



Removal of trivalent chromium from water using low-cost natural diatomite

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ARTICLE INFO

Article history:

Received 16 April 2007

Received in revised form 10 January 2008

Accepted 3 March 2008

Available online 8 March 2008

Keywords:

Chromium
Diatomite
Water pollution
Equilibrium
Isotherms
Kinetic

ABSTRACT

Trivalent chromium was removed from the artificial wastewater using low-cost diatomite in batch and continuous systems. In batch system, four different sizes and five different amount of sorbent were used. The effect of the temperature on sorption was evaluated with using three different temperatures. As a result of the experiments, 85% of the trivalent chromium was removed from the wastewater in conditions of using 1.29 mm grain material at 30 °C temperature for 60 min in batch system but chromium removal was 82% at 30 °C temperature for 22 min and 97% from the wastewater at 30 °C temperature for 80 min in continuous system. Also, the equilibrium adsorption isotherms have been analyzed by Langmuir and Freundlich models. The Langmuir isotherms have the highest correlation coefficients. Langmuir adsorption isotherm constants corresponding to adsorption capacity, q_0 , were found to be 28.1, 26.5 and 21.8 mg Cr³⁺/g diatomite at 15, 30 and 45 °C, respectively. Adsorption process was an exothermic process as a result of thermodynamic parameters calculations. The kinetic data of the sorption showed that the pseudo second-order equation was the more appropriate, which indicate that the intraparticle diffusion is the rate-limiting factor.

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1. Introduction

Chromium has a high hardness value and +2, +3, +6 oxidation states. Also, its compounds have many different colors. Moreover, +6 state of chromium has a magnetic property. So, chromium and its compounds are widely used in many industrial fields such as plating, alloying, dyeing, tanning, finishing, wood preserving and refractory technologies. Cr²⁺ is unstable state, Cr³⁺ is complicated and less toxic than Cr⁶⁺. Chromium is bioelement in +3 state. Cr³⁺ gives strong complexes with oxygen which is classified as a hard acid. Since the presence of chromium in water has led to an increasing awareness and concern of its detrimental effects to nature and human beings, chromium ions must be removed from the wastewater. Some typical treatment methods have been developed for removing chromium from water by using various methods: precipitation [1], ion exchange [2], membrane separation [3], reduction [4–6], biosorption [7,8] and adsorption [9,10].

Among these methods, the last two have been considered to be the most feasible methods of all. Because they are capable of removing many metals over a wider pH range economically and easily and to much lower levels than the others. Furthermore, they can often remove complex metals which would not be removed by conventional treatment processes. Removal of chromium from

water by holding methods has been reported by many researchers. The applicability of removal methods can be related to the decided economic advantage of low-cost adsorbents and holding efficiency and simple processing. By this purpose, activated carbon and natural mineral agents instead of extensive chemicals in packed beds are used widespread for removing chromium. Trivalent chromium was removed from wastewater by using activated carbon derived from agricultural waste material and fabric cloth [11]. Additionally, hexavalent chromium was removed from water by biomaterials or biomaterial-based activated carbons [12]. Many researches about this matter are summarized as reviews [13]. The ability of bentonite clay to remove Pb(II) from aqueous solutions and from nitric acid, hydrochloric acid and perchloric acid solutions ($1.0\text{--}1 \times 10^{-5}$) has been studied at different optimized conditions of concentrations, amount of adsorbent, temperature, concentration of electrolyte and pH. Maximum adsorption of Pb(II), i.e. >98% has been achieved in aqueous solutions, while 86% is achieved from 1.0×10^{-5} M HCl using 0.5 g of bentonite. The adsorption decreases by increasing the concentration of electrolytes [14]. Murathan [15] studied adsorbent production from horse chestnut and oak valonia to use wastewater treatment. They have found that the tannins from the different layers of oak valonia were extracted to remove copper II ions. It was found tannins have high-adsorption capacity and this value was 54.25 mg copper II per one gram of adsorbent. McKay and Porter [16] studied the sorption of three divalent metal ions – namely cadmium, copper and zinc – onto peat, in single component, binary and ternary systems.

