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Adsorption of Cadmium (II) onto Thiolated Graphene Oxide and Kinetic Investigations

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ABSTRACT: Cadmium is a very toxic metal that has adverse effects on human health and aquatic environments even at low concentrations. Therefore, efforts should be made to eliminate this metal from aquatic ecosystems. This study was carried out in order to remove cadmium ions from synthetic aqueous solutions by thiolated graphene oxide in a batch system. In this study, the effect of experimental parameters such as pH, adsorbent dosage and initial cadmium concentration was investigated. To characterize the adsorbent properties, SEM and FT-IR analyses were utilized. The results showed that with the increasing initial concentration of cadmium, the amount of adsorption decreased and increasing the dose of adsorbent and pH increased the percentage of cadmium removal. Comparison of isotherm and kinetic adsorption models showed that Langmuir and Pseudo-second order models, with R2 values of 0.97 and 0.99, respectively, had a better fitting and give a good description of adsorption data than other models. Therefore, as a general conclusion, it can be said that the synthesized adsorbent had a high capability to remove cadmium from aqueous solutions.

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1. INTRODUCTION

Cadmium (Cd), one of the most toxic environmental contaminants, exposes a great threat to human health and ecosystems due to its tendency for bioaccumulation and relative mobility in the environment. Therefore, efforts should be made to eliminate this metal from aquatic ecosystems [1]. The common techniques for removal of metallic ions are chemical precipitation, coagulation, ion exchange, chemical reduction, membrane separation, biological treatment and absorption [2]especially in arid and semi-arid regions of the world is exerting great pressure on resources and establishing more need to provide good quality water for human and other consumptions. Water recovery/recycle/reuse has proven to be effective and successful in creating a new and reliable water supply. Accordingly, attention is being paid to the effective treatment of alternative sources of water (apart from fresh water. The adsorption process is one of the most widely used methods for removal of pollutants from polluted media because of low cost, feasible design, facile application and insensitivity to toxic materials [3]. Among adsorbents, graphene nanoparticles are used to remove heavy metals due to their high potential, high absorption capacity and high surface area [4]. The functionalization of graphene oxide significantly increases the absorbent capacity to remove heavy metals from wastewater. Studies have shown that the thiol group tends to have a strong tendency to bond with soft metals such as cadmium [5]cyanuric chloride and sodium 2-mercaptoethanol in sequence as efficient ways to introduce amine and thiol functional groups onto the nanotube sidewalls. The synthesized amino and thiolated MWCNTs were characterized by Fourier transform infrared spectroscopy (FT-IR.

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2. METHODOLOGY

2.1. Batch adsorption experiment

To study the adsorption of Cd(II) ion from aqueous solution in a batch system, a 250 ml Erlenmeyer flask containing 100 ml of ion solution with magnet stirring at ambient temperature was used. The study was carried out by sampling at different times (5, 10, 15, 20, 30, 40, 50, 60 min) and equilibrium time was assumed to be 60 min. Cd(II) ion concentration in the solution was measured by the dithizone method and by using spectrophotometry at 480 nm [6]. In every experiment, adsorbent efficiency was determined according to maximum adsorption capacity (q_e, mg/g) as Eq. (1). [7]. Additionally, the removal percent of Cd(II) was calculated by Eq. (2).

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

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

2.2. Evaluation of adsorption process in batch system

Langmuir model suggests that adsorption is occurred on a mono layer in a homogenous surface without reaction of the adsorbed molecules. It is explained by Eq. (3), and Freundlich model is described according to Eq. (4).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

2.3. Study of adsorption kinetic

Pseudo-first order equation investigates the occupation of adsorption sites with respect to unoccupied sites. This model was described by Lagrange as Eq. (5).

$$Log\left(q_e - q_t\right) = Log q_e - \frac{k_1}{2.303} t \quad (5)$$

Pseudo-second order kinetic was expressed to describe adsorption of bivalence metallic ions as Eq. (6) [1].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

3. Results and discussion

As shown in Figure 1, by increasing the adsorbent dosage Cd(II) ion removal increased, which was due to a greater number of accessible active sites of the adsorbent, higher active surface area and dynamic factors such as higher availability of free bonds of the adsorbent in solution [8].

Figure 2 demonstrates the nonlinear Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms of Cd(II) ions onto the by GO/Fe3O4-Si-Pr-SH Nanoparticles and model parameters summarized in Table 1. Comparison of isotherm adsorption models showed that Langmuir and Freundlich, with R^2 values of 0.97 and 0.96, respectively, had a better fitting and describe adsorption data better than other models.

Table 2 and Figure 3 display the parameters and linear regression of pseudo-second-order rates. Data showed that pseudo-first-order kinetic models didn't show good fitness (in terms of R^2 values), while the pseudo-second-order model logically described a good fitness of data. All calculated q_{e2} values were close to those obtained experimentally ($q_{e\ exp}$). By increasing the Cd(II) concentration from 10 to 50 mg/l, slopes of the lines and constants of pseudo-second order equation (K_2) reduced which represents the fast saturation of adsorption active sites by metallic ions.

