REMOVAL OF TRACE CADMIUMFROM WASTEWATER USING BATCH FOAM FRACTIONATION

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ABSTRACT: In this research, a bath foam fractionation column of 5 cm inside diameter and 60 cm height was employed. The column was made of Pyrex. A sintered glass filter, which had pores of 30 micro meters, was installed as a gas distributor at the bottom of the column. The foam fractionation column wasemployed to remove cadmium ions from wastewater having ions concentration at a low level(10-50 mg/L). The effects of pH, surfactant (sodium dodecyl sulfate) concentration and Cd concentration on the Cd removal were studied. The results indicated that the percentCd removal increased with surfactant concentration increased, Cd concentration decreased and pH decreased. Within the range of parameters varied the maximum %Cd removal was 93% when Cd concentration, sodium dodecyl sulfate concentration and pH were 30 mg/L, 200 mg/L and 1.0, respectively.

Keywords:Cadmium removal, batch column, foam fractionation, wastewater treatment, sodium dodecyl sulfate

1. INTRODUCTION

Heavy metals are poisonous to aquatic environment even in relatively small concentrations [1, 2, 3, 4, 5]. Discharge of great amounts of heavy metals into the natural environment has contributed to a number of environmental problems [5, 6]. The existence of trace metals in the aquatic environment has been of large concern due of their carcinogenic properties, non-biodegradability and bioaccumulation [2, 4, 7, 8].

Cadmium is a heavy metal that is relatively widespread in the environment [2]. Cadmium mayconcentrate in the tissues of human body, causing nausea, diarrhea, salivation, muscular cramps, renal degradation, chronic pulmonary problems and skeletal abnormality [1]. It is therefore necessary to remove cadmium from various waste materials. Cadmium could enter wastewater discharges from the electroplating industry, the manufacture of nickel–cadmium batteries, fertilizers, pesticides, pigments, dyes, and textile operations [2, 7, 9, 10].

At the present time, many methods have been developed for removing heavy metal ions from waters, i.e., chemical precipitation, solvent extraction, ion exchange, filtration, membrane and electrochemical technologies [11, 12, 13, 14, 15, 16]. However, thesemethods are not economically feasible for treating large amount of wastewaters containing heavy metals at trace levels due to their high maintenance and operation costs that result from great quantities of chemicals and/or high energy consumption [12].

Adsorptive bubble separation, including foam fractionation, is based on the selective adsorption or attachment of solutesat the gas-liquid interface onto the surfaces of gas bubbles going up through a liquid solution [12, 17, 18, 19]. The foam fractionation of ions is like to ion flotation but incorporates an excess of surfactant to make stable foam [12].It could be used to concentrate and eliminate dissolved materials, including surface active and non-surface active solutes from aqueous solutions [12, 17, 19, 20]. Ion foam fractionation has several attractive features for removing very small concentrations of metal ions from aqueous solutions [12, 18]. This technique offers various advantages for the purification of industrial wastewaters compared to other separation processes, for examples, easy handling, accessibility of different sorbents, small space and energy requirements, easy design, operation and scale-up and lowerinvestment and operating costs [12, 17, 18]. Ion foam fractionation provides high metal removal efficiency at low feed metal concentrations[12].

In a foam fractionation process, gas bubbles move upwards through the column to generate foam. This froth is physically separated from the liquid bulk and the surface active solutes are also at the same time separated. Usually a small fraction of entrained liquid is taken with the bubbles into the froth because of the gravitational liquid film drainage. Once the foam collapses, the concentrated liquid that contains the surface active solute could be collected[12, 21].

There are two methods of conducting foam fractionation, simple method (batch wise or continuous), and complex method that includes enriching and/or stripping. The foam fractionation column can also be a single stage or multistage [12, 20].

Removing pollutants from water by foam fractionation has been widely studied [17, 18, 19, 20, 21, 22]. Many variables were found to have animportant effect upon solute removal efficiency, such as the surfactant concentration in feed, temperature, added electrolyte, sparger porosity, the height of the foam–liquid interface, the gas flow rate, the bubble diameter, and the solute concentration in feed [20].

Although the heavy metal removal from wastewater by foam fractionation technique is a well established topic, however, more experimental data will help a better understanding of the subject to justify its application in environmental issues. In this study the effects of feed pH, sodium dodecyl sulfate concentration and cadmium concentration on the Cd removal in a batch foam fractionation column were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Cadmium chloride dehydrates (CdCl₂.2H₂O) was purchased from Fluka (Switzerland).Anionic surfactant, sodium dodecyl sulfate (SDS), HNO₃, and NaOH wereobtained from Merck (Germany) and used without further purification. Deionized water was used in all experiments.

To measure solution pH and residual concentration of cadmium ions a pH meter of Jenway 3510 and an atomic adsorption spectrophotometer (PekinElmerAAnalyst 700, USA) were used, respectively.

2.2. EXPERIMENTAL SETUP

A schematic diagram of the experimental setup for batch foam fractionation is shown in figure 1. A bubble column of 5 cm inside diameter and 60 cm height was employed. The column was made of Pyrex. A sintered glass filter, which had pores of 30 micro meters, was installed as a gas distributor at the bottom of the column.

2.3. Feed preparation

A 1000mg/L stock solution of cadmium was prepared to perform the experiments by dissolving CdCl₂.2H₂O in dilute aqueous nitric acid and its volume was increased to oneliter by adding deionized water. Then the original stock solution was used to makefeed solutions of concentrations of 10, 20, 30, 40 and 50 mg/L.



