

Using selective sequential extraction techniques to evaluate tendency of soil fractions in Cd removal by Fe₃O₄ nanoparticles in continuous flow system

M. Mohammadiun^{1*}, B. Dahrazma¹, S.F. Saghravani¹ and A. Khodadadi Darban²

1. Faculty of Civil Engineering, Shahrood University of Technology, Shahrood, Iran

2. Department of Mining Engineering, Faculty of Engineering & Technology, Tarbiat Modares University, Tehran, Iran

Received 10 July 2017; received in revised form 22 December 2017; accepted 23 December 2017

*Corresponding author: malihemohamadiun@yahoo.com (M. Mohammadiun).

Abstract

Use of nanotechnology has proven to be a promising approach toward remediation of all phases of environment. The aim of this work is to investigate the effects of different parameters on using iron III oxide nanoparticles in a continuous flow configuration for the removal of Cd²⁺ ions from contaminated soils. Also selective sequential extraction tests are carried out to evaluate the nanoparticle tendency to remove cadmium from different fractions of soils. In order to achieve this goal, a specific flow rate of a nanoparticle solution was passed through a soil sample in a column with 3 cm diameter and 4 cm height. Up to 100% of cadmium removal was achieved by providing a nano-fluid concentration of 500 ppm, pH of 6.5, treatment duration of 24 hours, and flow rate of 0.5 mL/min. Evaluation of the results obtained showed that the tendency of the iron oxide nanoparticles to remove cadmium from different fractions of contaminated soil was in the order of exchangeable > carbonates > oxides and hydroxides > organic matter > residual. The results obtained from this work can be used to develop an appropriate remediation protocol for contaminated soils.

Keywords: *Selective Sequential Extraction, Iron(III) Oxide Nanoparticles, Continuous Flow Configuration, Cd²⁺ Removal.*

1. Introduction

Contamination of soils with heavy metals is a serious environmental problem throughout the world as it could threaten the ecosystems and human health [1]. Cadmium is considered as an extremely significant pollutant due to its high transfer rate from soil to plants and its strong bio-toxicity [2]. As many studies show, soil is an important source for human intake of cadmium [3, 4]; it is also a potentially toxic heavy metal, which can accumulate in human organs that may cause significant human health problems, specifically as lung, kidney, and liver deficiencies [5].

It is highly desirable to apply suitable remedial methods that can reduce the risk of heavy metal contamination in soils. Development of new low-cost, efficient, and environmentally friendly remediation technologies is one the goals of recent research activities in environmental science and technology [6, 7].

Soil washing is a technology that extracts heavy metals into a solution by either desorption or solubilization [8]. The effectiveness of washing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils. Acids, surfactants, electrolytes, and chelating agents have been widely used as the extracting solutions [9]. Recently, engineered nano-materials have been designed for the purposes of heavy metal removal, extraction, and remediation from aqueous solutions and soils [10]. Compared to the most commonly used traditional techniques suggested for soil remediation, unique physico-chemical properties and availability of different forms of nano-materials make them notable candidates for removal of organic and inorganic pollutants from the environment [11].

A survey of 155 articles (2004–2014) provides evidence that work is being carried out to remove heavy metals from wastewaters [12, 13] using inorganic nano-adsorbents. According to these studies, ZnO nanoplates show a complete removal of Cu(II) in aqueous solutions. Hierarchical structures such as flower-like shapes of Fe₂O₃ and titanium have been engineered to enhance the properties of metal oxides for heavy metal removal, and generally, the Fe₃O₄ nano-materials have been shown to have the appropriate ability for heavy metal removal from aqueous solutions [13]. Recently, nano-Fe₃O₄ has been successfully used to rapidly remove Cu, Ni, and Pb from aqueous solutions [14]. Iron(III) oxide nanoparticles are a non-toxic and environmentally friendly material, and in addition, a magnetic nano-scale iron particle (NIP).

Considering the efficiency of nano-scale iron particles in removal of heavy metals from aqueous solutions (i.e. water and wastewater), along with a lack of comprehensive studies on heavy metal removal from soils, this research work focuses on the use of Fe₃O₄ nanoparticles in the removal of cadmium from contaminated soils.

Toxic metals exist in various chemical forms and with different characteristics. The solubility and potential bio-availability of metals and their distribution in different fractions of soil are strongly related to their chemical speciation. [15]. Reactivity of the species or binding forms of heavy metals in solids could be assessed by various extraction media. One of the most popular methods of operationally defined speciation is selective sequential extraction (SSE). The first SSE procedure was introduced by Crawford and McLaren in 1973. Accordingly, trace elements in several fractions of the natural soil including exchangeable, residual, organic, and oxides were determined [16]. The BCR sequential extraction procedure devised by Community Bureau of Reference is another SSE procedure that is widely applied to soil and sediment samples [17]. Based on the BCR method, heavy metals could be extracted from three fractions of soils, namely exchangeable, reducible, and oxidizable. One of the best-known sequential extraction schemes by which heavy metals could be extracted from five fractions of soils and sediments, namely exchangeable, carbonate, iron and manganese

oxides, organic matter, and residual was proposed by Tessier in 1979 [18]. This procedure was adapted and improved upon by Yong in 1993 [19]. The Yong’s method is considered as the most complete SSE procedure, and has been implemented in many studies [20-22]. According to this procedure, heavy metals could be extracted from six fractions of soils and sediments, namely soluble, exchangeable, carbonates, oxides and hydroxides, organic matter, and residual.

Considering the efficiency of nano-scale iron particles in heavy metal removal from aqueous solutions (i.e. water and wastewater), in this work, iron(III) oxide nanoparticles were applied for the removal of Cd from contaminated soil. In addition, to evaluate the binding mechanisms, selective sequential extraction (SSE) using Yong’s method was employed, while the test was performed in a continuous flow configuration for a better adjustment to real conditions in contaminated sites. Thus the binding mechanism in this work was determined to evaluate the distribution of species in the solid phase.

2. Material and method

2.1. Nanoparticle solution

Nanoiron oxide (III) with a 99.5% purity and an average particle size of 44.5 nm was obtained from Pasteur Institute in Iran. It was stabilized by polyacrylic acid (PAA) (Sigma Aldrich Co.) based on the method proposed by Golzar et al. [23]. Accordingly, a specified value of the nanoparticles in distilled water of one-fifth of the final solution volume was placed in an ultrasonic bath (40 KHz, 50 W) for 30 min. In another flask, PAA (the weight ratio of PAA to the nanoparticles was 2:1) was mixed with four-fifth of the final volume of distilled water at a speed of 500 rpm for one h. These two solutions were mixed together and placed in the ultrasonic bath for one h.