4. CONCLUSIONS

In the present study, isothermal and kinetic manner of Cd(II) adsorption onto thiol-functionalized Graphene oxide were investigated. Data showed that Langmuir and Freundlich

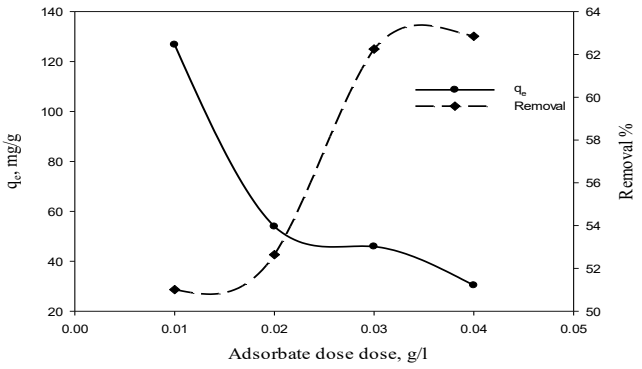

Fig. 1. Effect of adsorbent dosage on cadmium adsorption by GO/Fe_3O_4-Si-Pr-SH Nanoparticles.

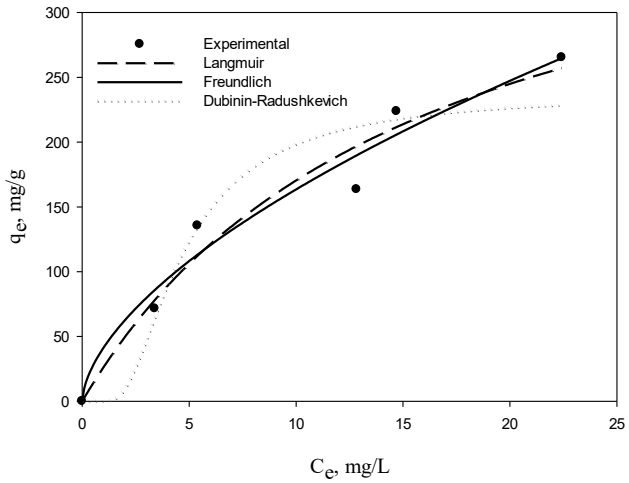

Fig. 2. Isotherm models for cadmium adsorption by GO/Fe_3O_4-Si-Pr-SH.

Table 1. Langmuir, Freundlich, and Dubinin–Radushkevich parameters for adsorption of Cd(II) onto GO/Fe_3O_4-Si-Pr-SH.

Models	**Parameters**		
Langmuir	$q_{m.exp}$ *(mg/g)*	*b (l/mg)*	R^2
	435.24	0.0644	0.97
Freundlich	*1/n*	K_f	R^2
	0.59	41.41	0.966
Dubinin–Radushkevich	q_m *(mg/g)*	*E (kJ/mol)*	R^2
	237.1	3.87	0.92

Table 2. Kinetic adsorption parameters obtained using Pseudo-first-order kinetics and pseudo-second-order models

Conc. (mg/l)	$qe_{(Exp)}$	Pseudo-first-order			Conc. (mg/l)		Pseudo-second-order		
		K_1	$q_{e2(\ mg/g)}$	R^2			K_2	$q_{e2(\ mg/g)}$	R^2
10	71/51	0.035	19.26	0.33	10	71/51	0.01	70.92	0.99
20	135.49	0.004	40.72	0.01	20	135.49	0.008	108.69	0.95
30	163.54	0.015	99.33	0.40	30	163.54	0.002	135.13	0.97
40	221.02	0.022	62.71	0.26	40	221.02	0.005	208.33	0.98
50	265.24	0.041	43.46	0.26	50	265.24	0.01	263.15	0.99

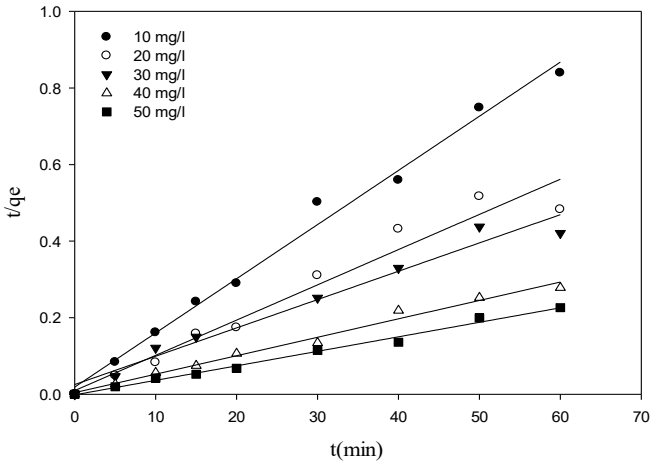

Fig. 3. Pseudo-second-order of cadmium adsorption onto GO/Fe_3O_4-Si-Pr-SH

isotherm models can logically describe the adsorption process. Pseudo-second-order had good fitness with data compared to the pseudo-first-order kinetic rate.

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