

Adsorptive Removal of Cadmium (II) from Aqueous Solution by Multi-Carboxylic-Functionalized Silica Gel: Equilibrium, Kinetics and Thermodynamics

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Abstract. In the present study, the adsorption behavior of cadmium (II) ion from aqueous solution onto multi-carboxylic-functionalized silica gel (SG-MCF) has been investigated in detail by means of batch and column experiments. Batch experiments were performed to evaluate the effects of various experimental parameters such as pH value, contact time and initial concentration on adsorption capacity of cadmium (II) ion. The kinetic data were analyzed on the basis of the pseudo-first-order kinetic and the pseudo-second-order kinetic models and consequently, the pseudo-second-order kinetic can better describe the adsorption process than the pseudo-first-order kinetic model. Equilibrium isotherms for the adsorption of cadmium (II) ion were analyzed by Freundlich and Langmuir isotherm models, the results indicate that Langmuir isotherm model was found to be credible to express the data for cadmium (II) ion from aqueous solution onto the SG-MCF. Various thermodynamics parameters of the adsorption process, including free energy of adsorption (ΔG^0), the enthalpy of adsorption (ΔH^0) and standard entropy changes (ΔS^0), were calculated to predict the nature of adsorption. The positive value of the enthalpy change and the negative value of free energy change indicate that the process is endothermic and spontaneous process.

1. Introduction

Cadmium, as well as other heavy metals such as mercury, chromium and lead, does harm to environment and human health even at relatively low concentration [1]. It has been classified as a human carcinogen and teratogen targeting lungs, kidneys, bones and reproductive organs [2]. Hence there is considerable interest in the development of techniques to remove cadmium (II) from contaminated and natural water.

A wide range of physical and chemical treatment methods to remove cadmium (II) from wastewaters have been reported previously, including chemical precipitation [3], ion-exchange [4], adsorption [5], membrane process [6] and electrodialysis [7]. Among them, the adsorption technology is found to be quite dependable, effective and economically feasible for the removal of cadmium from aqueous solution. And there are a large number of types of sorbents, including oxide minerals [8], zeolite [9], bio sorbent [10], agricultural wastes [11], organic/inorganic composite [12], activated carbon [13], resins [14], fibers [15] and modified silica gel [1], which have been employed to



eliminate cadmium (II) ion or to enrich trace amounts of it from aqueous solutions. It is necessary to further develop cheaper and available adsorbent with good performance for improving the efficiency of the adsorption process.

Silica gel has been extensively used as matrix to prepare adsorbents for removing heavy-metal-ions because not only does it have large surface area and its surface can be modified with organic ligands, but also presents good chemical stability even under acidic conditions [16]. Thus, silica gel has been received a great deal of attention recently due to its various excellent performance. With regard to the synthetic methods of modified silica gel are similar to make reacting silanol groups (Si-OH) of silica gel surface with organosilane, these functional groups grafted onto silica gel surface then are further modified according to special purpose.

In the present investigation, the multi-carboxylic-functionalized silica gel (SG-MCF) was selected as adsorbent for the adsorption cadmium (II) ion from aqueous solution by batch. In the batch studies, effects of such factors as pH, initial concentration, contact time and temperature on the sorption of cadmium (II) ion have been investigated. The thermodynamic parameters, the kinetics and the factors controlling the adsorption process were calculated and discussed in detail.

2. Material and methods

2.1. Adsorbent and adsorbate

The SG-MCF was prepared according to our previous work [1]. Surface area, pore volume and average pore diameter of the SG-MCF is 174.573 m²/g, 0.458 cm³/g and 9.380 nm, respectively.

CdCl₂·2.5H₂O used in this study was of analytical grade purchased from Beijing Yili chemical Co., Ltd, Beijing city, P.R. China. All other reagents used were also AR grade and without further purification. A series of cadmium (II) solutions of different concentrations were prepared by diluting 1000 mg/L of stock cadmium (II) solution which was obtained via dissolving a weighed quantity of CdCl₂·2.5H₂O in de-ionized water. In addition, the pH value of solutions was controlled by various buffer solutions: glycine acid/hydrochloric acid for pH 2.0 and 3.0, sodium acetate/acetic acid for pH 4.0, 5.0 and 5.5, and monopotassium phosphate/sodium hydroxide for pH 6.0 and 7.0.