2.2. Synthetic contaminated soil

The soil sample was prepared from clean standard materials to eliminate any interaction between pollutants that might appear in the natural soils. An appropriate composition was selected after several preliminary tests. This composition and the related weight percentages are presented in Table 1.

Table 1. Composition and weight percentages of soil structure.

Sand	Silt	Kaoline	Red clay	Organic matter	CaCO ₃	CaO
8%	40%	10%	20%	10%	10%	2%

The soil sample prepared with the above composition was mixed with 500 ppm of a cadmium solution, prepared from cadmium nitrate (Merck Co.). The ratio of the volume of the solution (mL) to the weight of the soil (g) was 20:1. The container was agitated for 48 h in a shaking incubator (Wise Cube 20-R) at room temperature (80 rpm). Then the supernatant solution was separated from the soil part using a centrifuge (3500 rpm for 20 min). In the last step, the soil was washed with distilled water to remove all the unabsorbed contaminants.

The prepared contaminated soil was dried at room temperature, and the sieve analysis was performed. A noticeable amount of the soil could pass from sieve No. 400 (opening size: 0.037 mm). Thus this part of the soil was analyzed using a Laser Particle Sizer ANALLISETTE 22 (FRITISH Co.). The contaminated soil composition was also tested by the XRD test.

2.3. Total Cd content of contaminated soil

In order to determine the total cadmium content, the soil was digested by the standard method recommended by Environment Canada (1990) as follows:

1. 1.00 g of the sediment was placed in a 1-L beaker.
2. 100 mL of 16 N nitric acid was added to the beaker over a minimum period of 2 min.
3. 40 mL of H₂O₂ (30%) was added to the beaker. The beaker was left for 5 min for the reaction to occur.
4. The beaker was placed on a hot plate (Fisher Stirring Hotplate) till boiling. Then it was removed from the heat and cooled to room temperature.
5. A solution of 1000 mL aqua regia was made through the following process:
 - 200 mL of concentrated nitric acid was added to a 1000-mL flask.
 - 500 mL of distilled water was added to the flask.
 - 50 mL of concentrated hydrochloric acid was added to the flask.
 - The flask was filled with distilled water to the 1000-mL mark.
6. 200 mL of aqua regia was added to the beaker.
7. The beaker was filled with distilled water to the 500-mL level.

The supernatant solution was analyzed by a UV spectrophotometer according to the procedure mentioned on Section 2.6. The total cadmium content of the contaminated soil was measured at 9500 mg per Kg of soil.

2.4. Soil washing procedure in continuous flow configuration

In order to evaluate the *in situ* approach for remediation of contaminated soils, the soil samples were washed with a nano-fluid in a continuous flow configuration. For this purpose, glass cylindrical cells (column) of 3-cm diameter and 4-cm height were used to wash 5 g of soil samples. Both the inlet and outlet tubings had the same diameter. A Masterflex peristaltic pump model 7518-00 was used to provide the dynamic head for the flow (Figure 1).

The nano-fluid was placed in a tank at room temperature. As the first try, the ratio of soil mass (g) to nano-fluid volume (mL) was adjusted to 1:150 (this ratio has been introduced as the optimum ratio in the batch test [24]). Ensuring the exhausting of air from the column, the flow was pumped and entered the column from its lowest level. The column was filled from bottom to top by Teflon rings, punctuated Teflon disc (as a filter), filter paper, 5 g soil, filter paper, punctuated Teflon disc, and Teflon rings. The flow rate was adjusted with a valve in the downstream of the column. The effluent was collected and the Cd content was then determined. The effects of a variety of parameters including the duration of treatment, multiple washing, and flow rate were optimized in the continuous flow configuration.

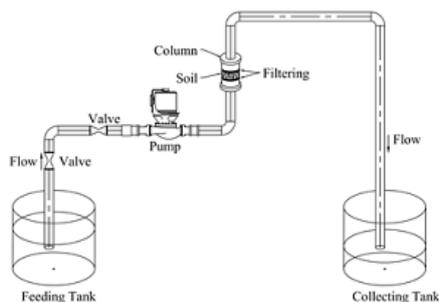


Figure 1. Schematic view of continuous flow configuration.

2.5. Selective sequential extraction (SSE) technique

The SSE procedure, proposed by Yong et al. (1993) [19], was adapted in this research work. After each step of the procedure, the solutions were completely separated from the solid phase using a centrifuge (3500 rpm for 20 min), followed by filtration. Moreover, the Cd concentration was determined by the UV spectrophotometer based on the procedure described in Section 2.6. Then the samples (soil that remained from the previous step) were washed with distilled water to be prepared for the next step. Subsequently, 1.5 g of soil (before and after the washing procedure) was taken, and SSE tests were performed according to the following procedure:

1. To determine the soluble fraction, the soil was washed by the nanoparticle solution and distilled water (as the control).
2. The exchangeable fraction was extracted after washing the soil at room temperature for 1 h with 8 mL of 1 M MgCl₂ (pH 7).
3. The soil obtained from the previous step was washed at room temperature with 8 mL of 1 M NaOAc¹ adjusted to pH 5 with acetic acid for 5 h to extract the carbonate phase.
4. The soil from (3) was washed with 20 mL of 0.04 M NH₂OH.HCl in 25% (v/v) acetic acid (pH 2.5) at 96 °C for 6 h to extract the oxide and hydroxide phase of the soil.
5. This soil (4) was washed with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ (pH 2) for 2 h at 85 °C, followed by 3 mL of 30% H₂O₂ (pH 2) at 85 °C for 3 h, and then 5 mL of 3.2 M NH₄OAcI in 20% (v/v) HNO₃ diluted to 20 mL at room temperature for 30 min, and the organic matter was extracted.
6. To extract the residual fraction, the soil from (5) was digested at 90 °C with 25 mL of diluted aqua regia (50 mL HCl, 200 mL HNO₃, and 750 mL water) for 3 h.

2.6. Spectrophotometric determination of Cadmium concentration

A UV spectrophotometer (CECIL CE 7000 Series) was used for the spectrophotometric determination of the cadmium concentration in the solution. In the present work, the APDC complex in Tween 80 media was used as a colorant agent. The detection limit for a good linearity was 0.05 µg mL⁻¹, and the maximum wavelength of the Cd²⁺ complex appeared at 324 nm [25].

