Removal of Cd(II) from polluted water by filtration using iron oxide coated sand media

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Abstract. Cadmium is a poisonous metal that may influence numerous organs in the human body; coated sand with iron oxide (IOCS) was prepared and utilized in this study as a filter media to investigate its removal efficiency of cadmium from Synthetic polluted water. The removal efficiency variation due to pH value, operation time, and the initial concentration were investigated. The results show good capability of the filtration media in removing cadmium ions which could reach about 95 % at a specific operating condition, optimal pH value, and operation time were 4, 30 min respectively while initial concentration higher than 1 mg/l would require longer operation time. In order to provide a practical tool to predict the removal efficiency under specific operating conditions a mathematical model and statistical analysis was applied; statistical analysis showed that the model had good representation capability.

Keywords: Iron oxide coated sand, Cadmium removal, Adsorption.

1. Introduction

Industrial workplaces such as industrial paints, rechargeable batteries manufacturing, and mining are some of common places that expect a cadmium exposure could take place in it. USEP water quality guidelines adopt the limits of 1 µg/l and 0.15 µg/l as a Short-Term and Long-Term exposure for cadmium at water hardness of 50 mg/l CaCO$_3$, while European Union exposure limits was 0.6 µg/l, and 0.09 µg/l as a Short-Term and Long-Term for cadmium at water hardness of 50 mg/l CaCO$_3$[1]. Short-Term exposure could cause potential health effects such as nausea, diarrhea, muscle cramp, liver injury, shock and renal failure, while Long-Term exposure could cause potential health effects such as kidney, liver, bone and blood damage [2]. Treatment of polluted water with cadmium is essential to prevent serious health risks; however adoption of a specific treatment method depends on many considerations such as efficiency, cost, and technology availability. Filtration was one of the oldest and widely used water treatment technologies but it’s mainly used for removal of suspended solids[3], improving filtration by improving the filter media to make it capable to remove dissolved material will be very helpful to extend removal efficiency for the filtration process.
Sand coating is a process designed to extend sand media capability to remove dissolved matter, coating may be done using manganese oxide\cite{4}, Graphene\cite{5}, aluminium oxide\cite{6}, and iron oxide\cite{7}. Iron oxide coated sand (IOCS) is an innovative media which can be used as a filter media in order to make filtration process capable to remove dissolve matter. Ching-Hsing reported that IOCS was achieving removal capability as much as 80 % of copper ions in polluted water, and the interaction was chemical bonds between both iron oxide and copper ions\cite{8}. Iron oxide coated sand was successfully reported used by many authors to remove arsenic\cite{9, 10}, Phenol Compounds\cite{11}, Cr (VI)\cite{12}, Copper (II) \cite{13}, while Ayoub G M gave a good comparison study between iron oxide and aluminium oxide coated filter media for phosphors removal\cite{14}. This study is designed to investigate the performance of iron oxide coated sand on cadmium ion removal efficiency under various operating conditions such as pH, operation time, and initial concentration, and establishes a mathematical model that could help in predicate the removal efficiency under specific operation conditions.

2. Materials and Experimental Setup.

2.1. Iron Oxide Coated Sand preparation.
The standard sand supplied by the General Company of Geological Survey in Baghdad / Iraq was used. Raw sand media sieve analysis described in Table 1. while physical properties is described in Table 2.

| Sieve No | Sieve size (mm) | Sieve weight (g) | Sieve weight + retained (g) | Retained (g) | Passing % |
|----------|-----------------|------------------|-----------------------------|--------------|-----------|
| 16       | 1.18            | 391.1            | 391.1                       | 0            | 100       |
| 20       | 0.85            | 366.5            | 392.6                       | 26.1         | 97.39     |
| 30       | 0.6             | 347.1            | 1299.7                      | 952.6        | 2.13      |
| 50       | 0.3             | 317.9            | 335.5                       | 17.6         | 0.37      |
| 100      | 0.15            | 296              | 296.2                       | 0.2          | 0.35      |
| 200      | 0.075           | 288.3            | 288.3                       | 0            | 0         |
| pan      | -               | 274.8            | 274.8                       | 0            | 0         |

