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Cadmium removal from industrial sewage by using Bentonite and Kaolinite absorbent gravels

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Abstract

Many types of water pollutants have been identified and categorized. Heavy metals is one of the most important and hazardous ones. Among all heavy metals, cadmium has a significant effect on all living organisms. Cadmium can be dissolved in water and be absorbed by Plants and then concentrates and moves up the food chain. Which causes toxication in Plants and causing Cancer and numerous other illnesses in humans and other living beings. Using surface absorption is proved to be a suitable method for removing heavy metals from industrial sewages. In this study, Bentonite and Kaolinite were used as surface absorption agents and White Cement was used as a binding agent to keep particles in a firm gravel shape. When poured into the current of sewage, surface absorbing gravels can remove Cadmium ions from sewage. Performance affecting factors such as optimum mass ratio between absorbent agent and binder agent, an optimum mass ratio between Bentonite and Kaolinite, gravels diameter, primary concentration of Cadmium, contact duration and sewage pH was separately examined and optimized by measuring post contact concentration of Cadmium of the samples. Results showed that gravels with absorbent: binder ratio of 3:1, absorbent mass made out of 80% bentonite and 20% kaolinite, when broken to a diameter of 4.75mm < D <6.35mm can refine sewage with 250ppm primary concentration of Cadmium and pH of 7.5 up to 99.97% in 5 hours contact duration.

Keywords: *Cadmium, Removal, Refinement, Bentonite, Kaolinite, Sewage, Industrial Sewage*

Introduction

Cadmium like other heavy metals has a lot of usage like plating, photo development, paint manufacturing, glass manufacturing, battery charging electrodes and light fiber production (Lide, 2000). Cadmium can be dissolved in water and be absorbed by plants then concentrate and move up the food chain (Appel and Ma, 2002; Mahmoud et al., 2015; Shukla et al., 2008; Kumar et al., 2008), causing toxication in plants and lung fibroses, ingestion problems, heart problems, kidney failure and a vast class of cancers in humans and animals (Darivasi et al., 2015; Nazari et al., 2015). Fortunately, the chance of Water being naturally contaminated with Cadmium is quite low and the usual reasons of cadmium contamination are human actions like pouring industrial, agricultural and mineral sewages into Water resources. There are a number of methods for removing dissolved cadmium such as chemical sedimentation, ion replacement, surface absorption, reverse osmosis and electric removal and each method had its own advantages and disadvantages (Masoumi et al., 2020). Previous studies showed that surface absorption is a proper method with high performance to refine such contaminations and factors like surface area, primary concentration, contact duration, pH and absorbent composition all have effect on refinement performance. Because heavy metals are dangerous even in very low dosages and removal of heavy metals from water is challen-

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ging, expensive, sophisticated and expensive methods are not economically convenient, using available material is a very efficient substitute (Barakat, 2011; Asrari and Bazrafken, 2019) and since Cadmium contamination in Water also leads to soil contamination, and both significantly increase the risk of Cadmium consumption by humans and causing illnesses; introducing a cheap and easy method, for that matter is urgent.(Asrari and Bazrafken, 2019; Asrari and Nejabat, 2021; Asrari et al, 2020). Studies of Abdel Halim and co showed the reactions which can remove chrome and Cadmium ions from water are very similar and methods used to remove chrome can also be used to remove Cadmium; sophomore, studies of Asrari and Bazrafkan (2019) and Asrari and Narimani (2020) showed that Bentonite and Kaolinite are significantly efficient absorbents to remove chrome ions from Water. After evaluating each method and identifying disadvantages, using gravels made of absorbents to remove Cadmium ions from Water is to be studied (Asrari and Bazrafkan, 2019; Asrari et al, 2020)

The main goal to this study is to design an efficient, flexible and cheap method to remove heavy metals from industrial sewage which can be used to reduce risk of heavy metal contamination by industrial sewage.

Materials and Methods

Materials used for this study are:

White Cement; Super active micronized Bentonite; Kaolinite; Cadmium Nitrate crystals; Nitric acid with 65% purity; Potassium hydroxide; Distilled Water.

