

Removal of Cd(II) from industrial wastewater using locally available Bentonite Clay

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Abstract. Water resources are increasingly polluted by toxic heavy metals such as Cadmium (Cd). Cd is particularly dangerous because it accumulates in living organisms leading to diseases affecting the kidneys, bones and lungs. As a result, researchers have been developing effective techniques to remove harmful heavy metals. Currently, purification techniques in Saudi Arabia and other parts of the world are inefficient and costly; thus, the development of a cheap, readily available, and natural material for the removal of Cd is of great interest. This work highlights the adsorptive potential of local Saudi bentonite clay extracted from Khulais region in western Saudi Arabia in the removal of toxic Cd(II) from aqueous solutions. We successfully synthesized bentonite clay beads that can be inserted in columns for filtering purposes. The effects of contact time, bentonite mass, PH, temperature, bentonite treatment (washing and calcinations), and the adsorptive potential of bentonite were evaluated. The results show excellent adsorptive capacity of bentonite.

1 Introduction

Water resources are increasingly polluted by toxic wastewater from factories. Heavy metals like cadmium (Cd) are One of the most dangerous types of toxins that is currently being discharged by such wastewaters include toxic heavy metals such as Cd (Godt et al., 2006). Even traces of Cd can cause adverse harmful effects. Cd is naturally found in the earth's crust and in rocks but is mainly introduced to the environment by industrial waste including production of NiCd batteries, phosphate fertilizers, solders, paint, and plastics as well as cigarette smoke. Due to the toxicity of this heavy metal, the removal of Cd from industrial waste is important and has received significant attention in recent years—mainly because Cd can readily be adsorbed by plants or animals and directly enter the human food chain (Lin et al., 2000). A number of water-treatment methods for the removal of heavy metals have been developed over the years. The removal of heavy metals from industrial wastewaters using various adsorbents is currently a hot topic in environmental science. Researchers at KACST are particularly interested in the use of clay because it is one of the most abundant resources in the Kingdom of Saudi Arabia. Clay minerals are hydrous aluminum silicates with a sheet-like structure and small particle size. The use of clay minerals such as bentonite for the removal of Cu, Pb, Ni, and many other heavy metals from wastewaters has been successful (Hefne et al., 2008). The goal of this research was to study the adsorptive potential of local Saudi bentonite clay extracted from the Khulais region near Jeddah in the removal of toxic Cd(II) ions from aqueous solutions. The effects of contact time, bentonite mass,

pH, temperature, bentonite treatment, and the adsorptive capacity of bentonite are evaluated. A future goal of this study is to develop a new market for bentonite applications for water treatment.

2 Experimental Techniques

2.1 Materials

Cadmium-nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was purchased from Merck; 0.1M hydrochloric acid (HCl) and 0.1M sodium hydroxide (NaOH) were used for pH adjustments. Ultra-pure water obtained from an E-pure (Barnstead, USA) purifier system to prepare all Cd solutions. Super purity Nitric Acid (SpA 68%) was obtained from ROMIL Ltd., UK and used in sample preparation. System calibrations used single element ICP standards from MV Laboratories Inc. USA. The adsorbent is natural bentonite obtained from the Khulais region of Saudi Arabia. The XRD pattern of the extracted bentonite clay shows that the main component is montmorillonite (68.74 %). The remaining components include K-feldspar (15.72%) and calcite (15.72%).

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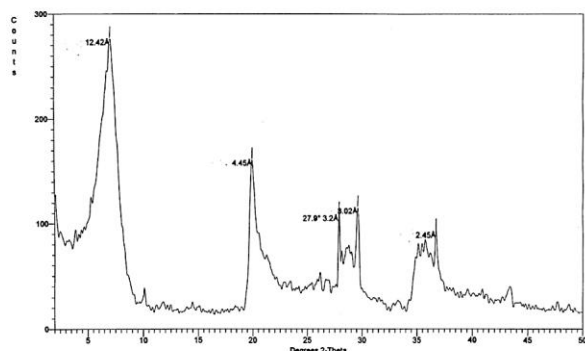


Fig. 1. The XRD pattern of natural bentonite.

2.2 Methods

2.2.1 Batch Adsorption Procedure

Adsorption of Cd with bentonite used a batch technique. Stock and test solutions of Cd were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Deionized water was used in all experiments. Standard Cd solutions ranging between 50 and 300 ppm were prepared by diluting the stock solutions. Adsorption experiments used polyethylene centrifuge tubes with 0.5 grams of bentonite mixed with 50 mL of Cd ions at different concentrations (50-300 mg/L). These tubes were then placed into a water shaker/incubator at 25°C with a 162 rpm stirring rate under natural pH conditions for defined times. Samples were then centrifuged. The equilibration time was 30 minutes. After centrifugation, the concentration of Cd remaining in the solution was analyzed by a Perkin-Elmer Sciex ELAN 9000 ICP-MS. All experiments were carried out in duplicate. The Cd ion uptake was simply calculated via concentration differences. The adsorbed percent of Cd was calculated as follows:

$$\text{Adsorption Percentage} = \left[\frac{(C_i - C_f)}{C_i} \right] \times 100 \quad (1)$$

Here, C_i and C_f are the initial and final Cd ion concentrations, respectively, and the resulting adsorption curves were estimated using these calculations.