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The particle size effect of selected adsorbent on adsorption of Cu^{2+} , Pb^{2+} and Zn^{2+} ions was investigated in a ternary system at constant temperature continuously. For this purpose, diatomite particles which have the size of 4.76, 3.15 and 2.00 mm were used. It was observed that adsorption capacity of diatomite increases with the decrease in particle size, proportionally. When smallest particle size has been used, it was obtained that diatomite has adsorbed these three metal ions in the descending order: $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$ [17].

Low-cost sorbents are needed for its application. Natural materials that are available in high reserves, or certain waste products from agricultural or industrial operations, may have potential as low-cost sorbents.

The aim of the present study was to investigate the effects of parameters on the chromium removal efficiency from aqueous solution by using diatomite which is a novel sorbent. Experiments were performed with discontinuous and continuous methods. Dynamic studies are carried out involving process parameters such as the initial Cr^{3+} concentration, solution temperature and contact time. Equilibrium calculations were conducted for understanding sorption process.

2. Materials and methods

50.0 ppm stock solution of Cr^{3+} was prepared from chrome nitrate salts ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in bidistilled water. All chemicals used were of analytical reagent grade. In all experiments, it was used 5.0 ppm Cr^{3+} solution was used that prepared from stock solution and it was kept at 6.0 pH. In this study, diatomite in 2.18 mm particle size from Ankara-Alacaatlı region of Turkey was used as sorbent and chemical composition of sorbent was obtained by XRD instrument. Specific surface area of sorbent was determined according to Nova Quantachrome 2200-E model sorptometer.

2.1. Batch experiments

Firstly, each of 50 ml 5.0 ppm Cr^{3+} solution was put in the six 100 ml plastic polyethylene bottles. Then, one bottle was kept as a blank solution and diatomite sorbent was added to each of other five bottles in different amounts. Experiments were carried out in a water-bath at 30 °C, 45 rpm for 480 min. The samples were filtrated and analyzed by PU 9285 Philips atomic absorption spectrophotometer. Before each analysis, it was prepared 1.0, 3.0 and 5.0 ppm standard solutions from stock solution and the spectrophotometer was calibrated. Working conditions were 357.9 nm wavelength, 12.0 mA wave voltage, 0.5 nm band slit, and 1.81/min fuel flow velocity. Air/acetylene flame was used as atomized. In all calculations, chromium holding on the bottle was subtracted from initial concentration of Cr^{3+} and it was calculated by holding on diatomite only. This value was 3.729 ppm for 5.0 ppm Cr^{3+} solution. It was calculated by 1.271 ppm adsorbed value from plastic polyethylene bottles. For this reason, initial concentration was taken as 3.729 ppm instead of 5.0 ppm. In these conditions, Cr^{3+} holding amount in polyethylene bottles was 25% according to 5.0 ppm initial concentration. These experimental conditions were also used for 1.85, 1.55 and 1.29 mm particle size sorbents.

In order to determine optimum treatment time for the Cr^{3+} adsorption on the sorbent, 50 ml of 5.0 ppm Cr^{3+} solution was put in the bottles. Then, sorbent at optimum particle size was added in each of the bottles at the optimum amount. Meanwhile, 30 °C temperature and 45 rpm shaking rate was kept as constant. Time variable were 15, 30, 60, 180 and 300 min. At the end of the each experiment, filtrates were analyzed by atomic absorption spectrophotometer and optimum treatment time was determined.

