

Groundwater Treatment from Heavy Metals

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Abstract: *The one of the most significant environmental problems in the last decades becomes the contamination of the soil and groundwater. The contamination can comprise the substantial risk for the environment and for human health. This work studies the reliability of using zeolite, which is one of the promising innovative in situ remediation methods, in removing cadmium from a contaminated shallow aquifer. In the batch tests, the influence of several operating parameters such as the effects of initial metal concentration (50-250 mg/L), time of contact of adsorbate with adsorbent (0-180 min), pH of the solution (2-8), adsorbent dose (0.15-2 g/100 ml), and agitation speed (200 & 270 rpm) were investigated. The optimum values of these parameters for cadmium on zeolite were 50 mg/L, 60 min, 6.5, 0.25 g/100 ml and 270 rpm respectively with achieved removal efficiency greater than 99.5%*

Keywords: Grand water, Heavy Metals, pollution

1. Introduction

The presence of toxic heavy metals in groundwater brings about significant changes in the properties of water resources and has to be avoided in order to preserve the environmental quality. These metals can be related to many anthropogenic sources, and their compounds are extremely toxic. Many heavy metals, such as mercury, chromium, and cadmium, accumulate in the aquatic food web reaching human beings through the food chain, and causing several pathologies [1]. The availability of fresh water of proper quality is a prerequisite for human well-being and the consequential social/economic development of communities. In the past, water requirements for humans were considerably lower than the available natural resources. Additionally, the negative impact on the quality of water resources was limited due to the relatively low-level community social/economic activities. Presently, the global population overgrowth coupled with the accelerating technological advances and the concomitant environmental pollution/climate change have all led to a significant reduction in water resource availability and appreciable deterioration of water quality. In the middle and southern regions of Iraq, the fresh water situation is especially acute leading, among other drawbacks, to an increase in desertification. A number of factors are to blame; foremost of which are water-impoundment projects in river-source countries (Turkey and Iran) and scanty rainfall due to Climate change. In many countries, groundwater is generally more reliable for use than surface water. For example, in the United States, 56% of the population relies on groundwater for their drinking water. However, groundwater resources are vulnerable because any chemical that is easily soluble and that can penetrate the soil is a prime candidate for a groundwater pollutant. Chlorinated hydrocarbons and heavy metals are two of the most serious pollutants threats continuously released to the groundwater as a result of many industrial operations and waste disposal [2].

1.1 Objective of the Present Study

The aim of this work is to investigate the potential application of zeolite for the removal of cadmium from the contaminated groundwater.

2. Experimental Work

2.1 Introduction

The description of the experimental setup and the analytical methods used in all experiments for obtaining experimental data and results were required in order to verify the accuracy and precision of all the measured parameters. The planned experiments, series of laboratory batch tests, were conducted in order to assess the potential of zeolite to reduce the concentration of selected toxic heavy metal (Cd^{2+}) from an artificially contaminated groundwater. The effects of contact time, pH, initial concentration, shaking velocity and dose of resin are covered here to get the best parameters for removing this contaminant.

2.2 Material

2.2.1 Zeolite

Zeolite is generally defined as aluminosilicates possessing three-dimensional frameworks of linked silicon-aluminum-oxygen tetrahedra. The isomorphous substitution of Al^{3+} for Si^{4+} results in a negative charge imbalance in the zeolite lattice that is balanced by exchangeable cations, typically hydrated Na^+ , K^+ and Ca^{2+} in nature. This means a high affinity for transition metal cations such as heavy metals, but a low affinity for anions and nonpolar organics exists [3].

However, a commercially zeolite pellets with diameter (35.96 mm) manufactured by (Dwax company for synthetic zeolite) were used as reactive materials. The resins were washed with 1M of NaOH and 1M of HCl in order to remove possible organic impurities, and then they washed with distilled water to remove all excess and basic. Finally the resins were dried for 24 hours. Table 2.1 shows the composition and reported physico-chemical properties of the zeolite used in the present study.