2.2.2 Effect of adsorbent dose and temperature

Different bentonite masses (0.1-5.0 g/50 mL Cd solution) at Cd(II) concentrations of 100 mg/L were used to study the adsorption of Cd onto bentonite while keeping the stirring speed at 162 rpm and maintain a 30 minutes contact time at room temperature. This experiment determined the optimal mass of bentonite needed for effective removal of Cd ions. Three temperatures were tested (i.e. 35, 40, and 50 °C).

2.2.3 Desorption studies

The significance of the desorption experiments in analyzing adsorptive potentials was highlighted in this work to estimate the metal-releasing capacity of the bentonite clay with Cd(II). Bentonite samples saturated with different adsorbed amounts of Cd ions were dried at 60°C and then 0.5 g of these samples were added to a glass reactor containing 50 mL of deionized water. In order to disperse the clay pellets, a vortex mixer was utilized. To illustrate, mechanical agitation was conducted for the suspensions for 24 hours at 162 rpm and 25°C. Finally, resulting supernatant was analyzed for its Cd content via ICP-MS.

2.2.4 Effect of bentonite pretreatment

The adsorption capacity and removal percentage of clay samples were studied under three different pretreatment conditions. First, the bentonite was used without any treatment and was named natural bentonite (NB). Second, the clay was washed several times with deionized water to release the dissolved salts into their constituents. This was termed washed bentonite (WB). In the third treatment, the clay samples were calcined or fired to 600°C. The purpose of this treatment is to investigate the effects of washing and heating on the clay's ability to adsorb Cd(II).

2.2.5 Synthesizing bentonite beads

Making bentonite beads in order to insert them in a column and test for Cd adsorption seemed to be of great interest if we wanted to implement filters using this clay technology. Small circular bentonite beads were synthesized by mixing 70 grams of the bentonite clay with 1200 mL of distilled water for 1 hour. Next, 20 g of alginate acid sodium salt (polymer extracted from seaweed) was stirred into the resulting mixture for two hours. The alginate acid helps the beads form their desired shape. A filtering apparatus was then used to pouring the mixture containing the water, bentonite, and polymer into a 3% calcium chloride solution so that when the drops fall into the solution, they form small stable beads that retain the circular shape. Next, the beads were spread out onto a tray and were left to dry for three days to obtain fully dried beads.

3 Results and Discussion

Various parameters were evaluated for their impact on Cd(II) removal by bentonite.

3.1 Kinetics of adsorption

The adsorption kinetics detail the rate of solute uptake and is a very important parameter for determining the adsorption efficiency of natural bentonite. Figure 2 demonstrates the effect of contact time on the Cd adsorption rate at 50 mg/L. Figure 2 shows that Cd

sorption was very fast. The slope indicates a fast adsorption rate. The removal of Cd(II) increases rapidly with time and then continues at a relatively slower rate until it reaches saturation in about 30 minutes. The removal of Cd(II) is initially very fast but becomes slower at later times. This is because a large number of vacant surface sites are first available for adsorption, but the remaining vacant sites are difficult to occupy at later time points due to repulsive forces between solute molecules of the solid and bulk phase (Bandyopadhyay 1998). The adsorption rate of natural bentonite seems to be excellent. Short adsorption times are always preferable to minimize energy consumption; therefore, bentonite is an excellent adsorbent for Cd with a very short adsorption time of about 30 minutes.

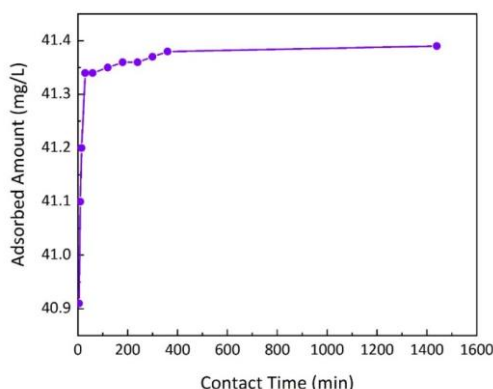


Fig. 2. Effect of contact time on Cd adsorption rate by bentonite (Cd concentration 50 mg/L, 25°C and bentonite dose = 0.5 g).

