Adsorption kinetic and desorption studies of Cu\(^{2+}\) on Multi-Carboxylic-Functionalized Silica Gel

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Abstract. In the present study, the adsorption behavior of copper (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 contact time on adsorption capacity of copper (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. And the adsorption mechanism of the process was studied by intra-particle and film diffusion, it was found out that the adsorption rate was governed primarily by film diffusion to the adsorption onto the SG-MCF. In addition, column experiments were conducted to assess the effects initial inlet concentration and the flow rate on breakthrough time and adsorption capacity ascertaining the practical applicability of the adsorbent. The results suggest that the total amount of adsorbed copper (II) ion increased with declined flow rate and increased the inlet concentration. The adsorption-desorption experiment confirmed that adsorption capacity of copper (II) ion didn’t present an obvious decrease after five cycles.

1. Introduction

Copper, 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 copper (II) from contaminated and natural water.

A wide range of physical and chemical treatment methods to remove copper (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 copper 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 copper (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 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 copper (II) ion from aqueous solution by batch. In the batch studies, effects of contact time on the sorption of copper (II) ion have been investigated. 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.

CuSO₄·5H₂O 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 copper (II) solutions of different concentrations were prepared by diluting 1000 mg/L of stock copper (II) solution which was obtained via dissolving a weighed quantity of CuSO₄·5H₂O 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 copper (II) ion
The concentration of copper (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 copper (II) ion solution of known concentration in separate 50 mL capped conical flasks. The concentration of Cu²⁺ was determined using ICP-AES. The percentage removal and adsorption capacity of Cu²⁺ 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 Cu²⁺ (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 contact time and adsorption kinetics
Fig.1 shows the effect of contact time on the adsorption capacity of copper (II) from aqueous solution at different temperatures. As seen here, the adsorption capacity of copper (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 copper (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 copper (II) ion at the early stage [17]. 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 [17]. 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 [17]. Therefore, in order to clarify the mechanism of adsorption process, some adsorption models were employed to evaluate the experiment data.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Effect of contact time on the adsorption of copper (II) ion onto the SG-MCF

3.1.1. Pseudo-first-order kinetics, The Lagergren pseudo-first-order kinetic model for the adsorption of solid/liquid system is given as [18].

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]  

(3)

Where \(q_t\) (mg/g) and \(q_e\) (mg/g) are the adsorption capacity of copper (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.2 (a) shows the

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** Laguerre first-order (a) and pseudo-second-order (b) kinetics of copper (II)

pseudo-first-order kinetic plot for the adsorption copper (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
Table 1. Kinetic parameters for the adsorption of copper (II) onto SG-MCF

| T (K) | $Q_e, exp$(mg·g$^{-1}$) | $k_1$ (min$^{-1}$) | $Q_e, cal$ (mg·g$^{-1}$) | $R_1^2$ | $k_2$ (g·mg$^{-1}$·min$^{-1}$) | $Q_e, cal$ (mg·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  |

3.1.2. **Pseudo-second-order kinetics**, the pseudo-second-order equation, which has been applied for analyzing chemisorption kinetic from liquid solutions, was defined as follows [18].

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}$$

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.2 (b) shows the pseudo-second-order kinetic plot for the adsorption copper (II) ion onto SG-MCF at different temperatures. As can be seen from Fig. 2 and Table 1, the adsorption process of copper (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 copper (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 [19]. 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 [18]. Similar phenomena have been observed by the adsorption copper ion onto modified silica gel [16], the adsorption iron ion onto amino functioned mesoporous silica gel.

3.1.3. **Intra-particle diffusion**, The adsorption process on porous sorbents mainly involves four stages. The first, the initial stage should be diffusion of solute from the bulk of the solution into boundary layer film bordering the solid surface by convection-diffusion. The second, the solutes pass through the film and reach the surface of solid phase. The third, the adsorption behavior is occurred gradually onto surface of adsorbent. The last stage, solutes transfer into interior pores through intra-particle diffusion process and combine with active sites of interior pores. In general, bulk diffusion and adsorption process are assumed to be rapid and they are not rate-controlled step [18]. Therefore, in order to determine whether intra-particle diffusion is rate limiting for the adsorption process or not, kinetic studies have to be investigated. The intra-particle diffusion model is expressed as follows [18].

$$q_t = k_3t^{0.5} + C$$

where $q_t$ is the adsorption capacity (mg/g), $k_3$ is the intra-particle diffusion rate constant (mg·g$^{-1}$·min$^{-0.5}$) and the intercept $C$ is an indicator to express the boundary layer thickness and it is obtained by extrapolation the linear portion of the plot of $q_t$ versus $t^{0.5}$.

As it can be seen from Fig.3, there is not a linear distribution of these points and the intra-particle diffusion occurred in the three stages for copper (II) ion onto the adsorbent. The first step in diffusion...
model is the external surface adsorption of copper (II) ion onto the SG-MCF. The second stage describes intra-particle diffusion of copper (II) ion onto the adsorbent. The third portion is attributed to the final equilibrium stage. It can be attributed to the fact that the bulk diffusion or exterior adsorption rate which is quite high, the subsequent linear portion is due to the

Intra-particle diffusion and plateau portion represents the equilibrium state [18]. The intra-particle diffusion constants and linear regression values were calculated and given in Table 2. The results indicated that intra-particle diffusion may play a role in the adsorption process because it is a factor to determine whether the whole process is rapid or not [20]. In addition, it is also observed from Table 2, the deviation of the curves from origin and intercept is positive values because of the effect of external film on the diffusion of the copper (II) ion from the bulk to the surface of the SG-MCF at initial stages of adsorption process [19].

