Cadmium ions adsorption from aqueous solutions by Bentonite clay, fixed bed column

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Abstract. Cadmium metal is discharged to the water from different industries. It can cause serious troubles for human being and aquatic ecosystems. The adsorption technique applied in this study to remove cadmium from simulated aqueous solutions onto bentonite clay by various experiments. Fixed bed system was implemented to verify the Impact of pH, initial cadmium concentration, adsorbent bed height, flow rates and the treatment time on cadmium ions removal. The results show up that when the pH of the aqueous solution was lowered, the cadmium removal efficiency increased. The cadmium removal efficiency decreased due to the increased initial cadmium concentration. Experiments have shown that increasing the contact time and the adsorbent medium in the column lead to more removal efficiency. Removal efficiency increased when the flow rate decreased. The best removal efficacy was (80%) when the pH of (3), initials cadmium concentration (3mg/l), height of the adsorbent bed (50 cm), flow rates (10 ml/min.) and the treatment time of (120 min.). Finally, the bentonite clay can be used for cadmium ions removal instead of more expensive adsorbents, because of its low cost, availability and perfect adsorption property.

Key Word: Cadmium, Bentonite, Adsorption, Removal Efficiency.

1. Introduction

The discharge from many industries contains different inorganic and organic contaminants. Amongst these contaminants are heavy metals that can be poisonous or carcinogen and hurtful to human being and other living organisms [1-2]. Heavy metals of most disturbing from different activities comprise cadmium (Cd), lead (Pb), zinc(Zn), arsenic (As), copper (Cu) and nickel (Ni) [3]. These metals come from various sources like fertilizers, pesticides, alloying, pigments, smelting [4]. There are many different techniques for removing heavy metals like chemical oxidation, chemical precipitation, reduction, ion exchange, ultrafiltration, reverse osmosis, electro dialysis and adsorption. Adsorption technique is the most Impactive because other techniques have ingrained limitations like low efficiency, generate a large quantity of sludge, expensive disposal and sensitive operational circumstances. It is considered an economic technology, and low cost absorbents material can be used in this technique This technique is a relatively new method and has emerged as a favorite possible alternate to remove the heavy metal because it provides high design flexibility, treat effluent with high quality and is reversible and the adsorbent material can be regenerated [5].
Cadmium is naturally existing in the environment through the gradual process of soil erosion and eroding rocks, and from volcanic eruptions and forest fires. So it is naturally found everywhere in soil, water, air and nutrients. The most famous cadmium metal is greenockite, cadmium sulfide (77.6% Cd). As a result, cadmium metal is mostly created as a by-product from smelting, refining and mining of zinc sulfide ores. Cadmium is a heavy metal that is significantly poisonous to human, animals and plants. Heavy metal is a particular concern as it is a non-degradable metal and thus stable. The key human source of cadmium in the environment is industrial waste like smelting, fertilizers, electroplating, pigments, alloy manufacturing, mining, plastic and pesticides [6-10].

There are many natural and enhancement adsorbents used to remove contaminant from contaminated water, soil and air. There are different examples of heavy metal adsorbents such as bio sorbents, resin, zeolite, metal oxide, clay, etc. Clay raw materials and their derivatives create large group with single microstructure and absorption properties for ecological fields. Clay is also used in food producing, pharmaceuticals, and various industrial fields [11]. Bentonite is clay in the nature with a layers of silicate 2:1. The surface of clay has a negative charge because substitution of magnesium and aluminum for silicon and aluminum. One of the most significant properties of bentonites is its large capacity to absorb the cations. Montmorillonite was the main component of bentonite, which is a 2:1 mineral with an octahedral sheet and two sheets of silica, making a layer. The forces of Van der Waals are Impact ing on these layer to keep them together. Water can simply permeate these layers and balance the cations as a result of these weak forces [12].

This study aims to investigate: (1) The ability of bentonite clay as an inexpensive, available and regeneration material for cadmium adsorption, (2) the impact of operating parameters like pH, initial cadmium concentration, height of adsorbent bed, flow rate and the treatment time on the adsorption of cadmium from the aqueous solution.

