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

Metin Gürü [a,*], Duygu Venedik [b], Ayşe Murathan [a]

[a] Gazi University, Engineering and Architectural Faculty, Chemical Engineering Department, 06570 Ankara, Turkey
[b] Gazi University, Institute of Science and Technology, Environmental Sciences Department, 06570 Ankara, Turkey

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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 Cr^{3+}/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.

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. Cr^{2+} is unstable state, Cr^{3+} is complicated and less toxic than Cr^{6+}. Chromium is bioelement in +3 state. Cr^{3+} 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 ($1.0–1 \times 10^{-5}$) 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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* Corresponding author. Tel.: +90 312 2317400/2555; fax: +90 312 2308434.
E-mail address: mguru@gazi.edu.tr (M. Gürü).

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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: $Cu^{2+} > Pb^{2+} > Zn^{2+}$ [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 ($Cr(NO_3)_3 \bullet 9H_2O$) 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 1.8 l/min fuel flow velocity. Air/acetylene flame was used as atomized. In all calculations, chromium holding on the bottle was substracted from initial concentration of Cr3+ 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 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.

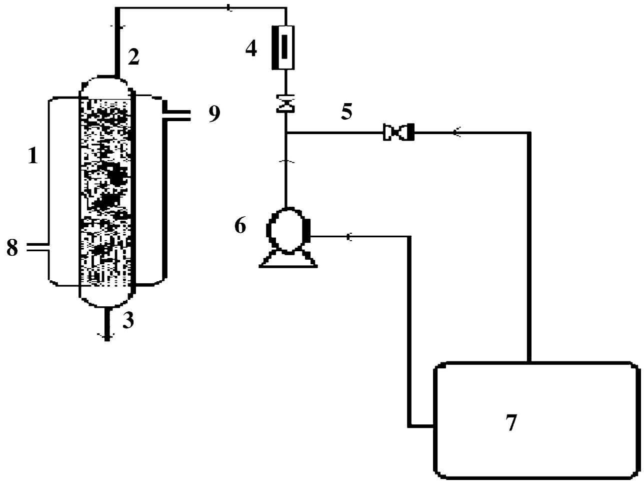

Fig. 1. Flow diagram of continuous experimental set-up. (1) Packed column, (2) liquid inlet, (3) liquid outlet, (4) liquid rotameter, (5) valve, (6) peristaltic pump, (7) liquid tank, (8) water inlet, (9) water outlet.

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 kg/m^2 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.