Table 2.1: Composition and physico-chemical properties of zeolite

Property	Percentage (%)
SiO_2	34.48
Al_2O_3	29.94
L.O.I	15.05
Na_2O	13.40
CaO	2.52
TiO_2	1.70

Bulk density (g/cm ³)	0.58
Particle density (g/cm ³)	1.2
Porosity (n _p)	0.34
Surface area (m ² /g)	1000
Cation exchange capacity (meq/100 g)	1.8

2.2.2 Contaminant

Cadmium was selected as a representative of heavy metal contaminants. To simulate the water cadmium contamination, a solution of Cd(NO₃)₂·2H₂O (manufactured by E. MERCK, Denmark) was prepared and added to the specimen to obtain representative concentration. Cd(NO₃)₂·2H₂O has a molecular weight of 169.5 g/mole and atomic weight of cadmium ions is 112.411 g/mole. For example, to prepare a water sample with cadmium concentration of 50 mg/l, 0.137 g of Cd(NO₃)₂·2H₂O dissolves in 1000 ml of distilled water.

2.3 Equipment's

- 1) Atomic absorption spectrophotometer (AAS) (Norwalk, Connecticut (USA)): was used to measure the concentration of soluble cadmium.
- 2) pH meter : was used to measure the pH of the aqueous solution.
- 3) Shaker: high-speed orbital shaker has an adjustable shaking (150, 200, 250, 270) rpm was used in the batch tests.

2.4 Batch Experiments

Batch equilibrium tests are carried out to specify the best conditions of contact time, pH, initial concentration, resin dosage and shaking velocity. This means that these tests are suited to identify the activity of the reactive material and the sorption isotherm. Series of 250 ml flasks are employed. Each flask is filled with 100 ml of cadmium solution which has initial concentration of 50 mg/l. About 0.25 g of adsorbent was added into different flasks. The solution in the each flask was kept stirred in the high-speed orbital shaker at 270 rpm for 2 hours. The measurements were carried out using atomic absorption spectrophotometer.

3. Results and Discussion

3.1 Batch Experiments

3.1.1 Equilibrium Time

Ion exchange is generally regarded as a relatively rapid process, and the time to reach equilibrium in batch systems is usually found to be less than 1 h, although it can reach 2 h. While variability in zeolite characteristics influences ion exchange, experimental conditions also affect the time to reach equilibrium in batch tests [3]. Figure 3.1 shows the effect of contact time on cadmium exchange using 0.25 g of zeolite added to 100 ml of metal solution for batch tests at 25±1°C. Equilibrium for the purposes of this study was taken as having been reached when the cadmium removal efficiency values plateau. This occurred at a reaction time of approximately 1 h. This value can be subsequently used for all batch tests.

It is clear from figure mentioned above that the percentage of metal ion sorbed (i.e., adsorption rate) was very fast initially and it's increased with increasing of contact time until reached the equilibrium time. This is crucial parameter for optimal removal ions from contaminated water [4]. Also this may be due to the presence of large number of resin sites available for the adsorption of metal ions [5]. However, further increase in contact time had no significant effect on cadmium removal. The maximum removal efficiency of cadmium using zeolite achieved in the present study was 99.8%.