3.2 Effect of bentonite dosage

Adsorption of Cd on bentonite was studied at different adsorbent masses [0.1, 0.3, 0.5, 0.7, 1.5, 2.0, 3.0, and 5.0 g/50ml] while holding the initial Cd concentration (100 mg/L), temperature (25°C), and contact time (30 minutes) constant. The adsorption of Cd increased with increasing adsorbent dose. Maximum removal was observed with the adsorbent dose of 0.5 grams (Figure 3). The increase in adsorption with adsorbent dose was indicated at the earlier stages. According to Tahir et al., this behavior is attributed to the increase in adsorbent surface area and the associated availability of more adsorption sites (Tahir and Naseem 2001). The fact that 0.5 grams of bentonite was sufficient for efficient removal is important for economic reasons particularly when industrial scale up is considered. Our results suggest that 0.5g or 5.0g yield almost the same result; thus, it is more economically favorable to use the bentonite with the lower mass.

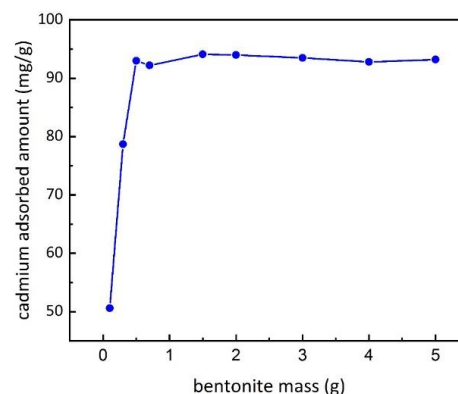


Fig. 3. Effect of bentonite mass on adsorbed amount of Cd (100 mg/L) at 25°C.

3.3 Effect of pH on Cd removal

The pH of the aqueous solution is an important parameter that controls the adsorption of Cd at the clay-water interface. Figure 4 illustrates the effect of pH on Cd(II) adsorption onto bentonite. Our experiments showed that adsorption experiments were not effective beyond pH 8 due to the precipitation of Cd(OH)₂ at pH 8; thus, the experiments were conducted from 2-8. At pH 2-8, the adsorption capacity increased with an increase in pH. The optimal adsorption was observed at pH 6 and then remains constant. Increasing Cd(II) adsorption with increasing pH reflects the presence of fewer H⁺ ions at higher pH values that could compete with Cd(II) cations for the available adsorption sites. The surface charge of bentonite is a strong function of the pH. Here, the point of zero charge (PZC) of natural bentonite is around pH 4. This indicates that the surface of bentonite is more protonated at pH values less than 4. This makes it less likely to retain Cd ions. Under these conditions, H⁺ competes with Cd ions resulting in active sites becoming protonated leading to the exclusion of Cd that might bind to the bentonite surface (Barbier et al., 2000). At pH values higher than 6, metal precipitation was evident and the clay became a bit deteriorated.

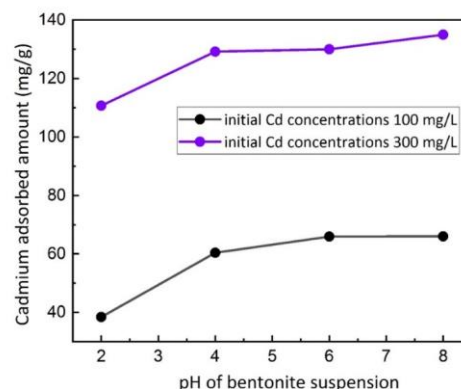


Fig. 4. Effect of pH on Cd removal by bentonite at 100 mg/L initial Cd; bentonite dose = 0.5 g as well as at initial Cd concentration of 300 mg/L with bentonite dose = 0.5 g.

Measuring the pH values of the bentonite suspension before and after Cd adsorption offered useful information. Figure 5 shows the pH values of the bentonite suspension before and after Cd(II) adsorption. There is a significant increase in the final suspension pH after Cd adsorption that might be due to the replacement of alkali and alkaline earth metals (Na, K, Ca, Mg) located in the exchange sites of the clay with Cd ions in the solutions. In addition, the carbonate that is already present in the bentonite structure might also be dissolved into the solution leading to an increase in the final solution pH.

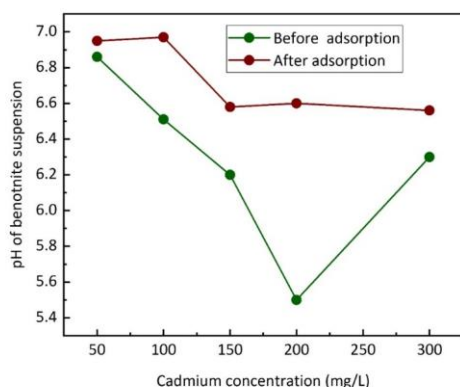


Fig.5. The measured pHs of bentonite suspension before and after Cd adsorption onto NB surface at 25°C.

