samples were characterized by SEM (Philips XL30 ESEM Holland). Figure 2 shows SEM micrograph of GO, where the exfoliated plates can be detected.

Figure 3 shows SEM images for PAN/GO-TA nanocomposite at two different magnifications. The GO-TA nanoparticles are well decorated in the PAN polymer matrix. In fact, strong interactions between the polymer and GO-TA nanoparticles dominated the agglomeration tendency of nanoparticles. Figures 4a and 4b present SEM micrograph and EDS image for GO-TA nanoparticles. The tendency of the nanoparticles for intermolecular interaction due to abundant functional groups of tannic acid (polyphenol) is detected in the form of agglomerate formation.

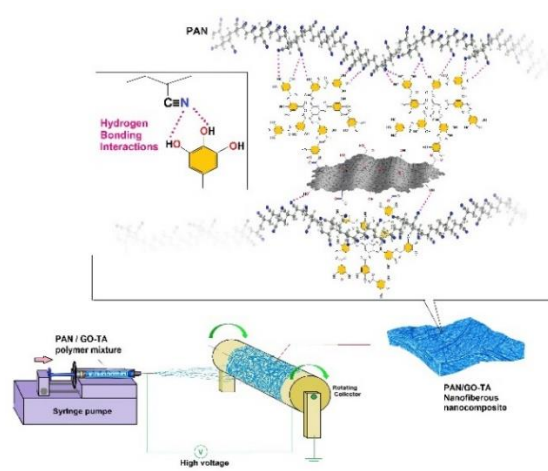


Figure 1. Electrospinning setup

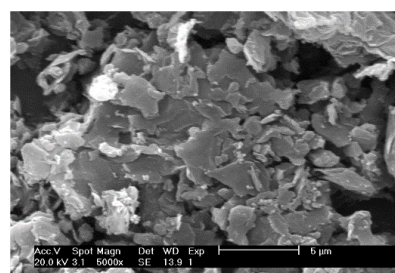


Figure 2. SEM micrograph of GO synthesized based on the modified Hummers method

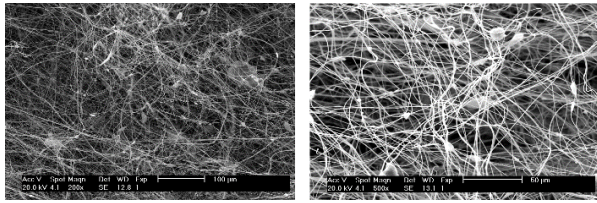


Figure 3. SEM micrograph of the PAN/GO-TA nanocomposite

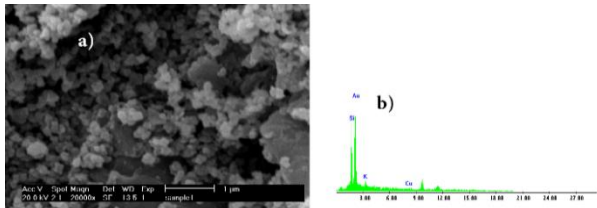


Figure 4. a) SEM micrograph and b) EDS of the synthesized GO-TA

4. EXPERIMENTAL DESIGN

Mathematical and statistical analysis was studied by Central Composite Design (CCD) under Response Surface Methodology (RSM) by applying the DoE software (Version: 7). In this research, four independent variables involving solution pH (A), nanoparticles weight percentage (B), heavy metal ions concentration (C) and contact time (D) were considered and then optimized for lead and cadmium adsorption. The ranges and levels of these variables are listed in Table 1.

The metal cation removal percentage (Y) was taken as a response of the software. The regression analysis technique based on the quadratic equation model Equation (1) was adapted to predict the optimum conditions.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

The favorability was chosen as maximum removal of heavy metal ions at optimum pH, nanoparticles weight percentage, heavy metal ions concentration and contact time.

TABLE 1. Ranges and levels of independent variables for lead and cadmium ions adsorption

Variable	Range and level				
	$-\alpha$	-1	0	1	$+\alpha$
pH	4.5	5	6	7	7.5
Nanoparticles weight percentage	0	1	3	5	6
Initial concentration (ppm)	5	12.5	27.5	42.5	50
Contact time (min)	15	30	60	90	105

5. RESULT AND DISCUSION

The heavy metal ions adsorption from an aqueous solution onto PAN/GO-TA nanofibrous composite was investigated through a batch process. The 1 M NaOH and HCl aqueous solutions were used to modify the pH of the solutions. Then, the samples were examined in terms of cadmium and lead ions concentrations with an atomic absorption spectrophotometer. The removal percentage of cadmium and lead ions from aqueous solutions were calculated by Equation (2).

$$R = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where, R is the removal percentage of a metal cation. C_i and C_f are the initial and final concentrations of a heavy metal.