A 1.0% (w/v) Tween 80 solution was prepared by dissolving 1.0 g of Tween 80 in 100 mL of distilled water in a volumetric flask with stirring. A phosphate buffer solution (pH = 7.0) was prepared by appropriately mixing 0.1 M KH₂PO₄ and 0.1 M NaOH (500 mL of 0.1 M KH₂PO₄ and 20 mL of 0.1 M NaOH were mixed, and then the solution was filled up to 1 L with distilled water). Since APDC slowly decomposes in aqueous solution, the 0.1% APDC solution was made whenever it was necessarily required [25]. Standard Cd²⁺ solutions were prepared in the range of 0.5-2.5 mg L⁻¹ of cadmium using a stock solution of 1000 mg L⁻¹. Also the latter was made of cadmium prepared by Cd(NO₃)₂ in 10-mL volumetric flasks. 0.5 mL of APDC and 1 mL of Tween 80 were added to each standard solution of Cd²⁺ in 1 mL samples. The solutions were then filled up to 10 mL with the phosphate buffer solution. A blank solution was also prepared by the above procedure without Cd solution. After 20 minutes, the Cd concentration could be determined by a UV-visible spectrophotometer [25].

2.7. Quality and control

All the materials used in this work were prepared from clean standard materials. Additionally, the verified and standard methods in several parts of experiments were as follow:

1. Nano-iron oxide (III) was stabilized by PAA based on the method proposed by Golzar et al. [23].
2. The soil was digested by the standard method recommended by Environment Canada (1990).
3. Selective sequential extraction was performed using the Yong method.
4. Spectrophotometric determination of the cadmium concentration in solution was done by the method proposed by Lee and Choi [25].
5. The test was repeated for several times (at least three times) to ensure the quality of the results.

3. Results and discussion

3.1. Size distribution of nanoparticles in solution

The results of the size distribution test for the stabilized nanoparticle solution in the optimum conditions is presented in Figure 2. The results of size distribution by number show that the peak number was attributed to the nanoparticles with the size of 216.7 nm.

¹ - Ac denotes acetate.

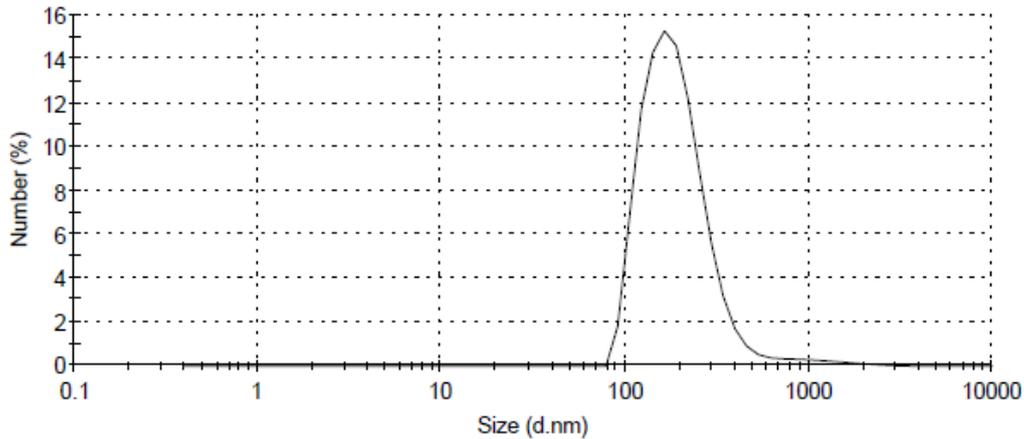


Figure 2. Size distribution of nanoparticles in solution.

3.2. Synthetic contaminated soil properties

The result of the sieve analysis is shown in Figure 3. Regarding this test, more than 54% of soil could pass from sieve No. 400 (opening size: 0.037 mm). Thus this part of the soil was analyzed by the Laser Particle Sizer ANALLISETE 22 (FRITISH Co.). The result obtained is presented in Figure 4.

According to the results of sieve analyses, based on the AASHTO soil classification, the sample contained 29% sand and 17% silt. On the other hand, according to the laser particle analyses, the fine part of soil consisted of 41% silt and 13% clay. Therefore, the soil consisted of 29% sand, 58% silt, and 13% clay.

The contaminated soil composition was also evaluated by the XRD test, and the result obtained was presented in Figure 5. According to the result, the main mineral composition of this artificial contaminated soil with maximum weight percent was 37.6% “Kutnohorite”, which is a member of the dolomite group and 31.2% quartz. The amounts of pH and EC of the contaminated soil were determined using the EPA SW-846 method 9045 (1:1 of soil to water) and EPA, 2006 (1:5 soil to water), respectively. The soil pH could be considered as the basic amount (pH 7.8), and EC was measured at 224 μ S/cm.

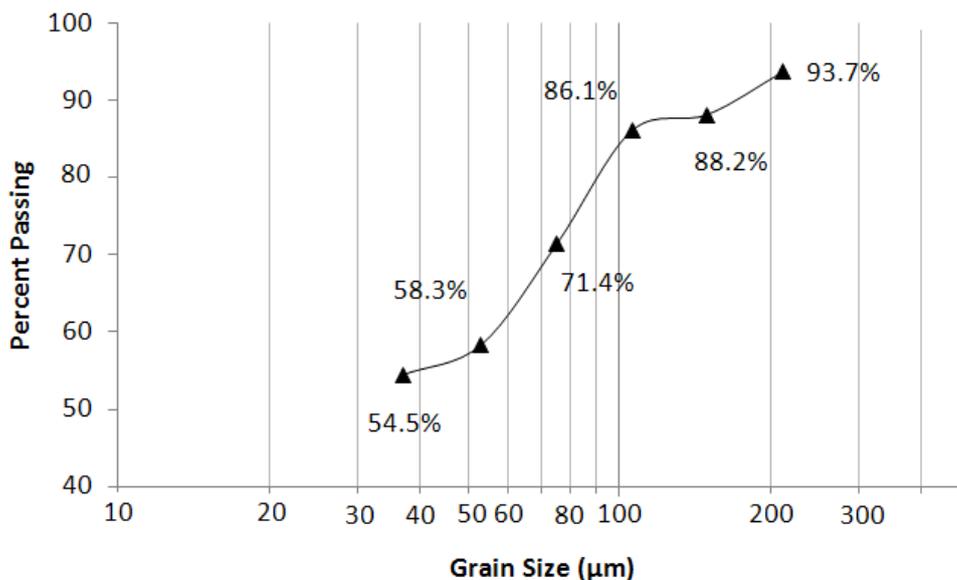


Figure 3. Size distribution of contaminated soil by sieving.