2.2. Analysis of cadmium (II) ion

The concentration of cadmium (II) ion solutions was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) (Perkin-Elmer-7000DV, USA).

2.3. Batch studies

Batch adsorption experiments were carried out by taking aliquots of 25 mL of cadmium (II) ion solution of known concentration in separate 50 mL capped conical flasks. The concentration of Cd²⁺ was determined using ICP-AES. The percentage removal and adsorption capacity of Cd²⁺ can be calculated according to the following equations.

$$\text{Removal rate (\%)} = \frac{(C_i - C_f)}{C_i} \times 100\% \quad (1)$$

$$q = \frac{(C_i - C_f) \times V}{1000W} \quad (2)$$

where q represents the adsorption capacity (mg/g); C_i and C_f are the initial and final concentration of Cd²⁺ (mg/L), respectively. V is the volume of the solution (mL); W is the mass used of SG-MCF adsorbent (g).

3. Results and discussion

3.1. Effect of pH

The effect of varying pH on Cd^{2+} uptake was investigated using the batch experiments. The adsorption experiments were triplicated. Considering the formation of precipitation of cadmium (II) at higher pH, pH above 7.0 was not investigated. It can be seen from Fig.1, the removal of Cd^{2+} increased as the pH value of the aqueous solution increased from 2.0 to 5.0 and the removal efficiency of cadmium (II) ions is low below pH 4.0. It can be explained by competition process between Cd^{2+} and H^+ for the same active sites and protonation of active sites [17], however, the concentration of the H^+ ion which exists in the aqueous solution will be declined as pH increased and will not give the chance to compete with Cd^{2+} onto the active sites of SG-MCF [18]. In the pH range of 5.0 to 7.0, the pH value has a minimal effect on the removal of Cd^{2+} , the removal efficiency of Cd^{2+} measures up to 89.44% at pH 7.0. At pH enhances to the range 5.0-7.0, where Cd^{2+} , $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_2$ forms are present in the solution[1], changing distribution of cadmium (II) ion species in the solution. In addition, at pH from 5.0 to 7.0, H^+ ion acted as competitor in the aqueous solution is less and the number of adsorption sites onto SG-MCF for Cd^{2+} is more [17]. This means that it is easier for Cd^{2+} and $\text{Cd}(\text{OH})^+$ ions to hook up the free binding sites of adsorbent under such conditions.

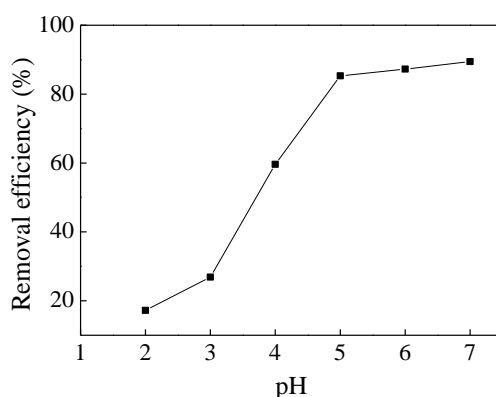


Figure 1. Effect of pH on the removal rate of cadmium (II) ion

3.2. Effect of contact time and adsorption kinetics

Fig.2 shows the effect of contact time on the adsorption capacity of cadmium (II) from aqueous solution at different temperatures. As seen here, the adsorption capacity of cadmium (II) increased with the time during the first 120 min and then the curve off as equilibrium was reached. In addition, there is a rapid uptake process within 90 min and the adsorption capacity of cadmium (II) ion does not change obviously with time after 120 min. It can be attributed to the fact that there is abundant availability of active sites on the SG-MCF which are available for the adsorption of cadmium (II) ion at the early stage [19]. After 120 min the active external vacant active sites are almost saturated, the adsorption process needs more time to occur depended on active intra-particle sites [19]. Almost all of the active sites onto the SG-MCF are supposed to saturation after 180 min and the system reaches equilibrium state. The analysis of kinetic data is necessary since it can provide the information about mechanism of adsorption process [19]. Therefore, in order to clarify the mechanism of adsorption process, some adsorption models were employed to evaluate the experiment data.