Three-dimensional plots for lead and cadmium ions removal percentage with PAN/GO-TA nanocomposite as a function of pH, nanoparticles weight percentage, initial concentration of the heavy metal ion and contact time are illustrated in Figures 5 and 6. Data in these figures shown that heavy metal cations adsorption is less efficient at lower pH value of ($\text{pH} < 5$). In fact, under acidic conditions, the functional groups such as $-\text{OH}$ and $-\text{COOH}$ on the surface of GO are protonated under acidic conditions while $-\text{O}^-$ and $-\text{COO}^-$ attract protons and metal cations. Furthermore, the adsorption process is lower at acidic pH values. In fact, the adsorbent considerably adsorbs H^+ ions in competition with metal ions from the solution. Therefore, positive charges are accumulated on the adsorbent surface where is unsuitable for cations adsorption. In other words, the cations adsorption increases when H^+ ions decrease ($5 < \text{pH} < 7$). Although lead and cadmium cations have a great tendency to precipitate in the forms of $\text{Pb}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$ when $\text{pH} > 8$. These figures also illustrate that lead and cadmium ions removal percentage increased with increasing the nanoparticles weight percentage up to 4.09 wt.%. In fact, this provides the adequate active sites for the cationic metal adsorption through the nanocomposite structure. However, nanoparticles weight percentage increment increases the number of active sites; but, it seems that the adsorption process was stopped in the studied range. Its reason may be due to lack of the unfilled active sites. The cadmium and lead ions removal percentage increased with increasing their initial concentrations from 12 to 37 ppm. Since active sites are saturated by the heavy metal ions in the nanocomposite adsorbent more than 37 ppm, the adsorption process decreased. The cadmium and lead ions adsorption increased with increasing the contact time from 15 to 69 min although they did not significantly increase by increasing the contact time more than 69 min. It is probably due to lack of the unfilled active sites.

