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FIXED BED STUDIES FOR Cd(II) REMOVAL FROM MODEL SOLUTIONS USING IMMOBILIZED BENTONITE/YEAST MIXTURES

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ABSTRACT. This work presents experimental results obtained in the process of Cd^{2+} removal from model solutions using batch (magnetic stirring) and fixed bed procedures. As adsorbent we used a mixture consisting of bentonite and baker's yeast (2, 4, 6 and 8 g in 1:0, 3:1, 1:1, 1:3 and 0:1 ratios), immobilized in calcium alginate. Adsorption capacities were calculated, and breakthrough curves were plotted in order to describe the influence of various working conditions (adsorbent type and ratio, initial cadmium concentration) over the process efficiency. Adsorption capacities up to 12.74 mg Cd^{2+}/g adsorbent were calculated.

Keywords: immobilized bentonite/yeast mixture, cadmium removal, adsorption, breakthrough curve

INTRODUCTION

Wastewaters contaminated with heavy metals represent a serious environmental problem because they do not undergo biodegradation and are accumulated [1] into vegetal and animal cells, with different toxic effects. Heavy metals can be released into the aqueous environment from a variety of sources such as metal smelters, effluents from plastic, textile, microelectronic and wood preservative-producing industry, and even fertilizer and pesticide usage [2]. In addition, mining, mineral processing and extractive-metallurgical operations also generate toxic liquid wastes.

Environmental engineers and scientists are facing with the challenging task to develop appropriate low cost technologies for effluent treatment [3]. Conventional methods for removing metals from aqueous solutions include

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chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation recovery. These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1-100 mg/L [4]. Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment becomes a costly issue and is not environmental friendly. Therefore, removal of toxic heavy metals to an environmentally safe level manner became a great importance process [3].

Cadmium is one of the most toxic heavy metals, heaving half-life of 10-30 years and its accumulation in human body affect kidney, bone and also causes cancer. Cadmium enters in the environment by natural (rock weathering, forest fires, and volcanic activities) and more important anthropogenic activities. Its use is increasing in industrial applications such as electroplating, pigments and electronic (batteries) industries. Mineral fertilizers applied on soil or solid wastes deposited in inappropriate places contains also cadmium compounds, which can be adsorbed on soil particles or can be mobilized in groundwater [5,6]. Because of its mobility in soil, cadmium may be transferred to plants and accumulated in roots, stems and leaves. As a consequence, because of the high toxicity of Cd^{2+}, the crops may become unfit for animal and human consumption, and crop yields may be drastically reduced [5].

Beside conventional methods presented above, eco-friendly processes such as biosorption and phytoremediation are used more often in order to eliminate heavy metals from different environments [3,7]. Biomaterials of microbial and plant origin interact effectively (adsorption and bioaccumulation) with heavy metals. Due to their unique chemical composition, metabolically inactive dead biomass sequesters heavy metal ions and metal complexes from solutions, which obviates the necessity to maintain special growth-supporting conditions. Metal adsorption by various types of biomaterials can find enormous applications for removing and recovery of heavy metals from their solutions [8].

For the economical reason, researchers have paid much attention to various by-products from fermentation industry, such as *Saccharomyces Cerevisiae*, because they are produced in large quantities. Although *Saccharomyces Cerevisiae* is a mediocre biosorbent, it is extensively examined as a biomaterial in biosorption studies for heavy metals removal [8]. Vieira et al. have shown that the questioned yeast has commercial application as biosorbent because at least four reasons. In the first place, *Saccharomyces Cerevisiae* is easy to cultivate at large scale; as a result it can grow with unsophisticated fermentation techniques and inexpensive growth media. Second, the biomass of *Saccharomyces Cerevisiae* can be obtained from various food and beverage industries. Third, *Saccharomyces Cerevisiae* is not usually a waste, but a commercial commodity and considered safe, therefore, biosorbent made from *Saccharomyces Cerevisiae* may be easily accepted by the public when applied in practice as it can be used at large scale with low cost, especially for treating of large amount of wastewater containing heavy metal in low concentration. Fourth, attempt is to use *Saccharomyces Cerevisiae* as biosorbent, but not the last, is an ideal model organism to identify the kinetics of the biosorption in metal ion removal, especially to investigate the interactions at molecular level [8].

Alginate beads are often used as a support for biomaterials because of their natural origin with no toxicity towards immobilised micro-organisms or environment and because of their biodegradability after utilisation [5].

Besides biomaterials, other natural cheap materials such as bentonite can be used with success to remove heavy metals from aqueous solutions. Removal of heavy metal ions such as lead, copper, cadmium, cobalt, iron, nickel, zinc from their solutions, was studied on bentonite (suspended in aqueous solution) from deposits situated all over the world [9-14].