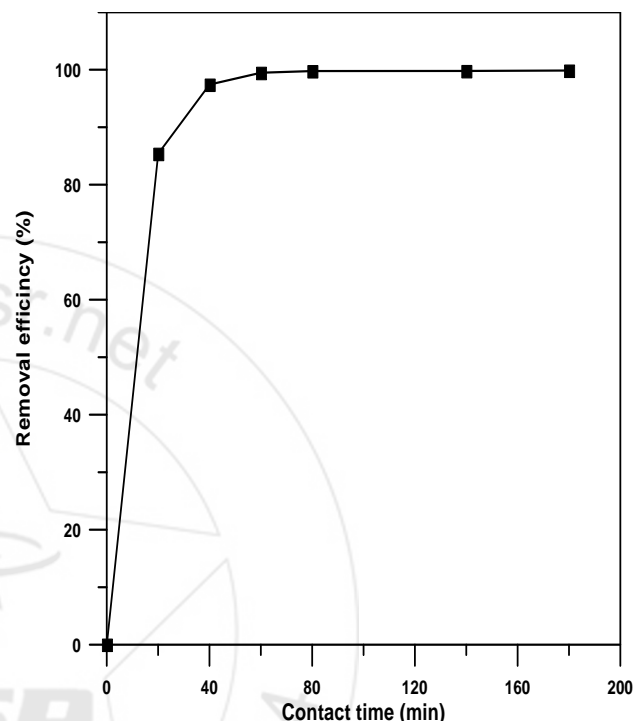


Figure 3.1: Removal efficiency of cadmium on zeolite as a function of contact time (pH= 6.5; c₀= 50 mg/l; dose=0.25 g; speed= 270 rpm; T= 25±1 °C).

3.1.2 Initial pH of the Solution

Because of the protonation and deprotonation of the acidic and basic groups of the adsorbents, its sorption behavior for metal ions is influenced by the pH value, which affects the surface structure of sorbents, the formation of metal hydroxides, and the interaction between sorbents and metal ions [6]. Therefore, the pH dependence of sorption for metal ions was investigated in detail. The sorption of cadmium on zeolite was studied as a function of contact time in the initial pH range 2–8 for a fixed resin dose of 0.25 g/100 ml at a constant initial ionic concentration of 50 mg/l and shaking speed of 270 rpm (Figure 3.2). This figure shows that the sorption behavior of metal ions is more sensitive to pH changes. A general increase in cadmium sorption with increasing pH of the solution has been observed up to pH equal to 6.5. There are no hydroxo complexes in the solution at pH less than 6.5; only dissociated aqua-ion-forming Cd (II) ions are present. Accordingly, the increase in the metal removal as the pH increases (i.e., as the solution becomes more basic) can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower columbic repulsion of the sorbing metal. However, further increase in pH values would cause a

decreasing in removal efficiency. This may be attributed to the formation of negative cadmium hydroxides $Cd(OH)_2^-$ which are precipitated from the solution making true sorption studies impossible. In addition, at low pH values an excess of protons can compete effectively with the Cd (II) ions for binding sites on zeolite surface. This effect has been attributed to the surface binding of low-affinity surface sites as high-affinity ones begin to reach saturation, leading to a reduction in the removal efficiency.

It is clear from figure 4.2 that the time required to reach equilibrium in batch systems is equal to 1 h, although the initial pH of the solution was varied from 2 to 8. Also, the maximum removal efficiency of cadmium was achieved at initial pH of 6.5.

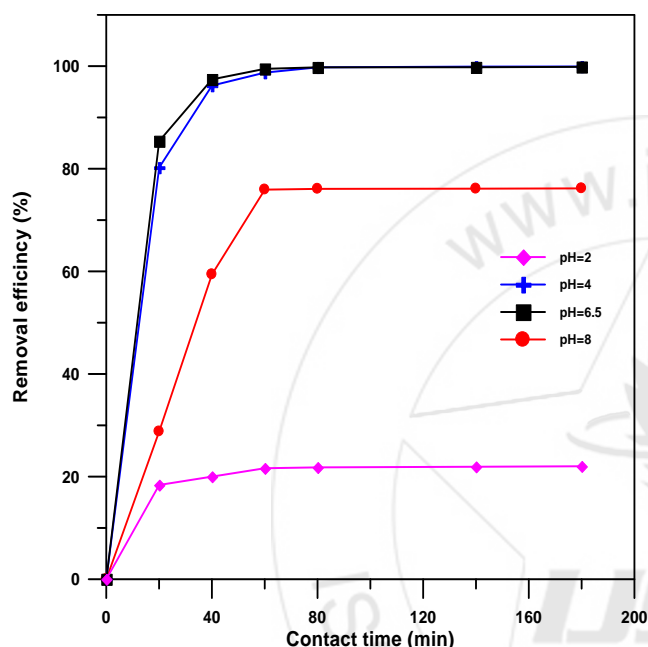


Figure 3.2: Effect of initial pH on removal efficiency of cadmium on zeolite as a function of contact time ($c_o=50$ mg/l; dose=0.25 g; speed= 270 rpm; $T= 25\pm 1^\circ C$)

3.1.3 Initial Cadmium Concentration

To study the effect of initial concentration of cadmium on the removal efficiency, the operating conditions were set as follows: volumes of solutions used were 100ml, concentration of cadmium ranging between 50 and 250 mg/l, were shaken with 0.25 g/100 ml of zeolite for 1 hour with initial pH of the solution is 6.5.

