REMOVAL OF CADMIUM FROM CONTAMINATED SOIL USING IRON (III) OXIDE NANOPARTICLES STABILIZED WITH POLYACRYLIC ACID

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Abstract. The aim of this study is to evaluate the effect of Fe3O4 nanoparticle, stabilized with polyacrylic acid on cadmium removal from the contaminated soils. To investigate the effect of important parameters, including nanoparticle concentration, pH, contact time, and the ratio of contaminated soil mass to nanofluid volume, several batch tests were performed. The maximum removal rate (100%) of cadmium was obtained in the following conditions: nanofluid concentration = 500 ppm, pH = 6.5, contact time = 24 hr and the ratio of contaminated soil mass (gr) to nanofluid volume (mL) = 1:150. Results of selective sequential extraction tests showed that the distribution of cadmium in different fractions of the soil was carbonates, oxides and hydroxides, residual fraction, exchangeable, and organic matter respectively. The tendency of nanoparticles for removal of Cd2+ from the soil fractions was in the order of: exchangeable > carbonates > oxides and hydroxides > organic matter > residual.

Keywords: soil contamination, iron (III) oxide nanoparticle, polyacrylic acid, cadmium removal, selective sequential extraction.

Introduction

One of the early generations of nanoscale technologies in the field of environment is iron nanoparticle technology (Wang, Zhang 1997). Medical treatment (medical devices), military installation, pollution sensing and detection, ecosystem monitoring and green chemistry are from important technologies in which nanotechnology has been applied effectively. Remediation/decontamination of pollutants in soils and groundwater has received significant benefit from nanotechnology. More researches are necessary to achieve the safe and beneficial applications of this new technology due to its novelty (Reddy 2010).

Many nanoscale metal oxides such as AgO_2, which is expensive, are toxic and unsuitable for injection into the environment, while nanoscale iron particles (NIP) with their environmentally-benign characteristics, favorable chemistry, relatively low cost, and ease of use are considered excellent candidate for environmental decontamination (Reddy 2010; Yuan *et al.* 2012).

With rapid urbanization and industrial development particularly by the beginning of the twentieth century, heavy metal pollution in the biosphere has now become one of the most serious environmental concerns due to its severe long-term implications on human health and the environment. Some of the heavy metals such as Zn, Fe, and Cu are essential for human metabolism but, at higher concentrations, can also lead to poisoning. Some others such as Cd and Pb are more dangerous hence, their concentrations should be as closest to zero as possible (Ozturk *et al.* 2017). Recently, several researches were done on dangerous effects of heavy metals including Mg, Fe, Cd, Zn, and Cu and their removal techniques (Vasarevičius *et al.* 2016; Strachel *et al.* 2017). Cd has high mobility and is accepted as carcinogenic element. Cd accumulation in plants causes adverse effects leading to growth inhibition and even death; it is also a potentially carcinogenic heavy metal, which can accumulate in human organs, so removal of this heavy metal from soil could be one of the environmentally valuable aspects of this study.

In recent decades, nanoparticles were used to remove heavy metals from contaminated water and wastewater.

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Cadmium ion removal by adsorption onto nano zerovalent iron (NZVI) particles from contaminated water sources and aqueous solutions (Boparai *et al.* 2011; Guler 2016) and for water treatment (Crane, Scott 2012) was studied. Use of Fe_3O_4 magnetic nanoparticles (MNPs) modified with 3-aminopropyltriethoxysilane (APS), copolymers of acrylic acid (AA), and crotonic acid (CA) for removal of heavy metal ions from water (Ge *et al.* 2012) are from researches which have proved effectiveness of using nano iron particles (NIP) for water, wastewater.

Soil washing is a common method for soil treatment. Different agents were employed for removal of heavy metals from contaminated soil. Soil washing with acetic acid and EDTA were applied on contaminated soils for Cd removal (Li *et al.* 2010; Gzar *et al.* 2014). NZVI has the capacity to remove all cadmium from contaminated soil (Shafai *et al.* 2012). Effect of soil washing with chelators or in combination with ferric chloride on heavy metals removal from soil was also studied (Guo *et al.* 2016).