Table.2. Physical Properties of the Standard Sand.

| Angular   | Sub Angular   | Rounded     | Sub Rounded |
|-----------|--------------|-------------|-------------|
| 8.7 %     | 40.22 %      | 7.61 %      | 43.47 %     |

Sand stock was washed and soaked in acid solution (1.0 M HCl) for 24 hours, then washed by deionized water and left to dry at 105°C for 24 hours in a drying oven in order to prepare the sand particles for surface coating, a 2M of Fe(III) was prepared by dissolving iron(III) chloride (FeCl$_3$) in deionized water, NaOH solution was used to set the iron(III) chloride solution to pH = 9.5, then the sand sample was added and mixed for 10 minutes, The sand – solution mixture dried at 105°C for 24 hrs, the produced coated sand then washed carefully with deionized water and finally dried at 105°C for 5 hrs\cite{15, 16}.

2.2. Preparation of Cd(II) stock solution.
Cadmium ion stock solutions with different concentrations were prepared using cadmium nitrate (Cd(NO$_3$)$_2$.4H$_2$O) and deionized water, Controlling the solution pH value was done using of 1.0 Mol/l of HNO$_3$ and pH meter\cite{17}. Atomic absorption spectroscopy (AAS) with graphite furnace (EPA Method 213.2) was used to determine cadmium ion solutions concentration.

2.3. Experimental setup.
A 2.54 cm diameter and 1 meter height PVC chemical resistance pipe was used as an experimental column (Figure 1.), the iron oxide coated sand media was packed in the pipe at 90 cm height, and then the experimental pipe was shaking gently in order to settle down the filtration media inside it. Filtration media flotation was prevented using perforated steel plates placed above and below the media. Experiments were carried out by upward flow of cadmium solution using peristaltic pump, while rotary flow meter and gate valve were used to measure and control the flow. At a flow rate of 50 ml/min the experimental solution requires approximately 10 min to travel through the one meter height experimental column, so with time step of 10 minutes to collect the samples we can insure a complete cycle of the experimental solution through the experimental column unit, therefore the samples were collected from the fully mixed solution tank in (10, 20, 30, 40, 50, 60 min). The removal efficiency ($R_e$) is calculated using the following equation:

$$R_e \% = \frac{C_i - C_e}{C_i} \times 100$$

(1)

$C_e$ is the Cadmium ion (Cd II) concentration in the collected samples from the solution tank under specific operating conditions, while $C_i$ is the initial Cadmium ion concentration.

Figure 1: Experimental column unit: (1) Chemical resistance PVC pipe; (2) Flow meter; (3) Motor with paddle mixer; (4) Peristaltic pump; (5) Gate valve; (6) Perforated steel plate; (7) iron oxide coated sand media; (8) Tank filled with experimental solution

3. Experimental results and discussions.

3.1. pH effect.

This first group of experiments was carried out to determine the effect of the hydrogen ion concentration (pH) variation on the removal efficiency of cadmium ions from the experimental solutions. Other experimental parameters such as operation time and initial concentration ($t_o$, $C_i$) were kept fixed on (60 min, 1 mg/l) respectively. The temperature of the experimental solution was within the range of room
temperature (20-25 °C), while solutions of 0.1 N NaOH and 0.1 N HCl were used to set pH initial values at (1, 2, 3, 4, 5, 6, 7, 8, 9, 10) respectively for the cadmium ion solutions for every experimental run. Figure 2. illustrates the experimental results, the figure shows that increasing the pH value increases the removal efficiency and that is due to the decreasing of the competition between hydrogen ions and Cd(II), however, at high pH, forming of Cd(OH)₂ due to the participation Cd(II) ions leads to decreasing of removal efficiency[18]. Highest removal efficiency was (95 – 85 %) which occurs within the pH range (4-7), and so the following sets of experiments will adopt pH = 4 as the optimal value of an operation condition.