Figure 3.3 illustrates the removal of Cd^{2+} ions by zeolite as a function of initial metal ion concentration. The results show that there was a higher removal of the metal in the first values of initial concentration. This removal was decrease with increasing of initial concentration up to 200 mg/l and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the zeolite samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the zeolite at equilibrium (the adsorption capacity) rapidly decreases at the low initial metal ions concentration and then it begins to a slight decrease with increasing metal concentration in

aqueous solutions in the length between 200 and 250 mg/l [7].

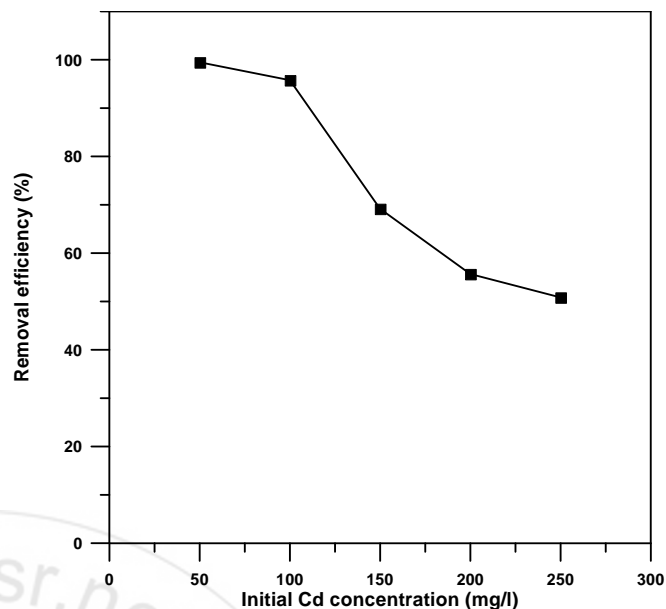


Figure 3.3: Effect of initial concentration on removal efficiency of cadmium on zeolite (pH=6.5; dose=0.25 g; speed= 270 rpm; contact time=1 h; $T= 25\pm 1^\circ C$)

3.1.4 Resin Dose

The dependence of Cd(II) sorption on adsorbent dosage was studied by varying the amount of zeolite from 0.15 to 2 g added to 100 ml of metal solution for batch tests at $25\pm 1^\circ C$, while keeping other parameters as follows; $c_o=50$ mg/l, pH=6.5, shaking speed=270 rpm and contact time=1 hour. Figure 3.4 presents the Cd (II) removal efficiency as a function of different amounts of zeolite. It can be observed that removal efficiency of the zeolite improved with increasing adsorbent dosage from 0.15 g to 0.25 g for a fixed initial metal concentration. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites.

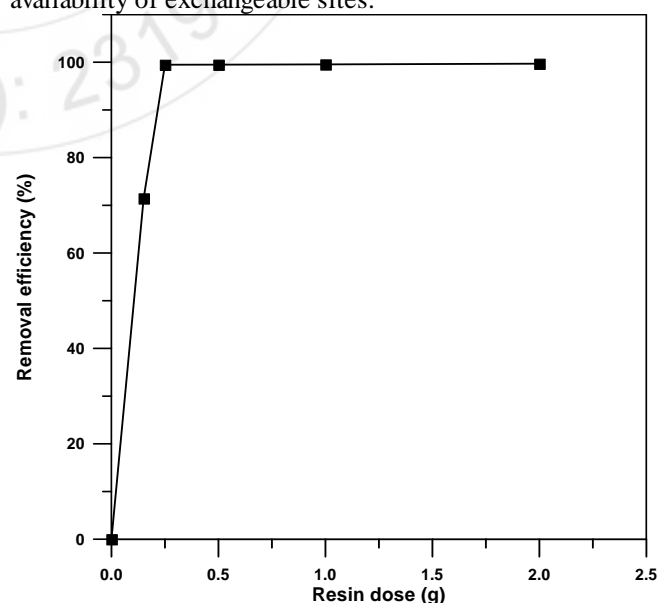


Figure 3.4: Effect of resin dosage on removal efficiency of cadmium ($c_o=50$ mg/l; pH=6.5; speed= 270 rpm; contact time=1 h; $T= 25\pm 1^\circ C$).