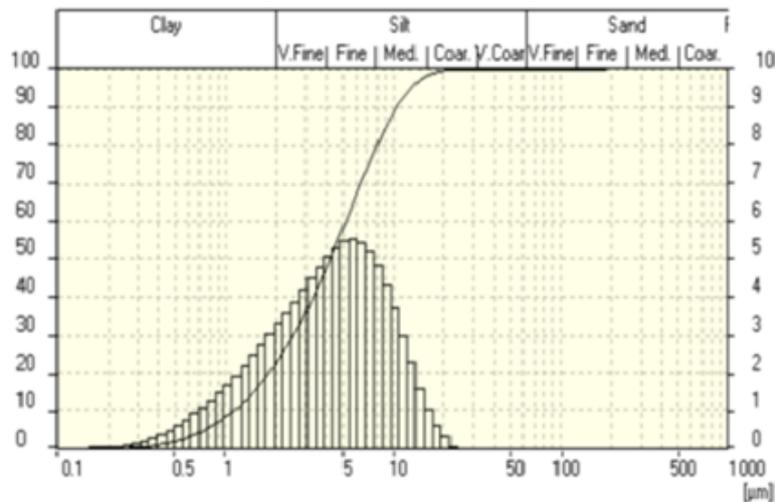


Figure 4. Results of laser particle sizing of soil.

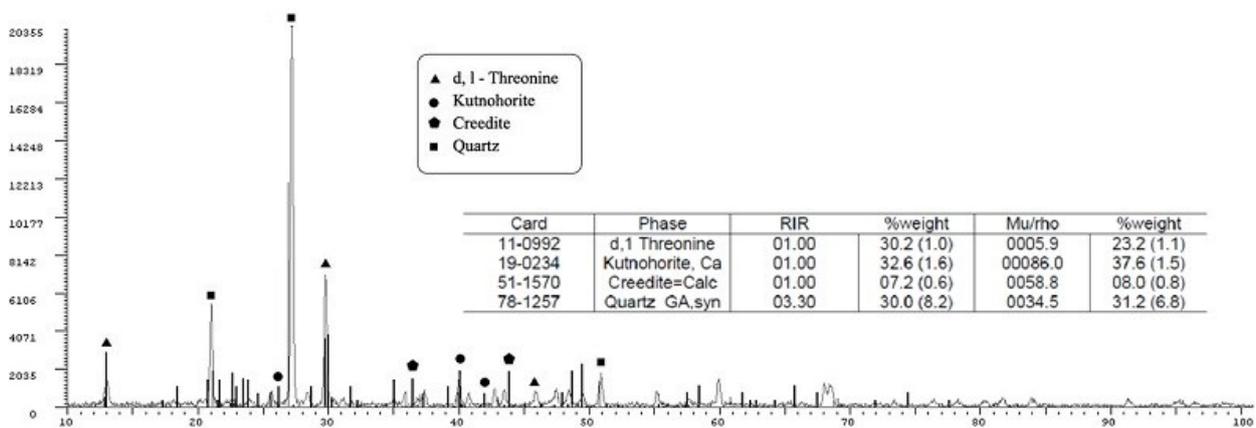


Figure 5. XRD test for contaminated soil.

3.3. Cd content in contaminated soil

The Cd content, determined by the method mentioned in Section 2.6, was 10000 mg in 1 Kg of the soil.

3.4. Study of nano-fluid concentration

5 g of contaminated soil was washed in the column with the blank (distilled water) and the nano-fluid of different concentrations including 100, 300, 500, and 1000 ppm. Other parameters were constant (flow rate = 2.5 mL/min, pH = 8.5, ratio of soil mass (g) to nano-fluid volume (mL) = 1:150). The results obtained are shown in Figure 6. The results of removal by distilled water are not

shown since cadmium was detected in the final solution.

The results obtained showed that the removal rate directly increased with increase in the concentration of the nano-fluid up to 85%, which occurred at 1000 ppm. As shown in Figure 6, the Cd²⁺ sorption rate has a direct relationship with the nano-fluid concentration. At higher concentrations, a higher amount of nanoparticles existed, so more sorption sites were found. Since the nanoparticles were coated with PAA, the higher concentrations are not practical due to the intense increase in the viscosity of the solution. Thus the concentration of 500 ppm with a removal rate of 80% was selected.

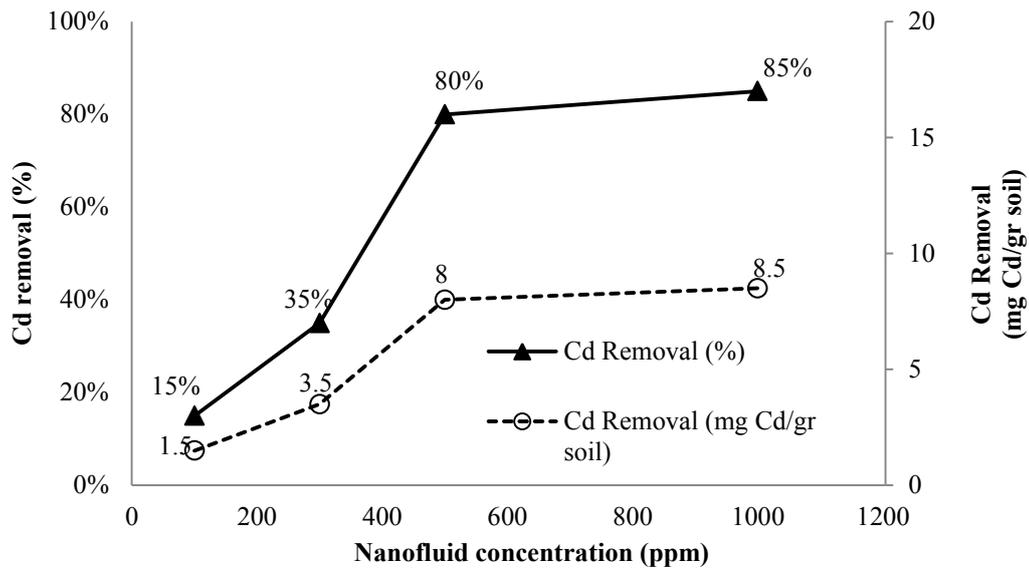


Figure 6. Removal of Cd by nano-fluid at different nano-fluid concentrations (flow rate = 2.5 mL/min, pH = 8.5, ratio of soil mass (g) to nano-fluid volume (mL) = 1:150).

3.5. Study of pH

In order to obtain the optimized amount of pH, 5 g of contaminated soil was washed in the column with 750 mL of 500 ppm nano-fluid at pH values varying from 5 to 10 with a flow rate of 2.5 mL/min. At pH values less than 5 and more than 10, the nano-fluid could not be stabilized; therefore, the range was limited to 5 through 10. The results obtained are shown in Figure 7.

According to the results obtained, the maximum Cd removal was recorded at pH = 6 (84%), and it was very similar to pH = 7 (83%). The percentage removal of cadmium at pH = 6.5 was also 84%, so this pH was selected.