It was also investigated the effect of temperature on adsorption at the recorded experimental conditions. In these experiments, the

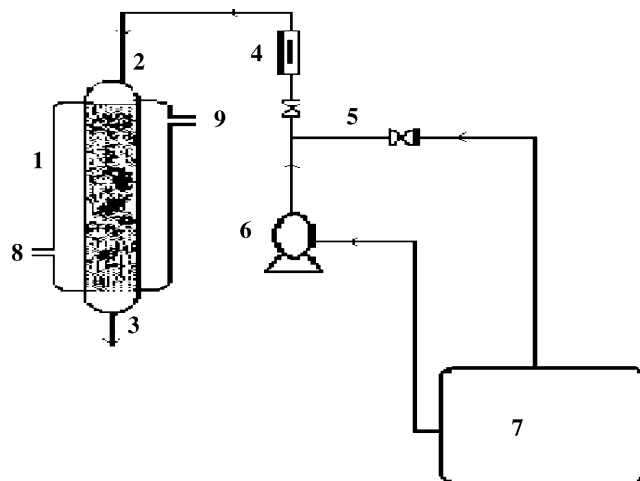


Fig. 1. Flow diagram of continuous experimental set-up. (1) Packed column, (2) liquid inlet, (3) liquid outlet, (4) liquid rotameter, (5) valve, (6) peristaltic pump, (7) liquid tank, (8) water inlet, (9) water outlet.

samples were treated at 15 and 45 °C. Filtrates were analyzed by atomic absorption spectrophotometer and optimum temperature was determined. Consequently, general optimization conditions which removed Cr^{3+} from water highest were determined and used from these results at continuous experiment.

2.2. Continuous experiments

After optimum conditions were determined in batch experiments, the removal of Cr^{3+} was studied in packed bed column (Fig. 1). Packed column used in experiments was made of pyrex material and it was a continuous system. Dimensions of reactor were in 20 cm height, 4.5 cm outer diameter and 3 cm inner diameter. Initial concentration of Cr^{3+} solution was 5.0 ppm, and this solution was fed to the top of the reactor at 6 ml/min ($1.5 \text{ kg/m}^2 \text{ s}$) by means of peristaltic pump. Packing materials were placed in the middle of the bed. Distilled water was passed through the bed before each trial. In all experiments, liquid flow-rate was kept constant and flow-rate was measured with a rotameter. Constant temperature was maintained by circulating water from a thermostatically controlled water-bath through the jacket surrounding the column. Cr^{3+} solutions were fed to the top of the packed column with a peristaltic pump. Samples were taken from the bottom of the column and immediately analyzed in atomic absorption spectrophotometer. The amount of adsorbed chromium was calculated from the observed difference between the input and output solution concentrations. It was chosen 30 °C as working temperature and 6.0 pH in the reactor [18].

3. Results and discussion

Specific surface area values of diatomite used in Cr^{3+} ions holding were given according to mean particle size in Table 1. As can be seen in Table 1, surface area of diatomite was increasing as mean particle size was decreasing. Chemical composition of diatomite determined by XRD instrument was given in Table 2.

In this study, optimum conditions were determined for the removal of Cr^{3+} ions from wastewater. For this purpose, particle size and amount of sorbent, contact time, and temperature effects on Cr^{3+} removal were studied.

Table 1
Specific surface area of diatomite according to mean particle size

| Mean particle size (mm) | Specific surface area (m ² /g) |
|-------------------------|---|
| 2.18 | 18.645 |
| 1.85 | 19.387 |
| 1.55 | 19.994 |
| 1.29 | 20.416 |

Table 2
Chemical composition of diatomite used

| Chemical composition | Content (m/m)% |
|--|----------------|
| pH | 8.80 |
| Silicium dioxide, SiO ₂ | 2.60 |
| R ₂ O ₃ (Al ₂ O ₃ + Fe ₂ O ₃) | 0.15 |
| Ferric oxide, Fe ₂ O ₃ | 0.00 |
| Sulfur trioxide, SO ₃ | 0.04 |
| Aluminium oxide, Al ₂ O ₃ | 0.15 |
| Calcium oxide, CaO | 50.95 |
| Magnesium oxide, MgO | 5.00 |

3.1. Batch experiments

As can be seen from Fig. 2, removal of Cr³⁺ from solution is increased with sorbent surface area. Consequently, Cr³⁺ ions on

diatomite are increased with decreasing particle size and with increasing sorbent amount. In Table 1, in spite of about 41% decrease in particle size there was 9.5% increase in surface area amount. It can be concluded that the removal efficiency of Cr³⁺ increased with increasing surface area of sorbent. In initial conditions, the effect of increase in sorbent amount was high in the removal of Cr³⁺ but it has no impact after about 3 g diatomite amount.