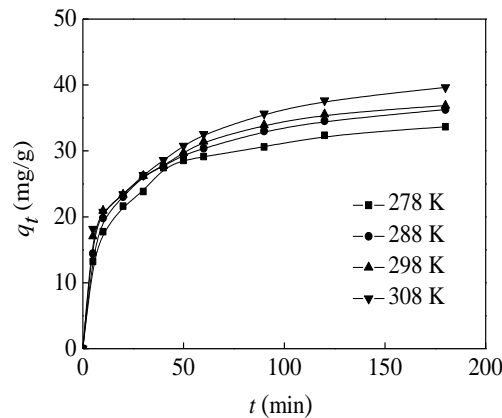


Figure 2. Effect of contact time on the adsorption of cadmium (II) ion onto the SG-MCF

3.2.1. Pseudo -first-order kinetics, The Lager Gren pseudo-first-order kinetic model for the adsorption of solid/liquid system is given as [20].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where q_t (mg/g) and q_e (mg/g) are the adsorption capacity of cadmium (II) at any time t and at equilibrium, respectively, k_1 (1/min) represents the rate constant of the first-order model. The rate constant, k_1 and correlation coefficients were calculated from the linear plots of $\ln(q_e - q_t)$ versus t and listed in Table 1. Fig.3 (a) shows the pseudo-first-order kinetic plot for the adsorption cadmium (II) ion onto SG-MCF at different temperatures. As can be seen from the results that the linear correlation coefficients of the plot is not good and the calculated values of q_e do not match the experimental ones. Thus, the results indicate that the adsorption process cannot be explained by the pseudo-first-order kinetic model.

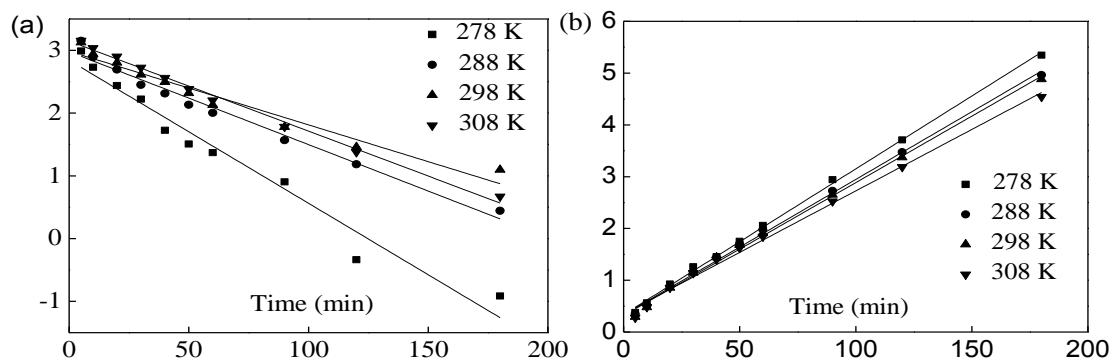


Figure 3. Lagergren first-order (a) and pseudo-second-order (b) kinetics of cadmium (II)

Table 1. Kinetic parameters for the adsorption of cadmium (II) onto SG-MCF

T (K)	$Q_{e, \text{exp}}(\text{mg} \cdot \text{g}^{-1})$	Pseudo-first-order rate equation			Pseudo-second-order rate equation		
		$k_1 (\text{min}^{-1})$	$Q_{e, \text{cal}} (\text{mg} \cdot \text{g}^{-1})$	R_1^2	$k_2 (\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$Q_{e, \text{cal}} (\text{mg} \cdot \text{g}^{-1})$	R_2^2
5	34.07	0.02279	17.14	0.961	0.002355	35.53	0.998
15	36.26	0.01481	19.66	0.978	0.002056	38.24	0.997
25	36.88	0.01173	19.79	0.952	0.002079	38.94	0.996
35	39.64	0.01434	23.28	0.992	0.001607	42.12	0.993