Cd removal from the soil using the nano-fluid depends on both the solubility of cadmium and the properties of nanoparticles. According to the solubility curve of cadmium, as the pH increases, its solubility is decreased. Therefore, by reducing the solubility of the ions in the nano-fluid at a higher pH, its separation from the soil is also reduced. The nano-fluid had the most stabilized situation at $\text{pH } 7.9 \pm 0.1$. The optimum pH for cadmium removal from the soil in this work (6.5) can be a result of both factors, the further Cd solubility at a low pH value and creation of a stable colloidal solution at a pH value of about 7.9.

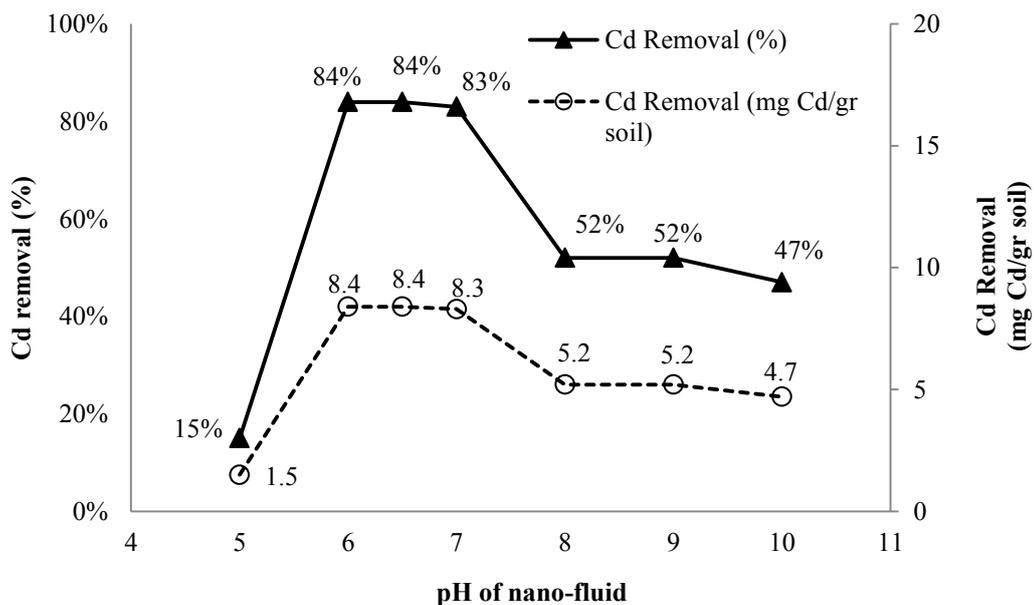


Figure 7. Removal of Cd by nano-fluid at different nano-fluid pH (nano-fluid concentration = 500 ppm, flow rate = 2.5 mL/min, ratio of soil mass (g) to nano-fluid volume (mL) = 1:150).

3.6. Study of flow rate

5 g of contaminated soil was washed in the column with a solution of 500 ppm iron (III) oxide nanoparticles at flow rates of 0.5, 1, 2.5, and 5 mL/min. The test was repeated with distilled water as the control. The other parameters were kept constant (pH = 6.5, ratio of soil mass to nano-fluid volume is equal to 1 (g): 150 (mL)). The results obtained are shown in Figure 8. The results of removal by distilled water are not shown since no removal was detected in this series of tests. As shown in Figure 8, 100% of removal occurred at 0.5 mL/min of flow rate.

The results obtained depict that the Cd removal increases considerably with decrease in the flow rate when the amount of nano-fluid is constant. Indeed, at a lower flow rate, a more desirable contact time for a specific volume of nano-fluid was prepared for desorption of cadmium from the contaminated soil. Similar results in evaluation of adsorption in continuous configurations (the adsorbent was fixed as a column, and the flow rate and other parameters of untreated water were studied) expressed that at higher flow rates, a more contact time, and accordingly, more adsorbent would be required to achieve the determined adsorption [26].

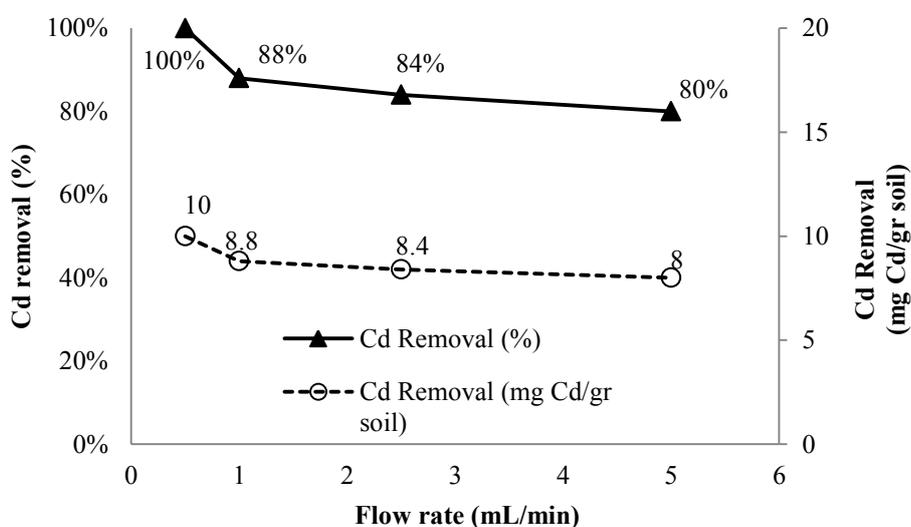


Figure 8. Removal of Cd by nano-fluid at different flow rates (nano-fluid concentration = 500 ppm, pH = 6.5, ratio of soil mass (g) to nano-fluid volume (mL) = 1:150)

3.7. Duration of treatment

To optimize the duration of treatment, 5 g of the soil in a column was washed with 500 ppm of nano-fluid (500 ppm of iron oxide nanoparticles) and a flow rate of 0.5 mL/min at pH = 6.5 for different durations of treatment including 15 and 30 minutes and 1, 5, 12, and 24 hours. The results obtained are shown in Figure 9. 0.5 mL/min was the minimum applicable flow rate in this continuous flow configuration, and it was not possible to achieve lower flow rates.

The results obtained depicted that Cd removal increased considerably with increase in the duration of treatment up to 24 h (from 2% in 15 min to 100% in 1440 min). Thus it was possible to remove the Cd(II) ions completely from the contaminated soil at optimized conditions.

In a continuous flow configuration, the specific amount of nano-fluid contacts with contaminated soil in the specific period of time. Thus with increase in the duration of treatment, more dosage of adsorbent would be available for Cd²⁺

adsorption. The same results were reported by Mohammad by evaluation of the adsorption capacity of a column [26].