There is lack of literatures for using nanoparticles as washing agent to remove heavy metals from contaminated soil. Recently, Adsorption of trace elements form contaminated soil with application of nano-maghemite (NM) (iron nano-oxide; Fe_2O_3) (Martínez-Fernández *et al.* 2014), assessment the effects of NZVI on heavy metal removal from calcareous soil (Shafai *et al.* 2012) and using NZVI for Cr (VI) removal from contaminated soil (Di Palma *et al.* 2015) were studied.

There are various methods to produce iron nanoparticles. In the recent years, several synthetic methods have been developed through various researches (Wang, Zhang 1997; Zhang 2003; Sun *et al.* 2006; Liu *et al.* 2015).

Many studies have been conducted to modify the nanoparticle surface properties (Elliott, Zhang 2001; Xu *et al.* 2005), and enhance the efficiency for field delivery and reactions (Elliott, Zhang 2001; Kanel *et al.* 2007). These extensive laboratory studies have demonstrated that nanoscale iron particles are effective for the transformation of a wide array of common environmental contaminants such as chlorinated organic solvents (Wang, Zhang 1997; Elliott, Zhang 2001; Zhang 2003; Nutt *et al.* 2005), organochlorine pesticides (Cao *et al.* 2003), Polychlorinated biphenyls (PCBs) (Zhang 2003; He, Zhao 2005), organic dyes (Liu *et al.* 2005), various inorganic compounds and metal ions such as As(III), Pb(II), Cu(II), Ni(II) and Cr(VI) (Alowitz, Scherer 2002; Xu *et al.* 2005).

Due to variation in the composition of the soils, including heterogeneous mixtures of organic and inorganic substances, the binding mechanisms for heavy metals are very different (Tokalioglu *et al.* 2003). This fact influences the bioavailability of heavy metals in the environment (Tessier *et al.* 1979). Identification of the adsorption procedure of trace elements on the several fractions of soils and sediments are important for designing the removal protocol. Selective sequential extraction (SSE) is widely used for this purpose (Tessier *et al.* 1979; Huang *et al.* 2012, 2016). Selective sequential extraction methods have been used for assessment of several heavy metals removal from soils, sediments, compost, sludge and wastewater and also the mobility of these metals have also been studied (Mulligan, Dahrazma 2003; Dahrazma, Mulligan 2006; Hseu 2006; Fan *et al.* 2012; Zaleckas *et al.* 2013; Zak *et al.* 2013; Uduma, Jimoh 2013; Ozbas, Balkaya 2014; Zhao *et al.* 2014; Pandey *et al.* 2015).

Varieties of SSE procedures are now available (Filgueiras *et al.* 2002; Gleyzes *et al.* 2002). The first SSE procedure was introduced by Crawford and McLaren in 1973 in order to remove elements from exchangeable, residual, organic, and oxides fractions of natural soil (McLaren, Crawford 1973). BCR (Community Bureau of Reference) and Tessier are from most common SSE methods (Tessier *et al.* 1979; Rico *et al.* 2009; Huang *et al.* 2012, 2016). The BCR procedure was proposed by European Union. BCR sequential extraction procedure has been widely applied to soil and sediment samples (terrestrial or marine originated) (Tokalioglu *et al.* 2003; Doelsh *et al.* 2008). According to Tessier procedure, heavy metals could be extracted from five fractions of soils and sediments, namely exchangeable, carbonate, iron and manganese oxides, organic matter, and residual (Tessier *et al.* 1979). This procedure has also been applied for heavy metal extraction in many studies (Quezada-Hinojosa *et al.* 2015a, 2015b). This procedure has been adapted and improved by Yong (Yong *et al.* 1993). The Yong's method is considered as the most complete SSE procedure that has been implemented in many researches for determination of heavy metals removal mechanism (Dahrazma, Mulligan 2007; Uduma, Jimoh 2013). The procedure, could determine concentration of heavy metals in six soil fractions namely, soluble, exchangeable, carbonates, oxides and hydroxides, organic matter, and residual fraction.

Considering the efficiency of nanoscale iron particles in heavy metal removals from aqueous solutions, water and wastewater, and also lack of comprehensive studies on heavy metals removal from soils using nanotechnologies, this research focused on the use of the iron (III) oxide nanoparticle for removal of cadmium from contaminated soil. The Yong's method of SSE was adopted in this study in order to assess the performance of iron nanoparticles on contaminated soil.