3.2.2. *Pseudo -second-order kinetics*, the pseudo-second-order equation, which has been applied for analyzing chemisorption kinetic from liquid solutions, was defined as follows [20].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where k_2 ((1/min)/(mg/g)) is the rate constant for pseudo-second-order model at the equilibrium. Among them, the rate constant k_2 , q_e and the corresponding linear regression correlation coefficient R^2 were calculated from the linear plots of t/q_t versus t and given in Table 1. Fig.3 (b) shows the pseudo-second-order kinetic plot for the adsorption cadmium (II) ion onto SG-MCF at different temperatures. As can be seen from Fig. 3 and Table 1, the adsorption process of cadmium (II) ion onto SG-MCF can be better described by pseudo-second-order kinetic model because the correlation coefficients are greater than 0.99 and the calculated q_e values depending on the pseudo-second-order model are good in agreement with the experimental ones. The results suggest that cadmium (II) ion can combine with active sites onto SG-MCF using covalent chemical bonds, involving valence forces between sorbent and adsorbate by sharing or exchanging of electrons [21]. The result can be expected because the common type adsorption processes are more rapid and mainly controlled by diffusion, however, the chelating adsorption process is slower and controlled either by particle diffusion mechanism or by second-order chemical reaction [20]. Similar phenomena have been observed by the adsorption copper ion onto modified silica gel [18], the adsorption iron ion onto amino functioned mesoporous silica gel.

3.3. Effect of initial concentration and adsorption isotherms

The effect of initial concentration on cadmium (II) ion uptake was investigated using a series of different cadmium (II) ion concentrations varied from 50 to 400 mg/L at different temperatures. Fig.4 shows the effect initial concentration on adsorption capacity. From Fig.4, it can be seen that the adsorption capacities are increased as initial concentration increased from 50 to 400 mg/L, and reach a plateau. This result can be explained in terms of the interaction of cadmium (II) ion with the SG-MCF. It can be attributed to the fact that there is the higher driving force for mass transfer as the concentration of cadmium (II) ion increased [22]. Adsorption isotherms are investigated for acquiring more information about the adsorption process. It is of fundamental importance to solid-liquid adsorption system and can provide a relationship between the concentration of the solute in the solution and the amount of solute adsorbed on the solid sorbent when the two phases are at equilibrium. Nevertheless, Langmuir and Freundlich equations are two common isotherm models to describe the behavior of adsorbent and the correlated adsorption parameters. In this work, the two models were used to investigate the adsorption properties of the SG-MCF for cadmium (II) ion.

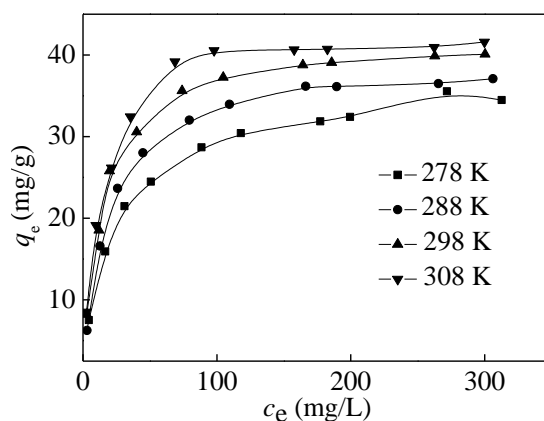


Figure 4. Effect initial concentration on adsorption capacity of cadmium (II)

3.3.1. Langmuir isotherm, The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a fixed number of binding sites. These sites are also assumed to be energetically equivalent and distant each other so that the molecule adsorbed has no effect on adjacent sites [23]. The Langmuir model can be described by the following equation [23].

$$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \quad (5)$$

where q_e is the amount of cadmium (II) ion adsorbed by per gram adsorbent (mg/g) and c_e is the equilibrium concentration of cadmium (II) ion in the solution. q_m and K_L are Langmuir constants related to the adsorption capacity (mg/g) and the adsorption energy (L/g), respectively. And the values of q_m and K_L can be obtained from the linear plot of c_e/q_e versus c_e .