From this result it has been seen that Cr³⁺ amount in solution was held in 85–95% according to sorbent particle size with 3.0 g of sorbent. Maximum holding efficiency could be obtained in 1.29 mm particle size diatomite. In this particle size, holding efficiency was about 100% with 6.0 g sorbent amount. For this reason, it was gone on with about 1.29 mm particle size and 6.0 g diatomite in after these experiments. It was investigated the effect of treatment time on holding efficiency at constant 30 °C temperature and 45 rpm shaking rate. As shown in Fig. 3, Cr³⁺ holding efficiency was increasing sharply in 30 min time, but increase in holding efficiency has no important in higher time. Increase in holding efficiency is decreasing over 60 min treatment time.

After these experiments, 60-min treatment time was used as constant. It was investigated the effect of temperature in holding efficiency at constant 60 min time and 45 rpm shaking rate with 1.29 mm particle size sorbent and 6.0 g sorbent amount. There is no

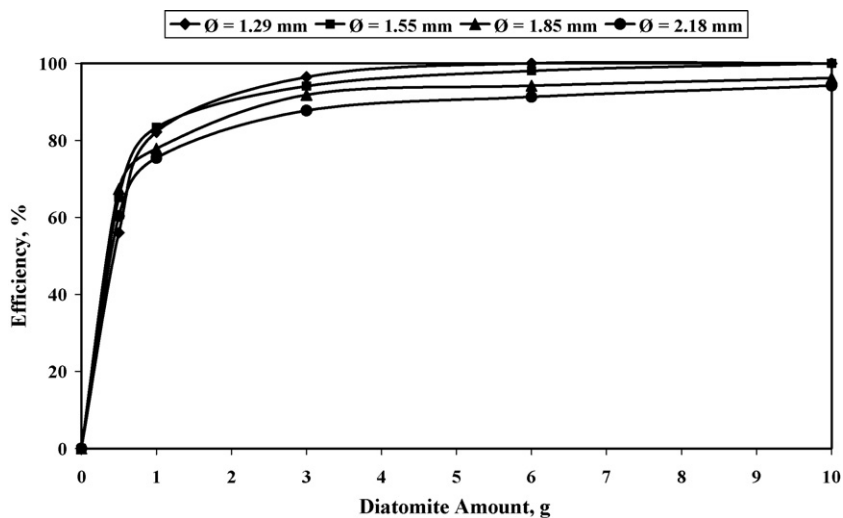


Fig. 2. Cr³⁺ holding efficiency by different size and amount of diatomite; 30 °C, 480 min, 45 rpm.

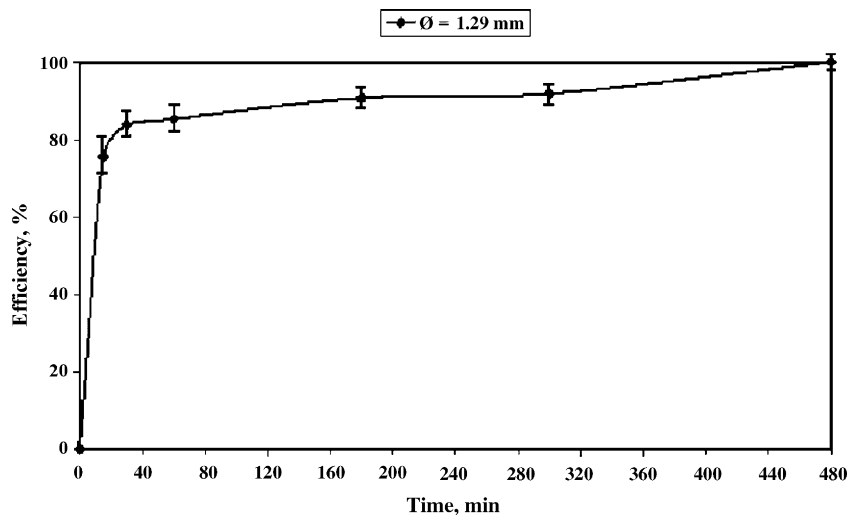


Fig. 3. Cr³⁺ Holding efficiency of diatomite for different times; 1.29 mm size and 6 g diatomite, 30 °C, 45 rpm.