![Figure 3. Intraparticle diffusion plots for copper (II) ion onto the SG-MCF at different temperatures](image)

![Figure 4. Bt versus time plots for SG-MCF at different temperatures](image)

| T (°C) | Film diffusion and pore diffusion | Intra-particle diffusion |
|-------|----------------------------------|--------------------------|
|       | Linear equation                  | Correlation coefficient | $k_i$ (mg·g$^{-1}$·min$^{0.5}$) | $C$ | $R^2$ |
| 5     | $B_t = 0.02277t + 0.2065$        | 0.973                    | 0.9589                          | 21.59 | 0.971 |
| 15    | $B_t = 0.01412t + 0.23339$       | 0.989                    | 1.6390                          | 17.58 | 0.987 |
| 25    | $B_t = 0.01111t + 0.27979$       | 0.967                    | 1.9172                          | 16.04 | 0.958 |
| 35    | $B_t = 0.01506t + 0.13969$       | 0.999                    | 2.1872                          | 15.14 | 0.977 |

3.1.4. Film diffusion and pore diffusion, the rate-limiting steps on porous sorbents for metallic ions are generally regarded by two steps, i.e film diffusion and intraparticle diffusion [21]. In order to clarify the mechanism of adsorption copper (II) ion onto SG-MCF further, the experimental data were analyzed by Boyd and Reichenberg equations. The film diffusion follows Fick’s law, but the sorbents particle should be assumed to be a sphere of radius ‘$r_0$' [18]. And the relevant equations are as follows [18]:

$$B_t = 0.02277t + 0.2065$$

$$B_t = 0.01412t + 0.23339$$

$$B_t = 0.01111t + 0.27979$$

$$B_t = 0.01506t + 0.13969$$

$$k_i (mg·g^{-1}·min^{0.5})$$

$$C$$

$$R^2$$
\[ \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left[ \frac{-D_i t \pi^2 n^2}{r_0^2} \right] \]  

(6)

or

\[ \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[ -n^2 B t \right] \]  

(7)

\[ B = \frac{\pi^2 D_i}{r_0^2} = \text{time constant} \]  

(8)

where \( D_i \) is the effective diffusion coefficient of ion in the adsorbent phase, \( r_0 \), the radius of the adsorbent particle, assumed to spherical, \( n \), an integer that defines the infinite series solution, \( q_t \) and \( q_e \) is adsorption capacity at time \( t \) and equilibrium time, respectively. Plot of \( B_t \) versus \( t \) was obtained from corresponding values of \( q_t \) and shown in Fig. 4. And the linear equations and correlation coefficients \( R^2 \) at different temperatures are shown in Table 2. The linearity of \( B_t \) versus \( t \) can be employed to distinguish between the film diffusion and particle diffusion governed the adsorption process. It is observed from Fig.4 and Table 2, all lines present fine linear relationship and all of them are without passing through the origin, the results indicate that the process of adsorption copper (II) ion onto SG-MCF may be controlled by the film diffusion to larger extent [17]. The result studied can be expected because the SG-MCF used in this study is modified only on the surface of silica gel.

3.2. Desorption and reusability study

The desorption of Cu (II) ion from the fixed bed is of crucial importance due to the fact that the Cu (II) ion adsorbed not only can be separated from the adsorbent but also the adsorption bed can be regenerated, making it can recover the ability to capture solute from aqueous solution. However, an important principle here is to separate the loaded solute from the column in the smallest possible volume of the eluted solution and the eluted solution is not posing any disposal problem waste. In order to the test stability and reusability of the SG-MCF adsorbent, 2.0 mol/L HNO₃ was applied to regenerate the fixed–bed column of the SG-MCF saturated with Cu (II) ion and the eluent at a constant flow rate of 0.25 mL/min. The adsorption-desorption cycles were repeated five times by dynamic experiments. The results of five cycles of adsorption-desorption of Cu (II) ion onto the SG-MCF are shown Fig.5. As shown in Fig.5, the results shown that after five cycles, the recovery efficiencies of Cu (II) ion still maintain above 91%, which indicate that the adsorbent had excellent stability and reusability.

4. Conclusion

The objective of this work was to investigate the dependence of adsorption on adsorbent (SG-MCF) and adsorbate (copper (II) ion) characteristics on the basis of batch. Conclusions from this present study could be summarized as follows.

(1) The adsorption process for copper (II) ion onto SG-MCF adsorbent was found to be strongly affected by pH value of aqueous solution containing copper (II) ion, the initial concentration of copper (II) ion and contact time. The adsorption capacity increased as pH value of the solution increased, and satisfactory adsorption capacity occurs in the pH range of 5.5-7.0, contact time prolonged or the initial concentration of copper (II) ion increased. When the initial concentration of copper (II) ion exceeds 150 mg/L or contact time reaches 90 min, they have a little influence on adsorption capacity of copper (II) ion.
(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) Adsorption mechanism was studied by intra-particle and film diffusion, it was observed that film diffusion is mainly rate-limiting step to the adsorption copper (II) ion onto the SG-MCF.

(4) The absorbent was regenerated by 2.0 M HNO₃ and was not observed to be obviously decrease for adsorption capacity of copper (II) ion after five adsorption-desorption cycles.

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