3.2. Effect of initial concentration.
With this group of experiments the parameters pH, to, were set fixed at 4, and 60 min respectively, setting pH at 4 was chosen based on the results obtained from the previous group of experiments which shows that maximum removal efficiency occurs at this pH, while the experimental solution temperature was within the range of room temperature. Cadmium ions initial concentrations were set to be at (0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10 mg/l) for every run of the experimental set.
Figure 3. shows the results which indicate that the removal efficiency decreases with the increasing of the initial concentration and that is referring to the increasing of the competition between the ions on the available active sites of the adsorbent[19]. However, we should remember that decreasing of the removal efficiency, do not mean decreasing of the total cadmium ions that were removed. At initial concentration 0.5 mg/l of Cadmium ions the removal efficiency reached its maximum value (97%), while minimum removal efficiency was 45 % at 10 mg/l initial concentration.
3.3. Effect of operation time.
Effect of operation time ($t_o$) on the removal efficiency ($R_e$) of the cadmium ions was investigated with this group of experiments; the time interval to collect samples was extended from zero to 90 min with 10 min interval for every sample that collected from the fully mixed experimental solution in the tank. Experimental solution temperature was at the range of room temperature, while other parameters such as pH and $C_i$ were sets fixed at 4 and 1 mg/l respectively. The results (Figure 4.) show that the removal efficiency increases rapidly for the interval from zero to 30 min where it reaches 93%, however, extending the operating time more than 30 min would not imply a significant increase in the removal efficiency.

Figure 3. Effect of intitial concentration on the removal efficiency of the cadmium ions

Figure 4. Effect of operation time on the removal efficiency of the cadmium ions

4. Mathematical modelling.
In order to model the experimental data, Polymath 6.1 computational system software was used. A nonlinear relation was chosen between the parameters ($C_i$, pH, $t_o$), as an independent variables, and
(R_e) as the dependent variable. Applying a regression analysis using polymath software introduced the following relation:

\[ R_e = A * C_i^B + C * pH^D + E * t_o^F \]  

(2)

By running 64 iterations the constants (A, B, C, D, E, F) fixed at the values shown in Table 3.

| Constant | A            | B           | C            | D            | E            | F            |
|----------|--------------|-------------|--------------|--------------|--------------|--------------|
| Value    | -66.91668    | 0.1715173   | -0.0023052   | 4.799459     | 124.6206     | 0.0666287    |

The relationship between calculated removal efficiency (R_e calc) and experimental removal efficiency (R_e exp) were shown in figure 5.

![Figure 5. Relation between experimental and calculated removal efficiency (R_e) as it was produced by polymath software](image_url)

Applying statistical analysis for the introduced model using polymath software yield the results shown in Table 4. which is shows that the coefficient of determination (R^2) that measure how well the model defines the experimental data was 0.969087 and that is indicated the good performance of the model. Root mean square deviation (Rmsd) that typically vary from zero to infinity was very close to zero, while Variance (σ^2) was equal to 17.00216 and that is indicates a good distribution of the data about its mean value.

| Parameter          | Determination coefficient (R^2) | Root mean square deviation (Rmsd) | Variance (σ^2) |
|--------------------|---------------------------------|----------------------------------|----------------|
| Value              | 0.969087                        | 0.8381936                        | 17.00216       |
5. Conclusions.
The study shows that IOCS was an effective adsorbent media for removal of Cadmium ions from polluted water. The efficiency of pollutant removal reaches as high as 97%, under specific operation conditions, the optimal pH operation value was found to be equal 4, while increasing the initial concentration of the cadmium ions in the polluted solution would increase the operation time required for optimal removal. The formula produced from the application of mathematical modelling will be very helpful to specify the best combination of operating conditions in order to reaches targeted removal value.

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