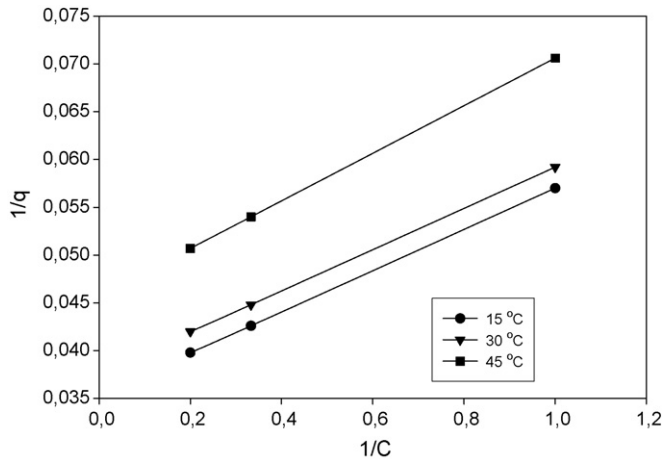


Fig. 4. Langmuir plots for the sorption of chromium ions on diatomite.

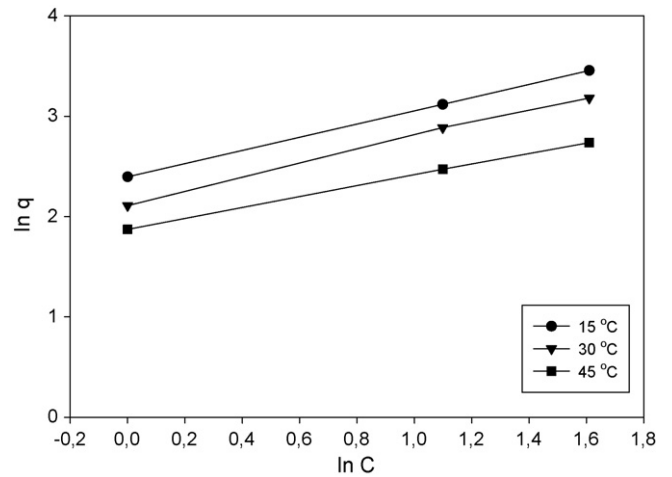


Fig. 5. Freundlich plots for the sorption of chromium ions on diatomite.

significant difference effect between 15 and 30 °C. However, it was obtained a slightly decrease in holding efficiency at 45 °C temperature. A decrease in holding efficiency may be explained because physical adsorption decreases with increasing temperature [19,20]. So, it can be recommended operation temperature up to 30 °C.

85% holding efficiency was obtained for 50 ml 5.0 ppm Cr³⁺ solution at constant 30 °C temperature and 60 min time and 45 rpm shaking rate with 1.29 mm particle size sorbent and 6.0 g sorbent amount. In this manner, 26.5 mg Cr³⁺/g diatomite of maximum specific holding capacity of diatomite was obtained. However, the maximum specific holding capacities of diatomite were recorded as 8.1 mg Cu/g diatomite, 3.6 mg Pb and 0.9 mg Zn/g diatomite in the previous study [18].

3.2. Sorption isotherms

The Langmuir and Freundlich sorption parameters were determined in the linear forms as follows:

$$\text{Langmuir isotherm : } \frac{1}{q} = \left(\frac{1}{q_0}\right) + \left(\frac{1}{K_L q_0}\right) \left(\frac{1}{C}\right) \quad (1)$$

$$\text{Freundlich isotherm : } \ln q = \ln K_F + \frac{1}{n} \ln C \quad (2)$$

Isotherms at three different temperatures of solutions are represented in Figs. 4 and 5, the Langmuir and Freundlich models, respectively.