The Langmuir plot for cadmium (II) ion adsorption onto SG-MCF adsorbent was shown in Fig.5. Langmuir constants and correlation coefficients (R^2) at different temperatures are given in Table 2. As it can be seen from Fig.5 and Table 2, the experimental data exhibited good linear relationship with Langmuir model ($R^2 > 0.995$) and the adsorption capacity values calculated are close to experimental ones, therefore, this means that the process of adsorption cadmium(II) ion onto the SG-MCF can be better described by Langmuir isotherm model.

In addition, the essential characteristic of Langmuir equation can be described using the dimensionless separation factor R_L , which can be defined as [23]:

$$R_L = \frac{1}{1 + K_L c_0} \quad (6)$$

where c_0 is the initial concentration of cadmium (II) ion (mg/L). R_L indicates the nature of the adsorption process. The calculated R_L values were found to from 0.0583 to 0.547 at 278 K, to from 0.0418 to 0.519 at 288 K, to from 0.0337 to 0.406 at 298 K and to from 0.0246 to 0.346 at 308 K for initial concentration of cadmium (II) ion of 50-400 mg/L. The result indicated that the adsorption process of cadmium (II) ion onto SG-MCF adsorbent was favourable adsorption process because all values of R_L lie between 0 and 1 at all temperatures studied [24].

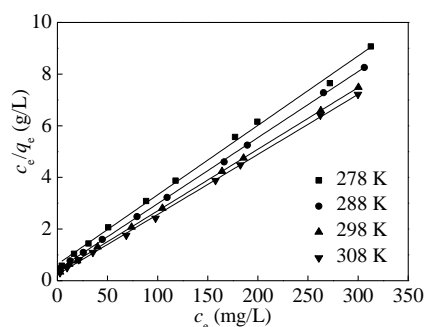


Figure 5. Langmuir plot for the adsorption cadmium (II) ion onto SG-MCF

Table 2. Langmuir and Freundlich isotherm constants for Cd (II) ions onto SG-MCF

T (K)	$q_{e, \text{exp}}(\text{mg/g})$	Langmuir isotherm			Freundlich isotherm		
		$q_{e, \text{cal}}(\text{mg/g})$	$K_L (\text{L/mg})$	R^2	$1/n$	$K_F(\text{mg/g})$	R^2
278	35.54	37.18	0.04228	0.9973	0.3376	5.7276	0.9233
288	37.09	39.09	0.06017	0.9997	0.3552	5.9284	0.8741
298	40.11	41.89	0.07535	0.9998	0.3123	8.0528	0.8721
308	41.58	43.01	0.09645	0.9993	0.3082	8.7259	0.8541

3.3.2. Freundlich isotherm, The Freundlich adsorption model is applicable to both monolayer and multilayer adsorption and to heterogeneous binding sites. The Freundlich equation is linearized as follows [23]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln c_e \quad (7)$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. And the K_f and n constants of Freundlich isotherm can be obtained by plotting $\ln q_e$ versus $\ln c_e$. Fig.6 presents the Freundlich isotherm plot for cadmium (II) ion adsorption onto SG-MCF adsorbent. The K_f and n constants of Freundlich isotherm and correlation coefficients (R^2) at different temperatures are given in the Table 2.