3.1.5 Agitation Speed

Figure 3.5 shows that about 77% of the cadmium ions were removed at shaking speed equal to 200 rpm when the contact time at equilibrium and that Cd removal increases with the increase in shaking speed. There was gradual increase in metal ions removal when agitation speed was increased from 200 to 270 rpm at which about 99.5% of Cd ions have been removed at equilibrium time. These results can be associated to the fact that the increase in the agitation speed improves the diffusion of metal ions towards the surface of the adsorbent. Figure 3.5 also shows that optimum equilibrium was reached at the agitation speed of 270 rpm. Therefore, higher uptake of metal ions could be possible at this speed of agitation as it will assure that all the sites are made readily available for metal ions uptake.

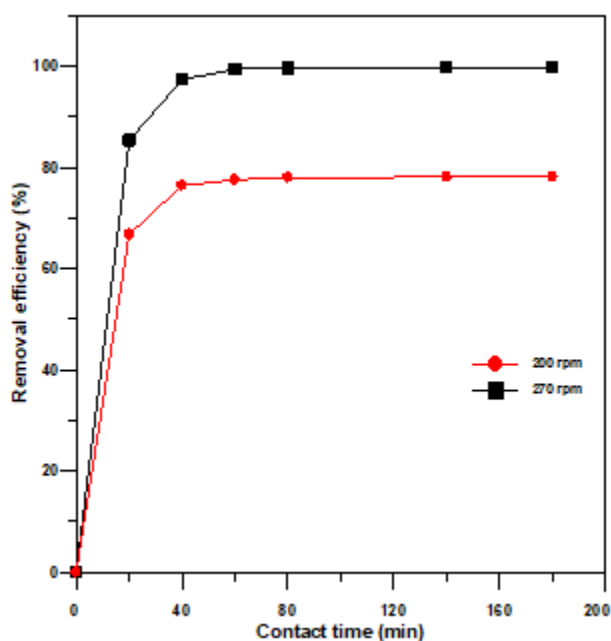


Figure 3.5: Effect of agitation speed on removal efficiency of cadmium as a function of contact time ($c_0=50$ mg/l; pH=6.5; resin dose= 0.25 g/100 ml; T= 25±1°C)

4. Conclusions

Based on the results obtained from the experimental measurements, the following conclusions can be drawn:

- The interactions between cadmium ions and zeolite have been investigated. The batch results indicated that several factors such as adsorption or equilibrium time, initial pH of the solution, initial metal ion concentration, resin dose and agitation speed affect the adsorption process. However, the optimum values of these factors will achieve the maximum removal efficiency of Cd²⁺ were 1 hr., 6.5, 50 mg/l, 0.25 g/100 ml and 270 rpm respectively.
- The adsorbed amount of cadmium ions can be:
 - Increased with increasing pH of the solution up to pH equal to 6.5. However, further increase in pH values would cause a decreasing in removal efficiency. This may be attributed to the formation of negative cadmium hydroxides Cd(OH)₂⁻ which are precipitated from the solution making true sorption studies impossible.
 - Decreased with increasing of initial concentration up to 200 mg/l and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau

represents saturation of the active sites available on the zeolite samples for interaction with metal ions.

- Increased with increasing adsorbent dosage from 0.15 g to 0.25 g for a fixed initial metal concentration. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites.
- Increased with increasing agitation speed from 200 to 270 rpm at which about 99.5% of Cd ions have been removed at equilibrium time. These results can be associated to the fact that the increase in the agitation speed improves the diffusion of metal ions towards the surface of the adsorbent.

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