As seen from Figs. 4 and 5, in the range 288–318 K, an increase in temperature does not affect sorption of chromium ions on diatomite significantly. This can be explained by physical adsorption decreases with increasing temperature [19,20].

As seen from Table 3, the value q_0 of maximum adsorption capacity, corresponding to monolayer coverage of the binding sites available in the sorbent, was obtained at 288 K.

On the other hand, the values of n between 2 and 10 shows good adsorption [21,14].

Table 3
The characteristic parameters of sorption process of chromium ions on diatomite

| | Langmuir isotherm | | | Freundlich isotherm | | |
|-----|-------------------|--------------|--------|------------------------------------|-------|--------|
| | K_L (l/g) | q_0 (mg/g) | R^2 | K_F (mg/g) (l/mg) ^{1/n} | n | R^2 |
| 288 | 1.642 | 28.100 | 0.9944 | 20.979 | 5.520 | 0.9856 |
| 303 | 1.751 | 26.500 | 0.9974 | 16.245 | 4.120 | 0.9922 |
| 318 | 1.843 | 21.800 | 0.9974 | 12.505 | 3.250 | 0.9889 |

The equilibrium sorption data at different temperatures fitted well to the monolayer Langmuir model according to regression coefficient, but Freundlich model results fitted according to n values too.

3.3. Thermodynamic study

Using the values of Langmuir constant, K_L and following equations one can calculate the variations of apparent enthalpy (ΔH , kJ/mol), apparent free energy (ΔG , kJ/mol) and apparent entropy (ΔS , J/mol K) of chromium sorption on diatomite (Table 4) according to Eqs. (3)–(5), where

R is the gas law constant and T is the absolute temperature.

$$\ln K_L = - \left(\frac{\Delta H}{RT}\right) + \text{constant} \quad (3)$$

$$\Delta G = - RT \ln K_L \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (5)$$

The negative value of apparent enthalpy change shows an exothermic physical adsorption, favoured by increased temperatures. The negative values of ΔG confirm that the chromium sorption on diatomite is a spontaneous process. It can be said that the driving force for sorption process is an entropy effect. This result was demonstrated by other experimental results [22].

3.4. Kinetic study

The kinetics of chromium sorption on diatomite was investigated using two different models: the pseudo-first-order and pseudo-second-order kinetics. The pseudo-first-order Lagergren model, is generally expressed by Eq. (6) where k_1 (1/min) is the Lagergren rate constant of the first-order sorption, evaluated from Fig. 6.

$$\log(q_0 - q) = \log q_0 - k_1 t \quad (6)$$

Table 4
The apparent thermodynamic parameters of sorption process of chromium on diatomite

| T (K) | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/mol K) |
|---------|---------------------|---------------------|----------------------|
| 288 | -1.185 | -1.100 | 0.295 |
| 303 | -1.409 | -1.324 | 0.280 |
| 318 | -1.614 | -1.529 | 0.267 |

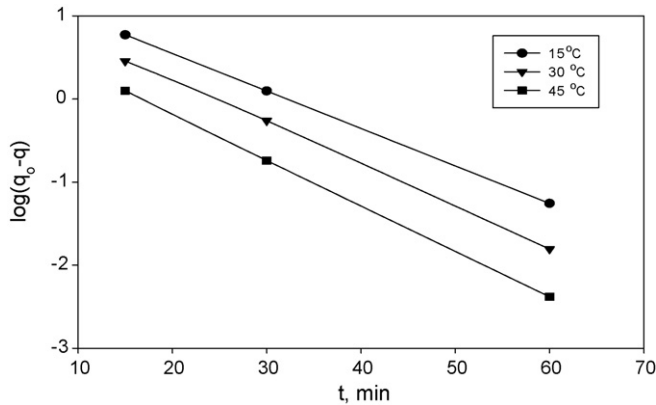


Fig. 6. The applicability of the first kinetic model to chromium on diatomite.