Cadmium extraction from contaminated soil by this method is considerably effective in comparison with the previous study's results. The efficiencies of cadmium removal from the soil using acetic acid and EDTA were 70.6% [27] and 87% [28], respectively. Study of Cd extraction from contaminated soil by NZVI as a nano-iron oxide showed a 100% removal rate [29]. Fe₃O₄ nanoparticles, as another important iron oxide nanoparticles, has been used for heavy metal adsorption from aqueous medium, and could remove Cu, Pb, and Cr with the removal rates of 99% [30], 98% [31], and 92% [32], respectively. There is lack of literature for the removal of Cd²⁺ ions from contaminated soil using Fe₃O₄ nanoparticles. The result of the present study illustrated that Cd was completely removed from contaminated soil by the iron(III) oxide nanoparticles.

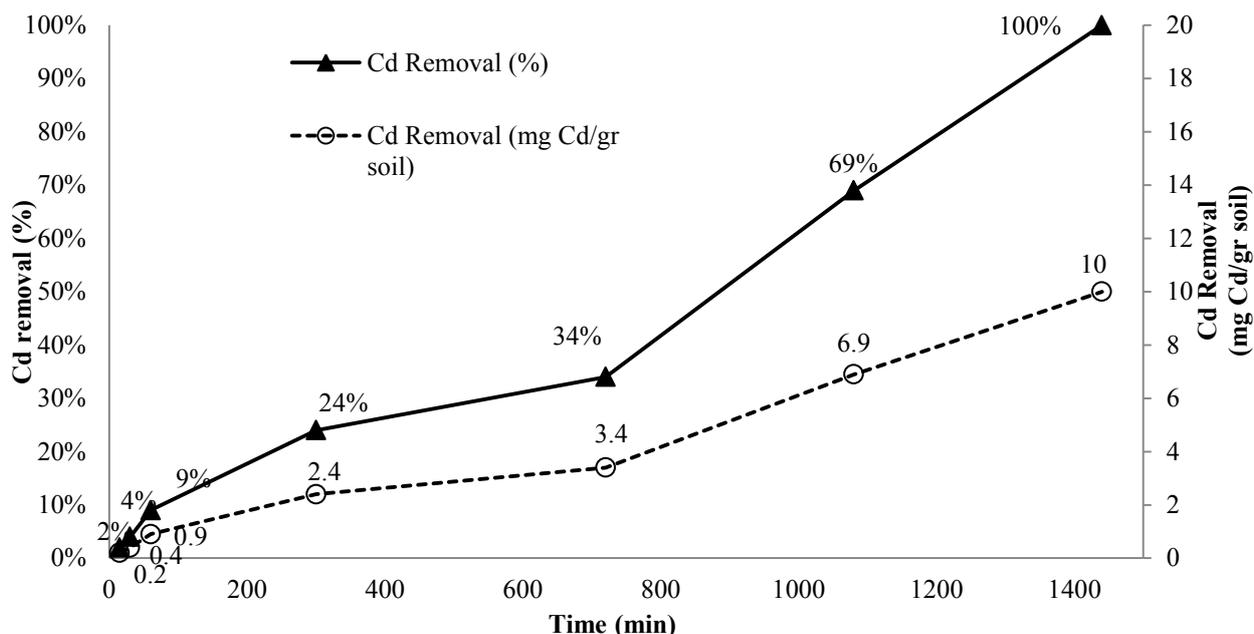


Figure 9. Removal of Cd by nano-fluid at different durations of treatment (concentration = 500 ppm, pH = 6.5, flow rate = 0.5 mL/min).

3.8. SSE tests

Considering the removal rate at optimized conditions, Cd was completely removed from all fractions of soil; thus it was not possible to determine the order of tendency of nanoparticles for removal of Cd²⁺ ions under this condition. Therefore, the test was repeated for a time less than the optimized duration of treatment (18 h).

The results of SSE for control samples indicated that Cd removal did not occur by washing the soil with distilled water. According to the results obtained, the accumulation of Cd in soil fractions was 0.0% in soluble, 4.82% in exchangeable, 54.99% in carbonates, 25.76% in oxides and hydroxides, 1.75% in organic matter, and 12.67% in the residual fraction.

The SSE results for samples that were washed for 18 h in the continuous flow configuration at pH = 6.5 showed that 68.56% of the Cd content was removed from soil by the nano-fluid (soluble fraction).

The order of Cd removal from other fractions of contaminated soil and their related changes

compared to the control samples after 18 h in a continuous flow system are shown in Figure 10.

Removal from the soil fractions using iron oxide nano-fluid in this study occurred as follows:

- Exchangeable: The highest removal (100%) occurred in this fraction, where cadmium was completely removed. The Cd content in this part was reduced from 4.82% to 0%;
- Carbonate: 82.75% of Cd was removed from the carbonate phase, and the Cd content decreased from 54.99% to 9.49%;
- Oxides and hydroxides: Cd removal occurred in this fraction with the mass fraction of 57.99%, and the Cd content changed from 25.76% to 10.82%;
- Organic matter: 48.03% Cd was removed from this fraction of soil. In this phase, the Cd content decreased from 1.75% to 0.91%;
- Residual: Cd was removed from this part of soil with a removal rate of 19.37%. The Cd content in this fraction decreased from 12.67% to 10.22%.