Devices used for this study are:

PG990 atomic absorption spectrophotometer made in UK for Cadmium concentration measurement; PHS-3F pH indicator; ED224S scale with 0.0001 g precision; MAHAK scale model 9800 with 2 g precision; volumetric flasks for liquification and dilution.

The method which the experiments were carried out was to make a mixture of absorbents, cement and water then let the grout turn rock hard and afterwards break the stone into gravels.

Then a synthetic swage using distilled water and cadmium nitrate Cd $(NO_3)_2$ was made and the primary concentration of cadmium in the liquid was measured by the molecular weight calculation. Gravels were poured into a reaction chamber into cadmium containing synthetic sewage with specified concentration of Cadmium, after passing the intended contact duration, secondary concentration of Cadmium still remaining in the water was measured with atomic absorption spectrophotometer that was calibrated according to PG990 atomic absorption spectrophotometer guidebook.

Then, the percentage of removal was calculated. After each experiment, affecting factors were optimized one by one.

Results and Discussion

Bentonite and Kaolinite have clay soil texture and cannot form a strong bind among their particles. Therefore, a binding agent like cement has to be added to the mixture so it can be shaped like gravels after drying. Since compression strength of the gravels is not needed to be specific, compression strength and erosion resistance of the gravels were evaluated relatively via visual observation (table 1). Because the goal for the gravels here is to have the most amount of absorbent for better removal percentage, sample 4 is chosen as the optimum absorbent: Cement ratio and gravels will be made with such as composition in further experiments.

Table 1. *Comparison of hardness and abrasion resistance according to the ratio of cement to bentonite*

Sample number	1	2	3	4	5	6
Absorbent: binder	1:1	1 :1.5	2:1	3:1	4:1	5:1
Observed compression strength after drying	Very hard	Very hard	Hard	Hard	Relatively soft	Soft
Observed erosion resistance after drying	Highly resistant	Highly resistant	Moderately resistant	Moderately resistant	Relatively low resistant	Lowly resistant

Effect of gravels diameter on cadmium removal

After the grout with the optimum absorbent: binder ratio has been made and dried out; the stone needs to be shattered into gravels in different sizes so that the performance of each size can be examined. Size categorizations were as in the table 2.

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Table 2. *Classification of gravels based on their diameter*

Sample number	**1**	**2**	**3**	**4**	**5**
Diameter (mm)	16 < D < 19	16 < D <12.7	12.7< D < 6.35	6.35< D < 4.75	D < 4.75

Afterwards, the gravels were separately poured into a synthetic sewage with 100 ppm of dissolved cadmium, pH:7.5 with 2.5-hours contact duration, then the sewage was strained and passed through a paper filter, after that the remaining cadmium concentration was measured and shown on the table 3. This experiment showed that the optimum diameter of gravels is 4.75mm < D < 6.35mm, which will be used for further experiments (Fig1).

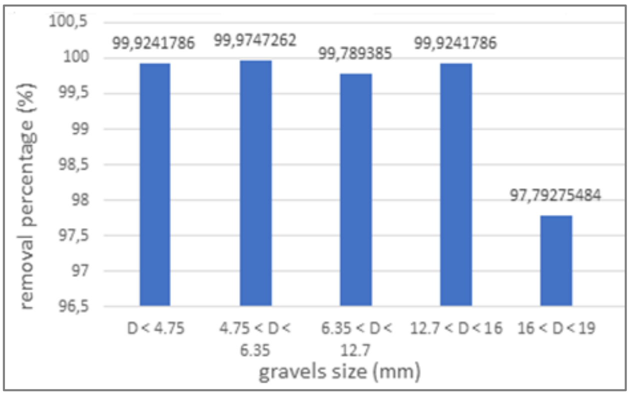

Figure 1. *The effect of aggregate size on removal percentage*

Table 3. *Effect of changing the size of aggregates on removal percentage (pH:7.5 and 150 minutes contact duration)*