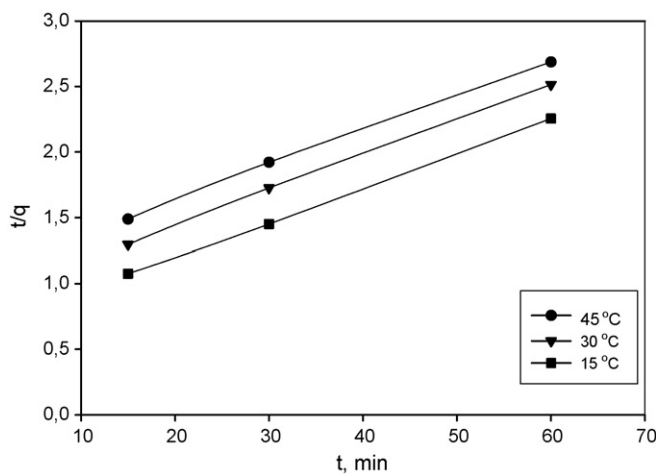


Fig. 7. The applicability of the second kinetic model to chromium on diatomite.

According to the pseudo-second-order model the chromium adsorption kinetic is described by Eq. (7), where k_2 is the rate constant of second-order sorption (g/mg min) and $k_2q_0^2 = h$ is the initial adsorption rate (mg/g min).

$$\frac{t}{q} = \frac{1}{k_2q_0^2} + \frac{t}{q_0} \quad (7)$$

The experimental kinetic data were adjusted according to the indicated models (Figs. 6 and 7) and the coefficients of correlation as well as the kinetic parameters of chromium sorption on diatomite are given in Table 5.

The results of Table 5 and Figs. 6 and 7 showed that the second-order equation model provided the best correlation with experimental results. This fact indicates that the sorption of chromium on diatomite follows the pseudo-second-order kinetic model and intraparticle diffusion is the rate-limiting factor.

Table 5
The kinetics parameters of sorption process of chromium on diatomite

| T (K) | Pseudo-first kinetic model | | Pseudo-second kinetic model | | R^2 |
|-------|----------------------------|--------|-----------------------------|----------------|--------|
| | k_1 (min ⁻¹) | R^2 | k_2 (g/mg min) | h (mg/g min) | |
| 288 | 0.0451 | 0.9715 | 0.0056 | 4.4221 | 0.9956 |
| 303 | 0.0582 | 0.9823 | 0.0036 | 2.5283 | 0.9975 |
| 318 | 0.0693 | 0.9855 | 0.0032 | 1.5212 | 0.9983 |

3.5. Continuous experiments

In batch experiments, it was obtained optimum conditions for Cr^{3+} removal by natural diatomite sorbent. By using these processes results, Cr^{3+} removal was investigated in continuous system as given in Fig. 1. In this system, Cr^{3+} removal yield was 82% at 22 min time and 97% at 80 min time. Selection of operation time was utilized from previous study [21]. This result showed that continuous system was more efficient than batch system for Cr^{3+} removal by diatomite. Also each of system can be used economically in Cr^{3+} removal by diatomite.

4. Conclusion

It is concluded that the Cr^{3+} pollutant in water can be removed by using natural diatomite which has no economical value. Inexpensive sorbent and low operating cost make this study a promising one for technological application. Optimum conditions recorded in this work may be applied to industrial scale economically and are environment-friendly. It was obtained 85% holding efficiency in batch system and optimum conditions were 30 °C temperature, 60 min time and 45 rpm shaking rate with 1.29 mm particle size sorbent and 6.0 g sorbent amount. Also it was obtained 82% Cr^{3+} removal yield at 22 min and 97% Cr^{3+} removal yield at 80 min in continuous system only. The equilibrium sorption data were analyzed using Langmuir and Freundlich models. The results fitted well to the two-parameter monolayer Langmuir model.

As a result of thermodynamic parameters calculations, Cr^{3+} sorption on diatomite was an exothermic process. The kinetic sorption data fitted well to the second-order kinetic model, indicating that the intraparticle diffusion is the rate-limiting factor.

Acknowledgement

This study was supported by State Planning Organizing of Turkey under project no. 2001 K 120590.

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