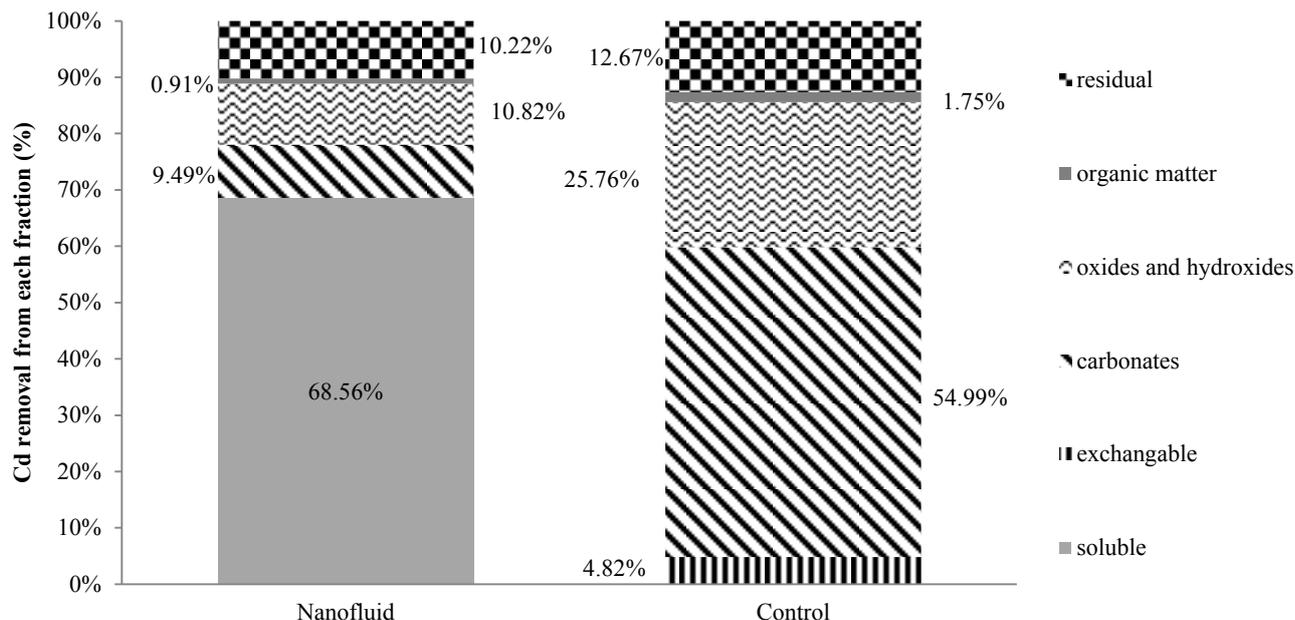


Figure 10. Sequential extraction of Cd in soil washed by iron(III) oxide nanoparticles (concentration = 500 ppm, pH = 6.5, flow rate = 0.5 mL/min, duration of treatment = 18 h).

4. Conclusions

Cadmium removal from contaminated soil in a continuous flow configuration would be affected by several parameters such as the nano-fluid concentration, pH, flow rate, and time. This process was investigated in the present work. According to the findings of this work, nano-Fe₃O₄ stabilized with PAA could remove up to 100% of cadmium (50 mg) from the soil in a column as a continuous flow system at the optimized conditions including nano-fluid concentration = 500 ppm, pH = 6.5, duration of treatment = 24 h, and flow rate = 0.5 mL/min. In this situation, the mass of adsorbent was 0.36 g, so the adsorption capacity was about 139 mg Cd/g adsorbent.

Then the tendency of iron(III) oxide nanoparticles to remove cadmium from each fraction of the soil was studied using the SSE technique. Accordingly, partitioning of cadmium in different fractions of the contaminated soil before washing tests was in the order of carbonates > oxides and hydroxides > residual fraction > exchangeable > organic matter. The tendency of nano-Fe₃O₄ to adsorb cadmium from different fractions of the soil was in the order of exchangeable > carbonate > oxides and hydroxides > organic matter > residual.

An economical assessment shows that this method is slightly more expensive than the traditional methods that have been used for real world projects. However, it was more economical than some other new methods proposed in the recent

research works such as using surfactants. In addition, it would be noticeable that the Fe₃O₄ nanoparticles are magnetic, and it is possible to recover them from the soil. Also these nanoparticles are recognized as harmless particles for the environment. It should also be considered that new technologies to produce nanoparticles are growing fast, and accordingly, their production costs are reduced. Thus considering the high removal rate (100%) of cadmium from contaminated soil and ability to remove contaminate from all fractions of the soil, iron(III) oxide nanoparticles stabilized by polyacrylic acid is strongly recommended to be considered as a washing agent for soil remediation.

References

- [1]. Niinae, M., Nishigaki, K. and Aoki, K. (2008). Removal of lead from contaminated soils with chelating agents. *Mater. Transactions*. 49: 2377-2382.
- [2]. Satarug, S., Garrett, S.H., Sens, M.A. and Sens, D.A. (2010). Cadmium, environmental exposure, and health outcomes. *Environ. Health Perspect.* 118: 182-190.
- [3]. Jarup, L. (2003). Hazards of heavy metal contamination. *Br. Med. Bull.* 68: 167-182.
- [4]. Chen, T., Chang, Q., Clevers, J.G.P.W. and Kooistra, L. (2015). Rapid identification of soil cadmium pollution risk at regional scale based on visible and near-infrared spectroscopy. *Environ. Pollut.* 206: 217-226.