Sample number	1	2	3	4	5
Diameter (mm)	16 < D < 19	16 < D <12.7	12.7< D <6.35	6.35<D < 4.75	D < 4.75
Primary Cadmium concentration (ppm)	100	100	100	100	100
Secondary Cadmium concentration (ppm)	0.009	0.003	0.025	0.009	0.262
Removal percentage (%)	99.79	99.92	99.78	99.97	99.92

Effect of primary concentration on Cadmium removal

One of the main affecting factors on removal percentage is the primary concentration of Cadmium in the sewage. While gravels composition and size is already determined, the effect of differentiating primary concentration of cadmium is to be experimented. Gravels were poured into separate synthetic sewages with Cadmium concentration of 25 ppm to 1000 ppm with pH:7.5 and contact duration of 2.5 hours. Then the sewage was strained and passed through a paper filter, then the remaining cadmium concentration was measured and shown on the table 4. Figure2, showed that the highest correlation between increasing of primary concentration and removal percentage is below 250 ppm. Afterwards the absorption terminals become saturated, and removal percentage will be reduced. Therefore, 250 ppm concentration of Cadmium is chosen as the optimum primary concentration to achieve the highest removal percentage.

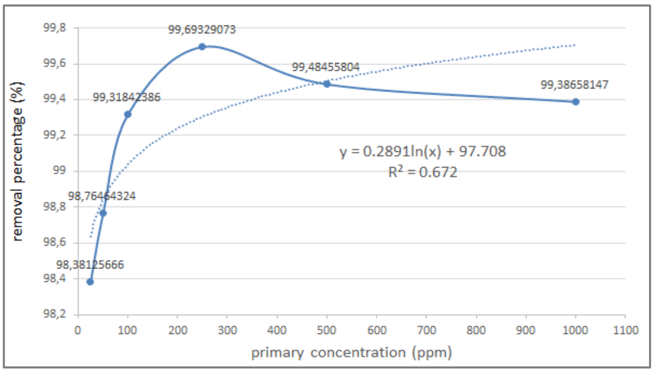

Figure 2. *The effect of initial concentration on removal percentage*

Table 4. *Effect of initial concentration on removal percentage (pH:7.5 and 150 minutes contact duration)*

Sample number	1	2	3	4	5	6
Primary concentration (ppm)	1000	500	250	100	50	25
Secondary concentration (ppm)	6.13	2.57	0.076	0.69	0.061	0.4
Removal percentage (%)	99.38	99.48	99.69	99.31	98.76	98.38

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Effect of secondary absorbent on Cadmium removal

Bentonite and Kaolinite both showed similar performance in previous studies, but the combination of these two absorbents was not tested. Therefore, while keeping the mass ration of 3:1 between absorbent and binder, different ratios between Bentonite and Kaolinite were mixed and turned into gravels. Gravels were poured into separate reaction chambers into sewage with 250ppm of Cadmium and pH=7.5 and were taken out after contact duration of 5 hours was passed. Then the sewage was strained and passed through a paper filter, then the remaining Cadmium concentration was measured and shown on the table 7.

Bentonite particle's average diameter is 38µm while Kaolinite particle's average diameter is 25µm, so as the amount of a Kaolinite was increased to 20% in the mixture, the average surface area's absorption terminal was increased and this improved removal but once the amount of Kaolinite exceeded 50% in the mixture, gravels surface turned smoother and fewer absorption terminals were available on gravel's surface which caused a decrease in removal. In Figure 5 can be seen, the optimum ratio between Bentonite and Kaolinite belongs to sample 2 with the ration of 80:20.