1. Material and method

1.1. Material

1.1.1. Soil mixture

To ensure the absence of other pollutants and elimination of any interaction between soil pollutants, after several trials and errors, based on the common natural soil compositions, the soil was prepared with clean standard materials as listed below:

- 161 Firuzkooh Sand (8%);
- Silt was prepared by Soil Mechanics Laboratory of Tehran University (40%);

– Kaolinite was prepared byIran China Clay Industries Co. (10%);
– Organic matter (10%);
– Red mud, which was excavated from a 2 meter depth pristine in the vicinity of the Shahrood City and passed through the sieve number 200 (20%);
– CaCo$_3$ (Merck Co.) (10%);
– CaO (Sigma Aldrich Co.) (2%).

1.1.2. Nanoparticles

Iron (III) Oxide Nanoparticles were produced in Pasteur Institute of Iran with 99.5% purity and average particle size of 44.5 nm.

1.1.3. Material for SSE

All chemicals for SSE procedure including MgCl$_2$, C$_2$H$_3$NaO$_2$, C$_2$H$_7$NO$_2$, H$_6$ClNO, HNO$_3$, H$_2$O$_2$, HCl and Acetic Acid were obtained from Merck Co.

Material for Cd spectrophotometric determination

All chemicals including Cd(NO3)$_2$ (Merck Co.), Ammonium Pyrrolidine dithiocarbamate (APDC) (Sigma Aldrich Co.), and Tween 80 (Sigma Aldrich Co.) were of guaranteed laboratory grade reagents.

1.2. Experimental procedures

1.2.1. Preparation of contaminated soil

The makeup soil was mixed with 500 ppm solution of cadmium nitrate for 48 h on a shaker with 80 rpm. To ensure the complete mixing, the ratio of the solution (mL) to the weight of the soil (gr) was 20:1. Then, the soil was removed from the solution. Using centrifuge (3500 rpm for 20 min) to remove all unabsorbed contaminant from the soil, this stage was repeated with distilled water. The soil was dried at the room temperature. The prepared soil was used for the course of this research.

1.2.2. Soil structure

After soil preparation, the contaminated soil was sieved according to ISIRI 4977. The result is shown in Figure 1. More than 54% of soil passed the Sieve No. 400 (opening size: 0.037 mm). This part was analyzed with Laser Particle Sizer ANALLISETE 22 (FRITISH Co.). The result is presented in Figure 2.

According to the results of sieve analyses, based on the American Association of State Highway and Transportation Officials (AASHTO) soil classification, the percentages of sand and silt were 29, and 17 respectively. Also, according to the laser particle analyses, the amount of the silt and clay were 41% and 13% respectively. Therefore, the grain size distribution was 29% sand, 58% silt and 13% clay.

1.2.3. Preparation of the nanofluid

For preparation of homogeneous nanofluid, the iron (III) oxide nanoparticles were stabilized with polyacrylic acid (PAA) (Sigma Aldrich Co.), according to the procedure
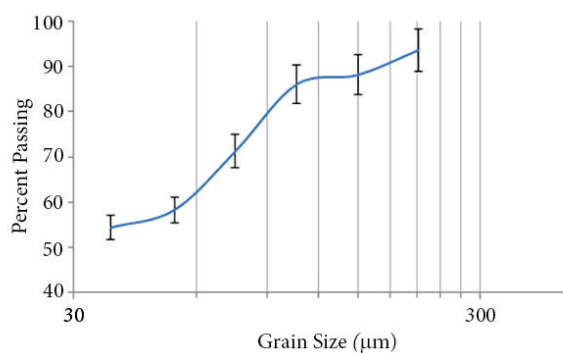

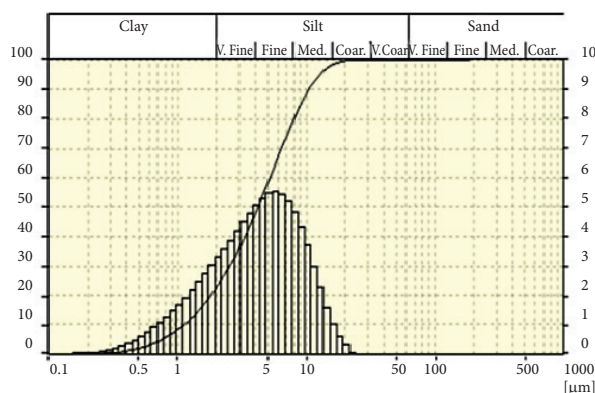Figure 1. The size distribution of the contaminated soil by sieving