In order to study the combined adsorptive properties of *Saccharomyces Cerevisiae* cells and bentonite, a series of mixtures consisting of bentonite and baker's yeast, immobilized in calcium alginate were used to establish adsorption capacities towards cadmium from aqueous solution.

RESULTS AND DISCUSSION

Batch study

The influence of the adsorbent type and ratio over the time evolution of cadmium concentration in batch conditions is presented in figure 1. Analyzing the decrease of concentration in time for all samples we observed some differences in the evolution of the adsorption process (cadmium concentration trends). In case of samples containing a higher quantity of baker's yeast (8g D, 6g D + 2g B) it is easy to observe that adsorption takes place in three distinct regions corresponding to cell surface adsorption, membrane diffusion and adsorption equilibrium, [15]. These regions are evidenced on the graph by the presence of two steps. As the baker's yeast quantity decreases, these specific regions are disappearing being replaced by a continuous decrease, evolution specific to inorganic adsorbents [14,16].

Adsorption equilibrium was reached in 90 minutes for betonite increasing to 150 minutes for the baker's yeast. This decrease of the adsorption rate in case of baker's yeast could be associated with the diffusion limitation of the heavy metal ions through the cellular membrane.

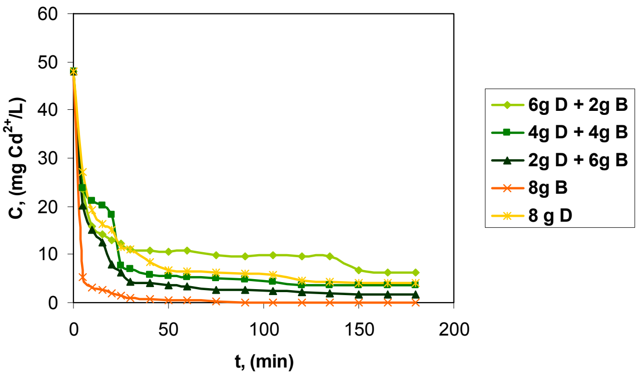

Figure 1. Influence of the adsorbent type and ratio over the time evolution of cadmium concentration in batch conditions (C_i = 40 mg Cd^{2+}/L, T = 20°C, pH = 5.4, 8g D, 6g D + 2g B, 4g D + 4g B, 2g D + 6g B, 8g B).

The influence of the adsorbent type and bentonite/baker's yeast ratio over the cadmium removal process, in terms of maximum removal efficiencies and adsorption capacities are presented in figures 2 and 3. The highest value of the removal efficiency was obtained in case of bentonite (100%). As the bentonite quantity decreases in the adsorbent mixture, figure 2, removal efficiency decreases to 87.08 % for the 6g D + 2g B mixture. When only the baker's yeast is present in the alginate beads, an increase of the removal efficiency to a value close to that corresponding to the 1:1 mixture ratio, 4g B + 4g D, (92.50%), 91.56% was calculated. Accordingly, the adsorption capacities (maximum values, calculated at equilibrium) will follow the same trend. The highest value was obtained when 8g of bentonite were immobilized, 0.6 mg Cd^{2+}/g adsorbent.

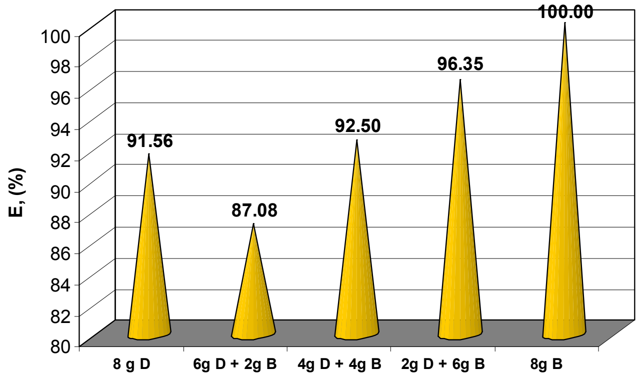

Figure 2. Maximum removal efficiency values for cadmium removal in batch conditions – influence of the adsorbent type and ratio (C_i = 40 mg Cd^{2+}/L, T = 20°C, pH = 5.4, 8g D, 6g D + 2g B, 4g D + 4g B, 2g D + 6g B, 8g B.