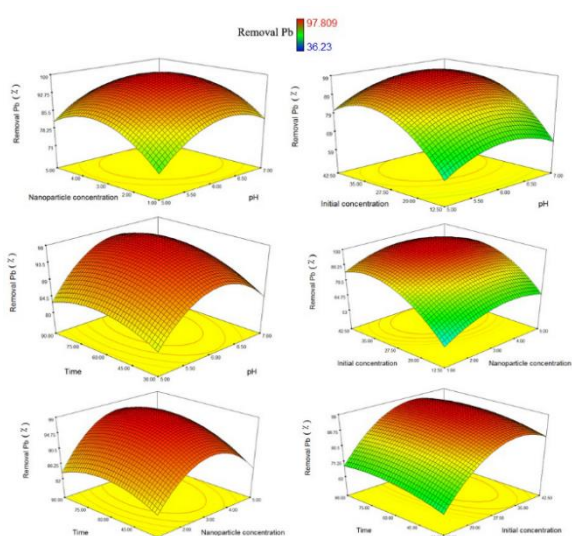


Figure 5. Effect of quadratic model variables on lead (II) removal percentage

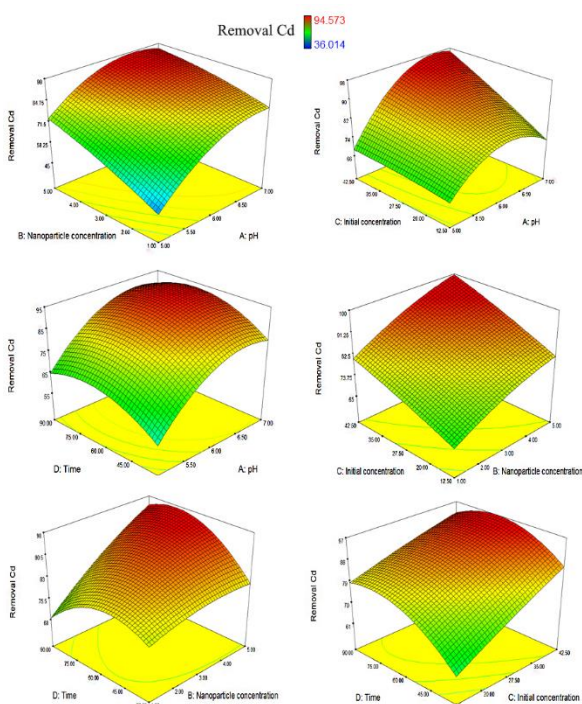


Figure 6. Effect of quadratic model variables on cadmium (II) removal percentage

6. OPTIMIZATION

The process was statistically optimized by maximizing the heavy metal ions removal. According to the software output, 99.82% of Pb(II) removal was found at pH of 6.2, nanoparticles weight percentage of 3.56 wt.%, initial concentration of lead ions of 31.78 ppm and contact time

of 72 min while 98.34% of Cd(II) removal was obtained at pH of 6.4, nanoparticles weight percentage of 4.95 wt.%, initial concentration of cadmium ions of 39.71 ppm and contact time of 69 min. For validation, two experimental runs were carried out at both sets of optimum conditions and 97.37% and 94.28% were respectively obtained for Pb(II) and Cd(II) removal. Absolute errors found for Pb²⁺ and Cd²⁺ ions adsorption were 2.52 and 4.31%, respectively. This clarifies that the statistical correlations can properly predict the adsorption process.

7. ADSORPTION ISOTHERMS

The lead and cadmium ions removal percentage are shown in Figure 7. The ions removal percentage dramatically increased in the first hour and then equilibrium occurred after 130 min (steady state condition was obtained). Interaction between the heavy metal ions and PAN/GO-TA nanofibrous composite was carefully studied by the adsorption isothermal models (at pH of 6.3, nanoparticles weight percentage of 4.26 wt.% and equilibrium time of 130 min). As shown in Figure 8a, the adsorption capacity increased with increasing the ions concentration and then the curves were found flat for both lead and cadmium ions (when the ions equilibrium concentrations were at 45 ppm). The adsorption equilibrium was studied using Langmuir and Freundlich isotherms, which can be defined by Equations (3) and (4), respectively [15,16]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_f q_m} \tag{3}$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{4}$$

where, C_e (ppm) is the equilibrium concentration, q_e (mg/g) is the adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption capacity, and k_f (g/mg) is the Langmuir constant. The k_f and 1/n are the Freundlich constants corresponding the adsorption capacity (mg/g) and adsorption intensity, respectively. Langmuir and Freundlich equations constants are determined from (C_e/q_e vs. C_e) and (Ln q_e vs. Ln C_e) graphs which are respectively shown in Figures 8b and 8c. Therefore, the values of q_m and k_f (for Langmuir model) were found from the slope and intercept of Figure 8b while the values of n and k_f (for Freundlich model) were obtained from the slope and intercept of Figure 8c. These results were tabulated in also the extract results from these plots are listed in Table 2.

As shown in Table 2, Pb²⁺ and Cd²⁺ ions adsorption on the PAN/GO-TA nanocomposite was properly fitted to Langmuir isotherm model with the excellent R² data.

Table 3 compares the maximum adsorption capacity of Pb²⁺ and Cd²⁺ ions on various adsorbents (based on literature) and this research.

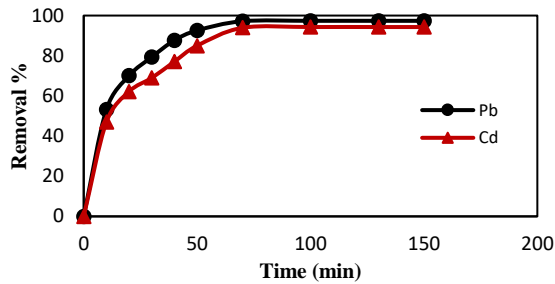


Figure 7. Pb^{2+} and Cd^{2+} ions removal percentage vs. time on PAN/GO-TA nanocomposite

TABLE 2. Langmuir and Freundlich models parameters

	Langmuir			Freundlich		
	q_m (mg/g)	k_l (L/mg)	R^2	n	k_f	R^2
Pb^{2+}	344.83	0.024	0.9944	1.30	2.38	0.9834
Cd^{2+}	312.5	0.021	0.9938	1.26	2.09	0.9876