Figure 2. Results of laser particle sizing for the soil

proposed by Golzar *et al.* (Golzar *et al.* 2014). Accordingly, specified value of the nanoparticles in the one-fifth of the final solution volume distilled water is placed in ultrasonic bath (40 KHz, 50 W) for 30 min. In the other flask, PAA (the weight ratio of PAA to nanoparticle is 2:1) was mixed with the four-fifth of the final volume distilled water at the speed of 500 rpm for one hour. These two solutions were mixed together and placed in ultrasonic bath (40 KHz, 50 W), for one hour. So for preparation of one liter of 500 ppm nanofluid 0.5 g of NIP in 200 mL distilled water was placed in ultrasonic bath and 1 g of PAA was solved in 800 mL distilled water, afterwards these two solutions were mixed and placed in ultrasonic bath again. Then this combination was kept in the room temperature for 24 h. The solution was placed in the same ultrasonic bath for 30 min each time prior to applying to the soil.

1.2.4. Determination of heavy metal content of the soil

To find the concentration of heavy metals in the soil, it was digested by the method recommended by Environment Canada (1990). According to this method 1.0 g of the soil was placed in a 1L beaker; 100 mL of 16N nitric acid were added to the beaker over a minimum period of 2 minutes; 40 mL of H$_2$O$_2$ (30%) were added to the beaker; the beaker was left for 5 minutes to react; the beaker was placed on a hot plate (Fisher Stirring Hotplate) until it boiled. Then, it was removed from the heat and cooled

to the room temperature; 200 mL aqua regia (50 mL HCl, 200 mL HNO_3 and 750 mL water) were added to the beaker; the beaker was filled to the 500 mL level with distilled water; the solution was prepared for analysis (Dahrazma, Mulligan 2007). The Cd content was measured at 9500 $mg.Kg^{-1}$.

1.2.5. Soil washing procedure

The soil was washed with nanofluid iron oxides in a batch configuration. To achieve the ultimate Cd removal by iron (III) oxide nanoparticle, the effective parameters including the nanofluid concentration, pH, contact time, and the ratio of the nanofluid (mL) to contaminated soil (gr) were evaluated and optimized. For this purpose 1.5 gr of soil was washed with nanofluid with different concentrations from 100 to 2000 ppm. After determination of optimized nanofluid concentration, pH was optimized in the range of 5 to 10. In the next stage contact time from 5 to 14400 minute was examined at the nanofluid concentration and pH which were determined in the first stage to achieve the maximum removal. Finally, soil was washed with different ratio of mass of soil to the volume of nanofluid in the range of 1:2 to 1:150 at the condition with the most removal in the previous steps of the test. All the tests were triplicated. The difference between test results never exceeded more than 5%. Parameters were optimized step by step and results of each step were used for the next parameter. All the tests were performed at 25 ºC.

The soil was placed in batch reactors and nanofluid iron oxide was added to the soil for Cd^{2+} removal. The samples were placed on a rotary shaker for a desired period of time. For analysis, the soils were separated from the solutions by centrifuge (3500 rpm for 20 min). The supernatant solutions were then decanted from the soils and the concentration of Cd^{2+} in solutions was measured using UV spectrophotometer.

1.2.6. Selective sequential extraction tests

The procedure used for the batch sequential extraction was similar to that of Yong *et al.* (1993) shown in the Table 1 Soil samples (1.5 g) were washed with the nanoparticle solutions and controls (Yong *et al.* 1993; Dahrazma, Mulligan 2006). Each fraction was collected and the concentrations of cadmium were determined by UV spectrophotometer according to the procedure presented in the next section. After each step, samples were washed with distilled water for the next step and then subsequently dried prior to next step. The amounts of Cd^{2+} extracted from each of the extractions were then determined and the percentage extracted by each solution was calculated.