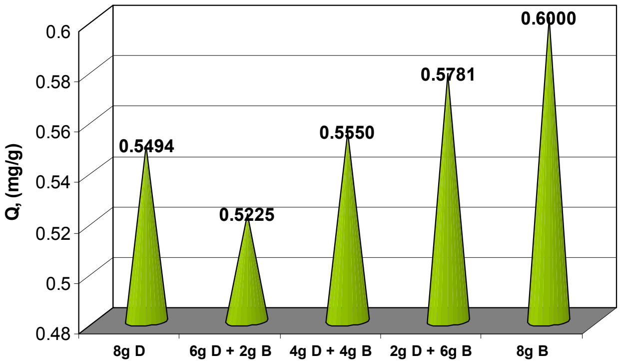

Figure 3. Adsorption capacity values for cadmium removal in batch conditions – influence of the adsorbent type and ratio (C_i = 40 mg Cd^{2+}/L, T = 20°C, pH = 5.4, 8g D, 6g D + 2g B, 4g D + 4g B, 2g D + 6g B, 8g B.

Fixed bed column study

Results obtained when the cadmium removal experiments were carried out in fixed bed column are presented in terms of cadmium concentration time evolution (breakthrough curves) and adsorption capacities at exhaustion point. As can be observed from figures 4 and 5, when only baker's yeast is present in the alginate beads, the breakthrough curve is steeper, concentration of cadmium at the outflow of the column increases faster, indicating a favourable kinetic in this case. We can concluded that using this flow rate, the adsorption in case of the baker's yeast takes place rapidly but only on the membrane cell, the diffusion through the membrane being restricted, therefore the adsorption capacity will be smaller. In all cases the breakthrough point is around 75 minutes, while the exhaustion point was reached after approximately 250 minutes.

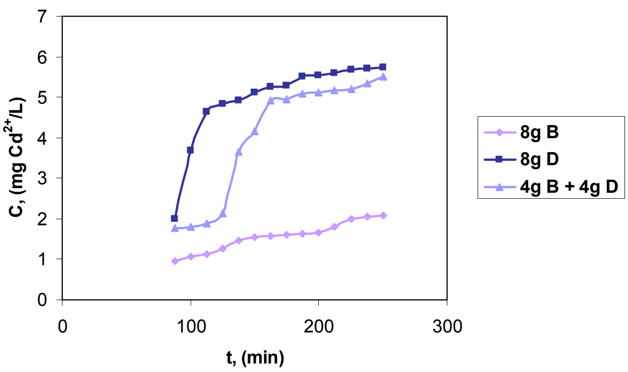

Figure 4. Influence of the adsorbent type and ratio over the cadmium concentration evolution in time in fixed bed studies – breakthrough region (C_i = 40 mg Cd^{2+}/L, T = 20°C, pH = 5.4).

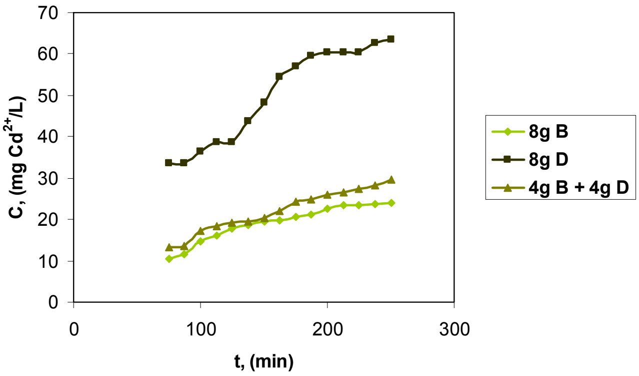

Figure 5. Influence of the adsorbent type and ratio over the cadmium concentration evolution in time in fixed bed studies – breakthrough region (C_i = 120 mg Cd^{2+}/L, T = 20°C, pH = 5.4).

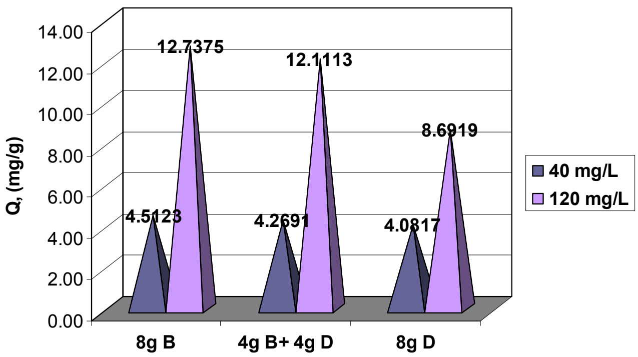

Figure 6. Maximum adsorption capacity values for cadmium removal in fixed bed – influence of the initial cadmium solution concentration, and adsorbent type and ratio (C_i = 40, 120 mg Cd^{2+}/L, T = 20°C, pH = 5.4, 8g D, 4g D + 4g B, 8g B).