- [5]. Comba, S., Martin, M., Marchisio, D., Sethi, R. and Barberis, E. (2012). Reduction of nitrate and ammonium adsorption using microscale iron particles and zeolite. *Water Air and Soil Pollut.* 223 (3): 1079-1089.
- [6]. Maheshwari, U., Mathesan, B. and Gupa, S. (2015). Efficient adsorbent for simultaneous removal of Cu(II), Zn(II), Cr(VI): kinetic, thermodynamic and mass transfer mechanism. *Process Saf. and Environ. Prot.* 98: 98-210.
- [7]. Nekouei, S.H., Nekouei, F., Tyagi, I., Agarwal, S. and Kumar Gupta, V. (2016). Mixed cloud point/soil phase of lead (II) and cadmium (II) in Water samples using modified-ZnO. *Process Saf. and Environ. Prot.* 99: 175-185.
- [8]. Semer, R. and Reddy, K. (1996). Evaluation of soil washing process to remove mixed contaminants from a sandy loam. *J. Hazard. Mater.* 45: 45-57.
- [9]. Wuana, R.A., Okieimen, F.E. and Imborvungu, J.A. (2010). Removal of heavy metals from a contaminated soil using organic chelating acids. *Int. J. of Environ. Sci. and Tech.* 7: 485-496.
- [10]. Sheet, I., Kabbani, A. and Holail, H. (2014). Removal of heavy metals using nanostructured graphite oxide, silica nanoparticles and silica/graphite oxide composite. *Energy Procedia.* 50: 130-138.
- [11]. Amin, M.T., Alazba, A.A. and Manzoor, U. (2014). A review of removal of pollutants from water/wastewater using different types of nanomaterials. *Advances in Materials Science and Engineering.* 2014: 1-24.
- [12]. Taman, R., Ossman, M.E., Mansour, M.S. and Farag, H.A. (2015). Metal oxide nano-particles as an adsorbent for removal of heavy metals. *J. Adv. Chem. Eng.* 5 (125).
- [13]. Ray, P.H.Z. and Shipley, H. (2015). Inorganic nano-adsorbents for the removal of heavy metals and arsenic: a review. *RCS Adv.* 5: 29885-29907.
- [14]. Kalantari, K., Ahmad, M.B., Masoumi, H.R., Shameli, K., Basri, M. and Khandanlou, R. (2014). Rapid adsorption of heavy metals by Fe₃O₄/talc nanocomposite and optimization study using response surface methodology. *Int. J. Molecular Sci.* 15 (7): 12913-12927.
- [15]. Tandy, S., Bossart, K., Mueller, R., Ritschel, J., Hauser, L., Schulin, R. and Nowack, B. (2004). Extraction of heavy metals from soils using biodegradable chelating agents. *Enviro. Sci. and Tech.* 38: 937-944.
- [16]. McLaren, R.G. and Crawford, D. (1973). Studies on soil copper: The fractionation of copper in soils. *J. Soil Sci.* 24: 172-179.
- [17]. Tokalioglu, S., Kartal, S. and Birol, G. (2003). Application of a tree-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. *Turk. J. Chem.* 27: 333-346.
- [18]. Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51: 844-851.
- [19]. Yong, R.N., Galvez-Cloutier, R. and Phadungchewit, Y. (1993). Selective sequential extraction analysis of heavy metal retention in soil. *Can. Geote. J.* 30: 834-847.
- [20]. Dahrazma, B. and Mulligan, C.N. (2007). Investigation of the removal of heavy metals from sediments using rhamnolipid in a continuous flow configuration. *Chemosphere.* 69: 705-711.
- [21]. Uduma, A.U. and Jimoh, W.L.O. (2013). Sequential extraction procedure for partitioning of lead, copper, cadmium, chromium, and zinc in contaminated arable soils of Nigeria. *Am. J. Environ., Energy and Power Res.* 1 (9): 186 -208.
- [22]. Georgiadis, A., Sauer, D., Herrmann, L., Breuer, J., Zarei, M. and Stahr, K. (2014). Testing a new method for sequential silicon extraction on soils of a temperate-humid climate. *Soil Res.* 52: 645-657.
- [23]. Golzar, M., Saghravani, S.F. and Azhdari Moghaddam, M. (2014). Experimental study and numerical solution of poly acrylic acid supported magnetite nanoparticles transport in a one-dimensional porous media. *Advances in Mater, Sci. & Eng.* pp. 1-8.
- [24]. Mohammadiun, M., Dahrazma, B., Saghravani, S.F. and Khodadadi Darban, A. (2015). Cadmium Removal Optimization from the Soil by Using nano Fe₃O₄. *International Conference of Environmental Science, Engineering and Technologies (CESET 2015).* University of Tehran. Tehran. Iran.
- [25]. Lee, S.K. and Choi, H.S. (2001). Spectrophotometric determination of cadmium and copper with ammonium pyrrolidinedithiocarbamate in nonionic tween 80 micellar media. *Bull. Korean Chem. Soc.* 22 (5): 463-466.
- [26]. Mohammed, N., Grishkewich, N., Waeijen, H.A., Berry, R.M. and Tam, K.C. (2016). Continuous flow adsorption of methylene blue by cellulose nanocrystal-alginate hydrogel beads in fixed bed columns. *Carbohydrate Polymers.* 136 (1): 194-202.
- [27]. Li, J., Sun, Y., Yin, Y., Ji, R., Wu, J., Wang, X. and Guo, H. (2010). Ethyl lactate EDTA composite system enhances the remediation of the cadmium contaminated soil by Autochthonous Willow (*Salix × aureopendula* CL 'J1011') in the lower reaches of the Yangtze River. *Hazard. Mater.* 181: 673-678.
- [28]. Gzar, H.A., Abdul-Hameed, A.S. and YounusYahya, A. (2014). Extraction of lead, cadmium and nickel from contaminated soil using acetic acid. *J. Soil Sci.* 4: 207-214.

[29]. Shafai, S.H., Fotovat, A. and Khorasani, R. (2012). Effect of nanoscale zerovalent iron (nZVI) on heavy metals availability in a calcareous soil. *J. Water & Soil.* 26: 586-896.

[30]. Davarnejad, R. and Panahi, P. (2016). Cu (II) removal from aqueous wastewaters by adsorption on the modified Henna with Fe₃O₄ nanoparticles using response surface methodology. *Sep. and Purif. Tech.* 158: 286-292.

[31]. Tan, Y., Chen, M. and Hao, Y.I. (2012). High efficient removal of Pb (II) by aminofunctionalized Fe₃O₄ magnetic nanoparticles, *Chem. Eng. J.* 191: 104-111.

[32]. Muliwa, A.M., Leswif, T.Y., Onyango, M.S. and Maity, A. (2016). Magnetic adsorption separation (MAS) process: An alternative method of extracting Cr(VI) from aqueous solution using polypyrrole coated Fe₃O₄ nanocomposites, *Sep. and Purif. Tech.* 158: 250-258.

استفاده از آزمایش‌های استخراج انتخابی متوالی برای ارزیابی حذف کادمیوم از بخش‌های مختلف خاک به وسیله نانو ذرات اکسید آهن سه ظرفیتی در سامانه پیوسته

ملیحه محمدیون^{۱*}، بهناز دهرآزما^۱، سید فضل اله ساغروانی^۱ و احمد خدادادی دربان^۲

۱- دانشکده عمران، دانشگاه صنعتی شاهرود، ایران

۲- گروه فرآوری مواد معدنی، دانشکده فنی و مهندسی، دانشگاه تربیت مدرس، ایران

ارسال ۲۰۱۷/۱۰، پذیرش ۲۰۱۷/۱۲/۲۳

* نویسنده مسئول مکاتبات: malihemohamadiun@yahoo.com

چکیده:

استفاده از نانو تکنولوژی یک روش اثبات شده برای حذف آلاینده‌ها از فازهای مختلف محیط‌زیست است. هدف از انجام این پژوهش، ارزیابی اثر پارامترهای مختلف در حذف یون‌های فلز سنگین کادمیوم از خاک با استفاده از نانو ذره اکسید آهن سه ظرفیتی در یک سامانه پیوسته جریان، همچنین ارزیابی توالی حذف کادمیوم از بخش‌های مختلف خاک آلوده با به کارگیری آزمایش‌های استخراج انتخابی متوالی بوده است. بدین منظور سیال حاوی نانو ذرات اکسید آهن در آب با دبی مشخص از ستون خاک آلوده به قطر ۳ cm و ارتفاع ۴ cm عبور داده شد. با ایجاد شرایط بهینه در این سامانه شامل غلظت نانو سیال برابر ۵۰۰ ppm، pH=۶/۵، زمان تماس ۲۴ ساعت و دبی ۰/۵ mL/min، ۱۰۰٪ کادمیوم از خاک آلوده حذف شد. ارزیابی نتایج به دست آمده نشان داد که تمایل حذف کادمیوم با استفاده از نانو ذره اکسید آهن سه ظرفیتی از بخش‌های مختلف خاک مورد آزمایش به ترتیب ذیل است:

بخش باقی‌مانده > بخش آلی > اکسیدهای آهن و منگنز > کربنات > تبادل پذیر

نتایج به دست آمده از این تحقیق می‌تواند برای ایجاد یک پروتکل پاک‌سازی مناسب برای خاک‌های آلوده استفاده شود.

کلمات کلیدی: استخراج انتخابی متوالی، نانو ذره اکسید آهن سه ظرفیتی، سامانه پیوسته جریان، حذف کادمیوم.