2. Material and Methods

2.1. Cadmium Stock Solution

The stock solution of cadmium was prepared from dissolution 1.85 g of cadmium nitrate tetrahydrate [Cd(NO3)2.4H2O] into 1 litter of distilled water. The different cadmium concentrations used in the tests were obtained by appropriate dilution of the stock solution by distilled water. pH of the solution was modify depending on the speciation of metal in order to prevent precipitation of metal and to guarantee the adsorption operation. Ammonium hydroxide and nitric acid were used to modify pH of the aqueous solution.

2.2 Adsorbent

Bentonite clay was collected from the western desert- Iraq. Raw bentonite clay was smashed into a rough powder and putted in the water. After that, the sample was left for four days until impurities precipitated in the bottom, and the suspended particles settle at the top of the colloidal solution. Then, clay particles were isolated from the sediments and sieved by (sieve, 63. μm) to eliminate the organic grains and rough impurities. The sample (dens slurry) was placed in a filter cloth and forced by a weighty mass of 5 kg. Then, the resulting dough was dry in the sun and subsequently in an oven at 100°C. The dried sample was ground and sieved by a (sieve, 125 μm). The use of resulting bentonite powder has been beneficial in column absorption and characterization studies [13].

2.3. Continuous adsorption system

Fixed bed column study of continuous system was conducted by several experiments in order to assessment the possibility of cadmium removal by treating cadmium stock solution under various cadmium concentrations, adsorbent bed height (bentonite clay), different flow rates and many pH
values of solution. Figure (1) shows a sketch of the adsorption system. The flow direction in the column is downwards because of gravity. The adsorption system consists of plastic container (5 liter) with inlet and outlet. Rotameter to evaluate of the flow rates. Glass column (2.54 cm ID) and height (60 cm). The adsorption column is filled with adsorbent medium at height of (10, 20, 30, 40, and 50 cm). The column was washed by distilled water double before starting operation. The adsorbent medium (bentonite clay) was filled in the glass column to the required depth. Adsorption experiment began by allowing the cadmium stock solution to flow through the column under the influence of gravity at a certain flow rate, cadmium concentration and pH, as shown in Figure 1.

![Figure 1. Sketch of the adsorption system.](image.png)

To obtain the best operating parameters for the adsorption process, the experiments were implemented at a stable temperature (25°C), pH values (3–10), initial cadmium concentration (3–60 mg/l), height of the adsorbent bed (10-50 cm), flow rates (10-50 ml/min) and the treatment time (10-120 min). The effluent samples were collected during the period of the experiment to analyze the cadmium concentrations in the effluent aqueous solutions by atomic absorption spectrophotometry. Table 1 shows the parameters of all experiments.
Table 1. Parameters of all experiments.

| EX. NO. | pH of aqueous solution (mg/l) | Initial cadmium conc. (mg/l) | Adsorbent bed height (cm) | Flow rate (ml/min) | Treatment time (min) | Objective of Exp. |
|---------|-------------------------------|-----------------------------|--------------------------|-------------------|---------------------|------------------|
| EX- 1   | 3–10                          | 3                           | 50                       | 10                | 120                 | Impact of pH     |
| EX- 2   | 3                             | 3–60                        | 50                       | 10                | 120                 | Impact of pH of initial cadmium concentration |
| EX- 3   | 3                             | 3                           | 10-50                    | 10                | 120                 | Impact of the adsorbent bed height |
| EX- 4   | 3                             | 3                           | 50                       | 10-50             | 120                 | Impact of solution flow rate |
| EX- 5   | 3                             | 3                           | 50                       | 10                | 10-120              | Impact of treatment time |

3. Results and Discussion

The cadmium removal experiments are achieved by a fixed bed column and in a continuous system under various parameters. The experiments were conducted at a constant temperature (25°C), pH of the aqueous solution, initial cadmium concentration \( C_0 \), height of adsorbent bed \( h \), the flow rate of the aqueous solution \( Q \) and the treatment time \( t \). Cadmium removal efficiency is calculated according to the equation 1.

\[
RE\, (\%) = \frac{\text{Initial conc} - \text{Residual conc}}{\text{Initial conc}} \times 100
\]  

Where:

RE: Removal Efficiency

3.1. Impact of pH

The pH has a significant Impact in the adsorption process. The impact of pH on the adsorption process has been studied in some experiments by changing the pH from 3 to 10. The experimentations were carried out at \( C_0 \) of 3 mg/L, h of 50cm, \( Q \) of 10 ml/min., \( t \) of 120 min.). The adsorption technique of cadmium from the cadmium stock solution based on pH of the solution, impact of charge on the absorbent material surface, the ionization degree and adsorbent species speciation. This may be due to the dependence of cadmium ionization on the pH value. Cadmium adsorption is minimal when the pH
values are high due to the driving force prevailing at higher pH values. At higher pH values, the cadmium ionized salts are easily formed leaving a negative charge on the cadmium ion [14]. The existence of OH\(^-\) ions on the adsorbent medium obstructs the adsorb of cadmium ions. pH value affects the properties of the adsorbent surface, i.e., the surface charge of the adsorbent. When the pH value decreases, the adsorbent surface would be enclitic by the hydronium ions, this enhances the cadmium reaction with sorbent binding sites by greater attractive powers [15]. Hence, the removal efficiency of cadmium increases when pH of aqueous solution decreases, as shown in Figure 2.

![Figure 2. pH of aqueous solution versus removal efficiency.](image)

3.2. Impact of initial concentration

Impact of initial cadmium concentration was analyzed by changing the cadmium concentration from 3 - 60 mg/L. The experiments were achieved at pH of 3, height of adsorbent bed (h) of 50cm, initial cadmium concentrations (C\(_0\)) of 3mg/L, flow rate (Q) of 10 ml/min., and treatment time of 120 min.. Figure 3 shows that when the cadmium concentration increases, the removal efficiency decreases. Where, the initial cadmium concentration has a limited Impact on the removal efficiency; and also, the adsorbent medium has a specified number of active places, which may become saturated at a specific concentration. Then, the amount of cadmium molecules contending of the existing functions sites on the adsorbent medium surface increases [14].
Figure 3. Initial of the cadmium concentration versus removal efficiency.

3.3. Impact of adsorbent bed height

Impact of bed height was analyzed by changing the height of the adsorbent bed in the column from 10 to 50 cm. The other conditions were (C₀ of 3 mg/l, pH of 3, Q of 10 ml/min, and t of 120 min.). Figure 4 shows that the cadmium removal efficiency increased when the height of adsorbent bed increased. This increase in efficiency because of an increase in the surface area of adsorbent and when increased height of bed the binding sites of adsorption also increased, then the cadmium removal efficiency increased [16].

Figure 4. Adsorbent bed height versus removal efficiency.

3.4. Impact of flow rate

Impact of flow rate was analyzed in the experiments at (pH of 3, h of 50 cm, C₀ of 3mg/L, t of 120 min.), and the flow rate varying from 10 to 50 ml/min. Impact of the flow rate on the adsorption efficiency of cadmium is shown in Figure 5. When the flow rate increased, the velocity of solution
flow in the bed column also increased. Hence, aqueous solution left the bed column before the adsorbent material adsorbs the appropriate amount of cadmium from the solutions to reach the best removal efficiency. But, when the flow rate decreased, the process changed and the contact time with the adsorbent medium (bentonite clay) increased. So, the amount of the absorbed cadmium increased, and then the removal efficiency increased [16-18].

Figure 5. Flow rate versus removal efficiency

3.5. Impact of treatment time

Figure 6 shows that, increasing the treatment time in the adsorption process led to an increase in the removal capacity of cadmium. The experiments were achieved by changing the treatment time from 10 to 120 minutes and at (C₀ of 3 mg/l, pH of 3, Q of 10 ml/min, and h of 50 cm). When treatment time of the process is increased, the aqueous solution took appropriate time in contact with the adsorbent medium (bentonite clay). Then, it allows the adsorbent medium to adsorbs largest amounts of cadmium and thus obtain the best removal efficiency [16].

Figure 6. Treatment time versus removal efficiency.
4. Conclusion

This study confirmed the success of using bentonite clay for cadmium removal from simulated aqueous solutions by fixed bed column system. In this study, the best removal efficiency of cadmium was (80%). The removal efficiency by using (bentonite clay) was increased as the pH of the aqueous solution, initial cadmium concentration and flow rate decreases. The removal efficiency was increased when the treatment time and height of adsorbent bed in column increased. Adsorption technique by (bentonite clay) can be considered one of more beneficial, economical and environmentally friendly technique.

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