1.2.7. Spectrophotometric determination of cadmium

UV Spectrophotometer (CECIL CE 7000 Series) was employed to measure the concentration of cadmium using APDC complexes in Tween 80 media. The detection limit for good linearity was 0.05 mgL^{-1} and the maximum

Table 1. Sequential extraction process
(adapted from Yong *et al.* 1993)

Se-quence	Chemical Reagents	Fraction
1	Overnight extraction of metals by nanoparticle solution and controls (distilled water) with 15 mL of solution	Soluble
2	Extraction of metals with 8 mL of 1 M $MgCl_2$ (pH 7) for 1 h	Exchangeable
3	Extraction of metals with 8 mL of 1 M $NaOAc^1$ adjusted to pH 5 with acetic acid for 5 h	Carbonates
4	Extraction of metals with 20 mL of 0.04 M $NH_2OH.HCl$ in 25% (v/v) acetic acid (pH 2.5) at 96 ºC for 6 h	Oxides and hydroxides
5	Extraction with 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 (pH 2) for 2 h at 85 ºC, followed by 3 mL of 30% H_2O_2 (pH 2) at 85 ºC for 3 h and then 5 mL of 3.2 M NH_4OAc1 in 20% (v/v) HNO_3 diluted to 20 mL at room temperature for 30 min.	Organic matter
6	Digestion at 90 ºC with 25 mL of dilute aqua regia (50 mL HCl, 200 mL HNO_3 and 750 mL water) for 3 h	Residual fraction

wavelength of Cd^{2+} complex appeared at 324 nm (Lee, Choi 2001). Standard Cd^{2+} solutions were made from 1000 mgL^{-1} stock solutions. A 1.0% (w/v) Tween 80 solution was prepared by dissolving 1.0 g of Tween 80 in 100 mL of water with stirring. Phosphate buffer (pH = 7.0) was prepared by appropriately mixing 0.1 M KH_2PO_4 and 0.1 M NaOH. Since APDC gradually decomposes in aqueous solution, 0.1% APDC solution was made whenever needed (Lee, Choi 2001).

Standard Cd^{2+} solutions were prepared in the range of 0.5–2.5 mgL^{-1} in 10 mL volumetric flasks. 0.5 mL of APDC and 1 mL of Tween 80 were added to each standard solution of Cd^{2+} and 1 mL of sample. The solutions were then filled up to 10 mL with phosphate buffer. Blank solution was also prepared by the above procedure without Cd solution. After 20 minutes, the cadmium concentration could be determined by a UV-Vis spectrophotometer (Lee, Choi 2001). By measuring the Cd^{2+} concentration, the mass of Cd^{2+} and the percentage of removal of Cd^{2+} by nanofluid was calculated based on the initial total content of Cd^{2+} in the soil.

2. Results and discussion

2.1. Effective parameters for Cd removal

The results of soil washing procedures and investigation on the effect of different parameters in Cd^{2+} removal using iron oxide nanoparticles are presented below.

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[1] Ac denotes acetate.

2.1.1. Effect of nanoparticles concentration

1.5 gr of soil was washed with the blank (distilled water) and nanofluid of different concentrations, 100, 300, 500, 1000, and 2000 ppm. Other parameters were constant (pH = 8.5, contact time = 24 hr). The results are shown in Figure 3. The results of removal by distilled water are not shown since cadmium was detected in the final solution.

Results illustrated that, removal rate directly increased by increasing the concentration of nanofluid up to 19%, which occurred at 2000 ppm. As shown in Figure 3, the Cd^{2+} sorption rate was positively correlated with nanofluid concentration. In higher concentrations, higher amount of nanoparticle existed, so more sorption sites were found. Since the nanoparticles were coated with PAA, the higher concentrations are not practical due to intense increase in the viscosity of the solution. The concentration of 500 ppm with removal rate of 11% was selected to continue, for the sake of workability of the solution.
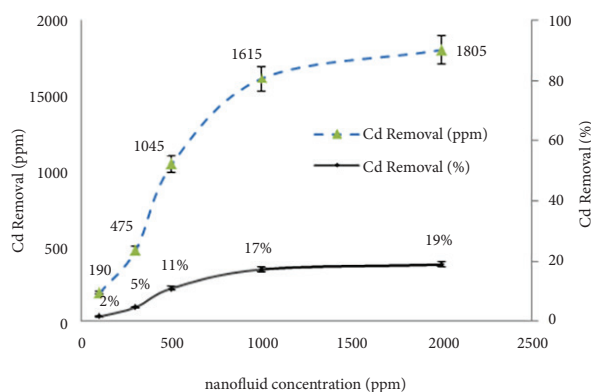

Figure 3. Removal of Cd by nanofluid at different concentrations (pH = 8.5, ratio of soil mass (gr) to nanofluid volume (mL) = 1:10, Contact time = 24 hr)