EXPERIMENTAL SECTION

We used a commercial bentonite (B) sample from Fort Benton distributed by Interker-Wein kft., Hungary. The bentonite sample was used as powder, (d < 0.2 mm), without any chemical treatment. We used also commercial baker's yeast (D) produced by Pakmaya (wet). All chemicals used in this study were analytical reagent grade ($Cd(NO_3)_2 \times 4H_2O$, alginic acid sodium salt and $CaCl_2$).

In order to obtain the bentonite/baker's yeast mixtures (we will refer to the bentonite-yeast mixture as adsorbent along the paper) immobilized in alginate beads we used the cross-linking procedure with calcium alginate, which is an adapted version of the method for treatment of fungi biomass outlined by Schiewer et al. (1995) and Zhao and Duncan (1997) [17,18].

For adsorbent immobilization, various quantities of bentonite (2, 4, 6, 8 g) and baker's yeast (2, 4, 6, 8 g) in different combinations (8g B, 6g B + 2g D, 4g B + 4g D, 2g B + 6g D, 8g D), were suspended in 50 ml distilled water. This suspension was next blended with a mixture formed from 1 g Na-alginate and 2 ml ethanol. The mixture was then dropped with a peristaltic pump into a 0.2 M $CaCl_2$ solution. During this process, alginate-bentonite-yeast mixture drops were gelled into beads with a diameter of 4.0 ± 0.2 mm. The Ca-alginate immobilized adsorbent beads were stored in 0.2 M $CaCl_2$ solution at 4°C for 1 hour to cure. The beads were rinsed with distilled water for remove excess of calcium ions and stored at 4°C prior to use.

For the heavy metal ion removal study we used model monocomponent solutions containing cadmium ions of 40 and 120 mg Cd^{2+}/L. The concentration of cadmium ions in solution was determined using a flame atomic absorption spectrophotometer (SensAA Dual GBS Scientific Equipment, Australia).

The heavy metal ions removal process was realized in a batch reactor under magnetic stirring (825 rpm), using 100 ml of cadmium solution in which Ca-alginate bentonite beads obtained from the desired quantity of adsorbent were suspended. For the fixed bed column experiments we used a 32 mm diameter column, in which Ca-alginate beads obtained from the desired quantity of adsorbent were placed. Cadmium solution passes the fixed bed with a flow rate of 4 ml/min.

In order to determine the exact concentration of cadmium ions and establish the evolution of the removal process, in batch conditions, samples of 1 mL (dilution in each case was 25) from the supernatant were collected at different time intervals, every 5 minutes for the first 30 minutes and next every 15 minutes until equilibrium was reached. In case of the fixed bed experiments, 50 ml solution is collected at the outflow of the column every 12.5 minutes until the adsorbent is exhausted (exhaustion point).

We studied the influence of the bentonite and baker's yeast quantity, cadmium concentration in solution over the process efficiency in batch and fixed bed conditions. The experiments were carried out at room temperature (20°C) and without any modification of the pH value (pH 5.4 of the initial cadmium solution).

The amount of adsorbed cadmium (adsorption capacity Q, mg/g) was calculated using equation 1 (the calculated values of removal efficiencies and adsorption capacities should be regarded according to the precision of the determination methods we used). We also calculated the removal efficiencies (E, %), equation 2, in order to establish the effectiveness of the considered adsorbent in the heavy metal ion removal process, in batch conditions.

$$Q = \frac{(C_0 - C_t)}{w} \cdot \frac{V}{1000} \tag{1}$$

where,

C_0 is the initial cadmium concentration (mg Cd^{2+}/L),
C_t is time t cadmium concentration (mg Cd^{2+}/L),
V = 100 ml, and
w is the quantity of the adsorbent (g).

$$E = \frac{C_0 - C_t}{C_0} \cdot 100 \tag{2}$$

CONCLUSIONS

The bentonite sample, yeast biomass and their mixtures, proved to be efficient for the removal of cadmium from model solutions.

The highest adsorption capacity was obtained when only bentonite was included in the Ca-alginate beads in batch conditions. As the bentonite concentration decreases, the adsorption capacity decreases as well, even if the amount of yeast increases in batch conditions, excepting the case of the pure yeast sample, which has an intermediate value.

When the removal process was realized in fixed bed conditions, also the most efficient sample was the immobilized bentonite. The mixture containing the same quantity of bentonite and yeast (4 g) has intermediate values for both cadmium initial concentrations. The breakthrough point for fixed bed experiments was observed at 75 minutes in all cases.

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