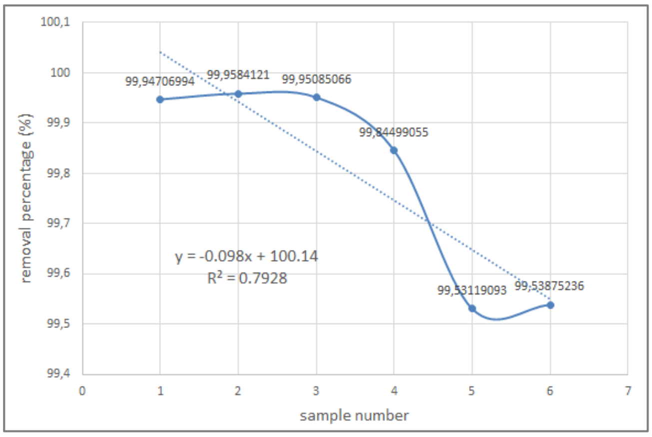

Figure 5. *Effect of adding secondary adsorbent on removal percentage*

Table 7. *The effect of adding a secondary adsorbent on the removal percentage (pH:7.5 and contact duration of 300 minutes)*

Sample number	1	2	3	4	5	6
Mass of Bentonite in the mixture (%)	100	80	60	40	20	0
Mass of Kaolinite in the mixture (%)	0	20	40	60	80	100
Primary concentration (ppm)	250	250	250	250	250	250
Secondary concentration (ppm)	0.13	0.10	0.12	0.38	1.17	1.15
Removal percentage (%)	99.94	99.95	99.95	99.84	99.53	99.53

The optimum amount for each variable.

The experiments showed the optimum amount for each variable is as the table 8.

Table 8. *The optimum amount for each variable*

Variable	Optimum amount
Absorbent: binder ratio	3:1
Bentonite: Kaolinite ratio	80:20
Gravels size	(4.75mm < D < 6.35mm)
Primary Cadmium concentration	250ppm
Contact duration	5 hours
pH of sewage	7.5

Cadmium removal from real sewage.

So far, all the experiments were carried out in a laboratory with synthetic sewage, so the performance of the gravels had to be tested in real sewage; a sample of sludge from the bottom of a lagoon at the stream leaving Shiraz industrial park and going to Shiraz sewer treatment facility was taken.

The sludge was placed into a beaker with some distilled water and placed in a mixer for 10 minutes, then Cadmium concentration in the beaker was measured and noted as 58ppm and the pH of the sewer was measured 8.5. Then gravels with optimum composition and size were poured into the reaction chamber into the sewage and left for 2 and 5 hours.

After that the sewage was strained and passed through a paper filter, then the remaining Cadmium concentrations was measured and shown on the table 9. The results from actual situation are closely similar with the results from laboratory situations, which indicates validity of the synthetic sewage simulation to real sewage and the performance of gravels in reallity.

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Table 9. *Real situation removal*

Real sample number	1	2
Primary concentration (ppm)	58	58
Contact duration (hours)	2	5
Secondary concentration (ppm)	0.23	0.01
Removal (%)	99.61	99.97

Conclusions

Gravels made with 3:1 ratio between absorbent and binder showed enough compressive strength and erosive resistance and having the mass ratio of 80:20 between Bentonite and Kaolinite enhanced removal. Although covering the surface of a concrete shape as (Asrari and Bazrafkan, 2019) did create an absorbing surface to remove heavy metals from water but this method offers a limited contact surface and has limited absorption life span while pouring absorbent gravels into the stream provides a tremendous contact surface and has a way higher life span as the performance of the gravels enhanced from 97.79% to 99.97% when gravels diameter was reduced from (16mm<D<19mm) to (4.75mm<D<6.35mm). As for the effect of primary concentration, study of (Asrari and Bazrafkan, 2019) showed that removal is correlated to concentration increase for concentrations lower than 250 ppm and will slake at higher concentrations due to saturation of absorption terminals, which was also observed to be true in this study. The study of (Asrari and Bazrafkan, 2019) showed that removal and pH are corelated in removing chrome ions and here It was also seen that removal is higher in acidic situations and increased from 99.95% in pH=10 to 99.99% in pH=2, which shows acceptable performance in both acidic and alkaline enlivenments. Contact duration is a key factor in removal as it was studied by (Asrari et al., 2020) which showed that removal percentage peaks at 8 hours but in this study, removal had the sheerest slope in the first 2 hours that reached 99.81% and came to peak at 5 hours period to 99.94%. Finally, testing laboratory circumstances optimized parameters in real industrial sewage and observing similar removal of 99.97% insure validity of the experiments and test results.

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