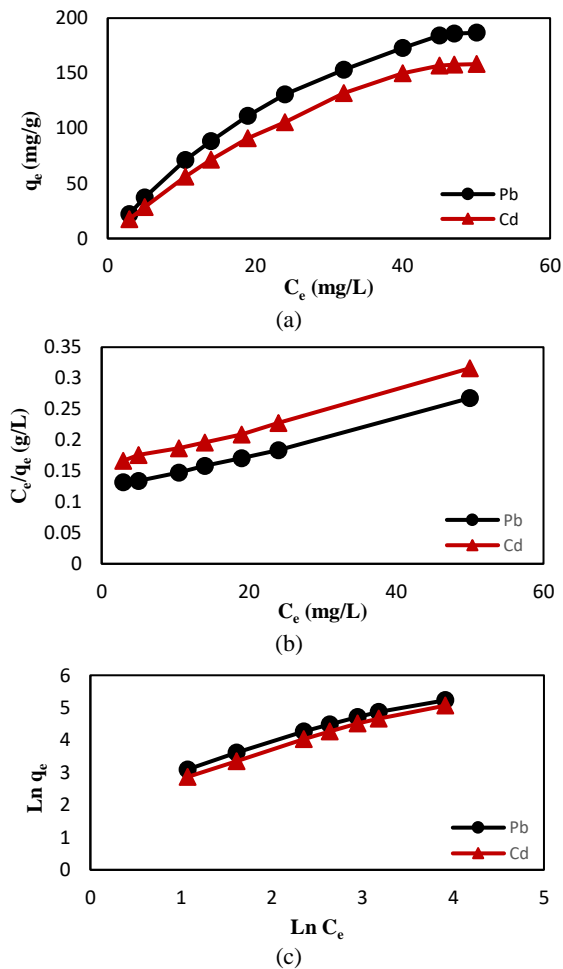


Figure 8. a) Adsorption isotherms, b) Langmuir and c) Freundlich model for Pb^{2+} and Cd^{2+} ions adsorption on PAN/GO-TA nanocomposite

TABLE 3. Maximum adsorption capacity of Pb^{2+} and Cd^{2+} ions on the various adsorbents

Adsorbent	q_m (mg/g) for Pb^{2+}	q_m (mg/g) for Cd^{2+}	Ref.
Poly(vinyl alcohol)/chitosan composite nanofiber	266	148	[17]
Phosphorylated PAN-based nanofiber	98.06	18.89	[18]
Aminated polyacrylonitrile/ γ -AIOOH electrospun composite nanofibers	180.83	114.94	[19]
Poly ethylene oxide /Chitosan Electrospun nanofiber	214.80	232.30	[20]
Graphene oxide/polyacrylonitrile nanofibrous composite	344.83	312.50	This study

8. CONCLUSION

In the present study, PAN/GO-TA nanofibrous composite were prepared to remove $Pb(II)$ and $Cd(II)$ from the aqueous solutions. CCD under RSM was applied to study the effect of solution pH, nanoparticles weight percentage, initial concentration of heavy metal ions and contact time. The model terms had substantial effect on the adsorption of $Pb(II)$ and $Cd(II)$ ions because $Prob > F$ was less than 0.050. The optimum conditions for 97.37% of Pb^{2+} and 94.28% of Cd^{2+} ions removal were meanly obtained at pH of 6.3, nanoparticles weight percentage of 4.26 wt.%, metal ions concentration of 35.74 ppm and contact time of 70.5 min. Furthermore, the Langmuir isotherm model could fantastically model Pb^{2+} and Cd^{2+} ions adsorption on the PAN/GO-TA nanocomposite.

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Persian Abstract

چکیده

در این مطالعه گرافن اکسید توسط تانیک اسید عامل دار شده و به روش الکتروریسی نانوالیاف پلی آکریلونیتریل/گرافن اکسید به منظور حذف دو فلز سنگین سرب و کادمیم از محلول‌های آبی تهیه شده است. نتایج حاکی از آن است که این نانو جاذب توانایی جذب کاتیون‌های فلزی سرب و کادمیم را به خوبی دارد. شرایط بهینه برای حذف ۹۷/۳۷ و ۹۴/۲۸ درصد سرب و کادمیم در pH ۶/۳، ۴/۲۶ درصد وزنی از نانوذرات، غلظت ۳۷/۷۴ ppm یون‌های فلزی و زمان تماس ۷۰/۵ دقیقه می‌باشد. حداکثر ظرفیت جذب برای سرب و کادمیم به ترتیب ۳۴۴/۸۳ و ۳۱۲/۵ میلی‌گرم بر گرم بود.