3.4 Effect of temperature on Cd removal

Figure 6 shows the adsorbed amount of Cd by bentonite at different temperatures (35, 40, and 50°C). The temperature increase obviously increases the amount of Cd adsorbed onto the bentonite clay. This increase in adsorptive potential is due to the increase of the kinetic energy of the Cd ions with heating. This increases the frequency of collisions between the bentonite and Cd ions thus increasing the adsorption of Cd onto the bentonite surfaces as discussed by Hefne et al. (Hefne et al., 2008).

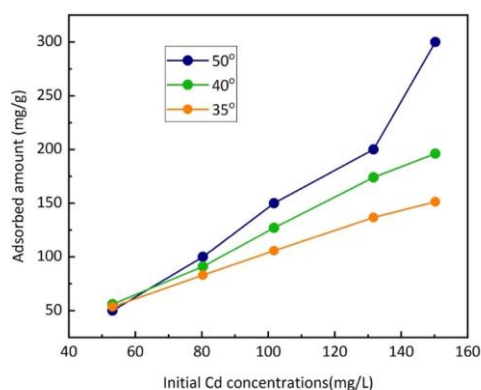


Fig. 6. Adsorption isotherms of Cd onto natural bentonite at different temperatures.

3.5 Desorption

Studying desorption of an adsorbent is very important in the metal ion removal process. The desorption experiments used deionized water as a desorbing agent. The bentonite samples were loaded with different adsorbed amounts of Cd(II) ions (initial Cd concentration 100 and 300 mg/L) and placed in 50 mL of deionized water. After one day, the amount of Cd(II) desorbed into the water was measured. Cd(II) retention within bentonite was about 98% indicating strong contact between Cd(II) ions and bentonite surfaces. A strong acid such as HCl is needed to promote desorption within the samples.

3.6 Effect of bentonite pretreatment

The amount of Cd adsorbed onto the washed bentonite was significantly higher than the natural and calcined bentonite samples. This may be because the excess salts located in the exchange sites of natural bentonite were removed with washing. Consequently, more exchange sites were now available on the bentonite surfaces to increase Cd adsorption. This outcome is a result of the heat treatment of the bentonite clay that lead to its subsequent dehydration and dihydroxylation. There is decreased cationic exchange capacity and decreased surface area. Thus, the adsorption capacity decreased (Alkan et al., 2005). Therefore, in this work, the adsorption capacity of NB decreased upon heat treatment at 600°C and increased upon washing with deionized water.

4 Conclusion

Industrial waste is increasingly polluting water bodies. This poses a great threat to the environment, aquatic life, and human health. Although many technologies are available for removing pollutants—they are usually expensive especially for poor countries who face the biggest threat. Therefore, there is a need to develop affordable technologies for water purification. In this study, we demonstrated that natural bentonite clay can be used as an efficient adsorbent for the removal of heavy metal Cd that contaminates industrial wastewaters. In batch mode adsorption studies, metal ion removal increased with increasing contact time, amount of adsorbent, pH, and temperature. With these parameters, only a small amount of bentonite (0.5 g) was needed to effectively remove Cd(II) ions. In addition, less than 2% of Cd(II) desorbed from the bentonite surfaces which indicates the strong affinity between bentonite surfaces and Cd(II). Pre-washing the bentonite increased the absorption capacity relative to natural bentonite and calcined bentonite. Thus, bentonite filtering applications can be implemented in the near future.

5 References

1. J. Godt, F. Scheidig, C. Grosse-Siestrup, P. Esche, P. Brandenburg, A. Reich, D. Groneberg, J. Occup Med Toxicol, **1**, 22 (2006)
2. S. Lin, S. Lai, H. Leu, J. Hazard Mater., **76**, 139-153 (2000)
3. J. Hefne, W. Mekhamer, N. Alandis, O. Aldayel, T. Alajyan, Int. J. Phys. Sci., **3**, 281-288 (2008).
4. A. Bandyopadhyay, R. Panda, T. McNulty, F. Mohammadi, S. Danforth, A. Safari, RAPID PROTOTYPING J., **4**, 37-49 (1998)
5. S. Tahir, R. Naseem, Chemosphere **63**, 1842–1848 (2006)
6. F. Barbier, G. Duc, M. Petit-Ramel, Colloids Surf. A:Physiochem. Eng. Aspects. **166**, 153-159 (2000)
7. M. Alkan, M. Karadas, M. Dogan, O. Demirbas, J. Colloid Interface Sci., **291**, 309-318. (2005)