Figure 1.Schematic diagram of experimental setup.

2.4. Operation

All experiments were conducted in a batchwisemode with respect to liquid. The feed solution was poured into the column from the top of the column. Air by using an air compressor was introduced from the bottom of the column and the air flow rate was keptconstant at 100mL/min using a rotameter. Because of insignificant influence of temperature on the heavy metal removal performance of foamfractionation column in the range of 15-34°C [12], all the experiments were conducted at room temperature, 26-28°C. The exit foamsfrom the top of the column enter a foam collector where they were collapsed by their self. The foam height was 60 cm during the experiment. Samples of the feed solution and the effluents were collected and analyzed for cadmium concentrations. All taken samples were acidified with concentrated nitric acid to a pH lower than 2 to preserve them. The concentration of cadmium ions was determined by an atomic adsorption spectroscope.

2.5. Calculations

The performance of the investigated batch ion foam fractionation column was evaluated by calculating the %Cd removalaccording to the following formula:

$%Cd removal = 100(C_iV_i - C_eV_e)/C_iV_i$

In the above formula, C_i is the cadmium concentration in the influent (feed) and C_e is the cadmium ion concentration in the effluent stream, and V_i and V_e are the volume of feed and effluent, respectively.

3. RESULTS AND DISCUSSION

The original concentration of cadmium, pH of the solution and concentration of SDS were the main variables to study the effects on the %Cd removal.

3.1. Effect of feed Cd concentration %Cd removal

Influence of cadmium concentration on removal efficiency of cadmiumwas investigated at different feeds of ion Cd concentration under the conditions of 10, 20, 30, 40, and 50 mg/L as shown in figure 2. During all experiment the air flow rate was kept constant at 100 mL/min. The initial feed pH and SDS concentration were 3 and 200 mg/L, respectively. No pH adjustment was done afterward during the column operation. The time of air bubbling was 60 minutes. The results were demonstrated in figure 2. The figure indicated that the percent cadmium removal from water decreases as the cadmium concentration in the feed increases.At constant initial SDS concentration, the relative availability of SDS to a specific amount of cadmium ions decreases as the cadmium in the feed concentration increases and consequently less cadmium could be removed. 100



Cd concentration in feed (mg/L)

Figure 2.Effect of Cd concentration in feed on %Cd removal.

3.2. Effect of initial pH on %Cd removal

The effect of pH on the efficiency of separation of cadmium is shown in figure 3. The pH in the feed solution was investigated under the conditions of 1, 2, 3, 4,and 5. The initial cadmium concentration and SDS concentration were 30mg/L and 200mg/L respectively. The initial pH of the solution was adjusted by NaOH or nitric acid. No further pH adjustment was made during the separation. The foaming time was 60 minutes during all experiments of this part. As shown by figure 3, increasing the pH of the feed decreases the cadmium removal efficiency. The maximum Cd removal efficiency was about 93% at pH 1 while at pH 5 the efficiency reduced to 45%. This could be ascribed to the fact that as pH is increased less ionic mercury is available to react with surfactant thus the cadmium removal efficiency is reduced considerably [22].

In the aqueous solution the SDS dissolved is ionized to Na^+ and DS⁻. Cadmium chloride and water ionization produce other ions such as Cd^{2+} , Cl^- , H^+ , OH^- . It isanticipated that



Figure 3.Effect of initial feed pH on %Cd removal.

4. CONCLUSION

A bubble column of 5 cm inside diameter and 60 cm height was employed to investigate the batch foam fractionation for trace Cd^{2+} removal from wastewater. The effects of three important parameters(pH, cadmium concentration and surfactant concentration) on the removal of Cd^{2+} were studied. The results indicate that the percent Cd removal increasesas surfactant concentration increases, Cd concentration decreases and pH decreases.Within the range of parameters varied the maximum %Cd removal was 93% when Cd concentration,SDS concentration and pH were 30 mg/L,200 mg/L and 1.0, respectively. The method applied is well suited for Cd removal at trace concentrations at low pH (acidic mediums) solutions.

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 Mohan, D. and Singh, K. P., "Single- and multicomponent adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste", *Water Res.*, 36(9):2304–2318 (2002). positive ions such as Na⁺, Cd²⁺, and H⁺ would compete to make interaction with surfactant ions (DS⁻). At low pH value or higher H⁺ concentration it seems that Cd²⁺ makes chelates more easily with surfactant ions (DS⁻) and therefore the cadmium removal increases. However, as the pH increases some Cd²⁺ probably attached to OH⁻ as hydroxides that resulted in lowering cadmium removal [18].

3.3. Effect of surfactant concentration on %Cd removal

The effect of surfactant concentration on the efficiency of cadmium separation was studied and the results were shown in figure 4. The initial SDS concentration in the feed solution was studied under the conditionsof 50, 100, 150,200, 250, 300, and 350 mg/L. The initial cadmium concentration and pH were kept at 30 mg/L and 3 respectively. The time of air bubbling was 60 minutes for all experiments of this part. The removed cadmium ions efficiency is increased up to 88% by increasing surfactant concentration to 350 mg/L. This may be attributed to the higher SDS/Cd molar ratio at higher SDS concentration that provides better conditions of Cd ions removal.



Figure4.Effect of surfactant concentration on %Cd removal.

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