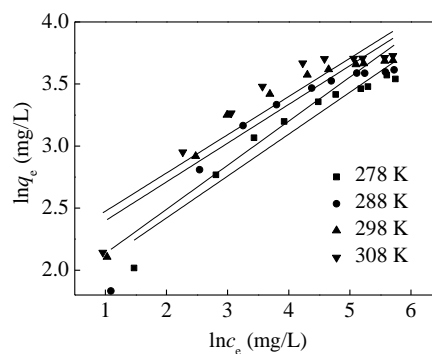


Figure 6. Freundlich plot for the adsorption cadmium (II) ion onto SG-MCF

As seen from Table 2 and Fig.6, the correlation coefficient (R^2) of Freundlich isotherm was 0.9233, 0.8741, 0.8721 and 0.8541 at different temperatures respectively. It means that the plot of $\ln q_e$ versus $\ln c_e$ was nonlinear, which obviously demonstrated that the adsorption process of cadmium (II) ion onto SG-MCF adsorbent does not obey the Freundlich isotherm model [22].

Comparing the correlation coefficient (R^2) of Langmuir and Freundlich isotherm, there was an excellent linear relationship between c_e/q_e and c_e , indicating the adsorption process of cadmium (II) ion onto SG-MCF adsorbent could be described via Langmuir isotherm.

3.4. Adsorption thermodynamics

To determine the parameters of adsorption thermodynamics are of significance because they can conclude whether the process is spontaneous or not and acquire an insight into the adsorption behaviors. These thermodynamics parameters, including free energy of adsorption (ΔG^0), the heat of adsorption (ΔH^0) and standard entropy changes (ΔS^0), can be calculated according to the following Eqs.

$$\Delta G^0 = -RT \ln K_L \quad (8)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

where R is the gas constants ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and T is the absolute temperature (K). ΔH^0 and ΔS^0 are obtained from the slope and intercept of the line plotted by $\ln K_L$ versus $1/T$, respectively. The obtained thermodynamic parameters for cadmium (II) ion onto SG-MCF were listed in Table 3. As it can be seen from Table 3, the negative value of ΔG^0 means the feasibility of the reaction and the spontaneous nature of the adsorption of Cd (II) ions by SG-MCF [22]. The positive value of ΔH^0

indicates that the adsorption process is endothermic [25]. However, the positive value of ΔS^0 reflects that there was an increase in the randomness at the solid-solution interface during the adsorption of Cd^{2+} ions onto the surface of SG-MCF [26].

Table 3. Thermodynamic parameters for the adsorption of Cd (II) ions by SG-MCF

ΔG^0 (KJ·mol ⁻¹)				ΔH^0 (KJ·mol ⁻¹)	ΔS^0 (J·mol ⁻¹ ·K ⁻¹)
278 K	288 K	298 K	298 K		
-19.56	-21.10	-22.39	-23.78	19.25	139.81

4. Conclusion

The objective of this work was to investigate the dependence of adsorption on adsorbent and adsorbate characteristics on the basis of batch and column experiments. Conclusions from this present study could be summarized as follows.

(1) The adsorption process for cadmium (II) ion onto SG-MCF adsorbent was found to be strongly affected by pH value of aqueous solution containing cadmium (II) ion, the initial concentration of cadmium (II) ion and contact time.

(2) The adsorption process could be better described by the pseudo-second-order model than pseudo-first-order model, adsorption capacities calculated to be 35.53, 38.24, 38.94 and 42.12 mg/g at 278, 288, 298 and 308 K, respectively, were closed to the experimental ones.

(3) The Freundlich isotherm and Langmuir isotherm model were applied to describe the adsorption process for cadmium (II) ion onto SG-MCF adsorbent, but the experimental data could be better fitted by the Langmuir isotherm model and correlation coefficients were found to be 0.9973, 0.9997, 0.9998 and 0.9993 at 278, 288, 298 and 308 K, respectively.

(5). Thermodynamics parameters of the adsorption process, including free energy of adsorption (ΔG^0), the heat of adsorption (ΔH^0) and standard entropy changes (ΔS^0), were obtained from adsorption isotherms at different temperatures. The result indicates that the adsorption process of cadmium (II) ion onto SG-MCF adsorbent was found to be endothermic and spontaneous.

Acknowledgments

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