2.1.2. Effect of pH

According to the preliminary tests, at pH = 4 and also at pH = 11 the nanofluid was unstable and settled. This is shown in Figure 4(a) and Figure 4(b). So the optimization of pH was performed in the range of 5 to 10.
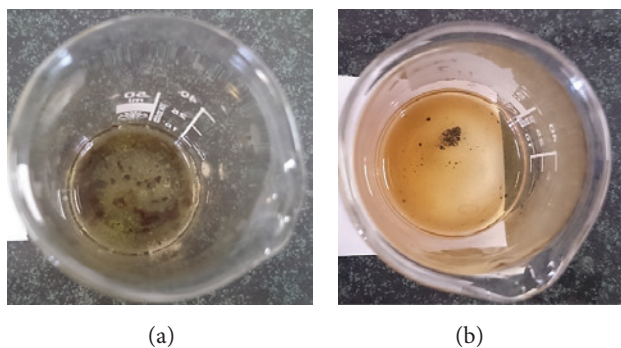

(a)   (b)

Figure 4. Nanofluid at pH = 4 (a) and pH = 11(b)

For optimizing pH, 1.5 g of soil was washed with 15 mL of 500 ppm nanofluid at pHs, including, 5 through 10, for 24 hr. The results are shown in Figure 5.
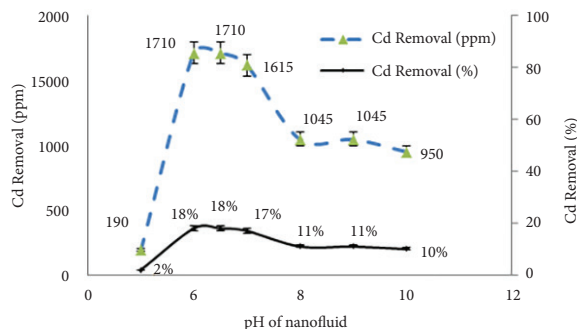

Figure 5. Removal of Cd by nanofluid at different pH (Concentration = 500 ppm, ratio of soil mass (gr) to nanofluid volume (mL) = 1:10, Contact time = 24 hr)

As per the results, maximum Cd removal was recorded at pH = 6 (18%) and it was very similar to pH = 7 (17%). The percentage of removal of cadmium at pH = 6.5 was 18% too, so this pH was selected.

Hetzer *et al.* (2006) further justified this fact as well. Several other researchers affirmed that optimal pH for the adsorption of cadmium is situated around 6 (Asci *et al.* 2007; Quintelas *et al.* 2009). Similar results have also been presented by Chowdhury *et al.* (2011) in the evaluation of adsorption mechanism of dyes (Chakravarty *et al.* 2010), and also by Ebrahimi *et al.* (2015) in assessment of biosorption of Cd(II) from aqueous solutions.

Cd removal from the soil by nanofluid depends on both the solubility of cadmium and the properties of nanoparticles. According to the solubility curve of cadmium, by increasing the pH, its solubility is decreased (Bradl 2005). Therefore, by reducing the solubility of the ion in nanofluid at higher pH, separating it from the soil is also reduced.

Magnetite nanoparticles were prepared by alkaline hydrolysis of the highly concentrated mixed solution of iron(II)- and iron(III)-salts. So excess amount of proton and therewith its surface charge depends on the pH (Tombacz *et al.* 2006). Magnetite is an amphoteric solid, which can develop charges in the protonation and deprotonation reactions of Fe-OH sites on surface. These surface reactions can be interpreted as the specific adsorption of H^+- and OH^-- ions at the hydrated solid/water interface (Tombacz 2002). Colloidal solution nanofluid achieve to the highly stabilized condition at the point of zero charge (PZC) where surface charge density is also zero. The PZC of nano Fe_3O_4 seems to be at pH 7.9±0.1 (Tombacz *et al.* 2006). The optimum pH for the cadmium removal from the soil in this study (6.5) can be a result of both factors, the further Cd solubility in low pH and creation of a stable colloidal solution at pH of about 7.9.

2.1.3. Effect of contact time

To optimize the contact time, 1.5 gr of soil was washed with 15 mL of nanofluid with concentration of 500 ppm at pH = 6.5 for 5, 10, 15, 60, 300, 720, 1440, 2880, 4320, and 14400 minutes. The results are shown in Figure 6.
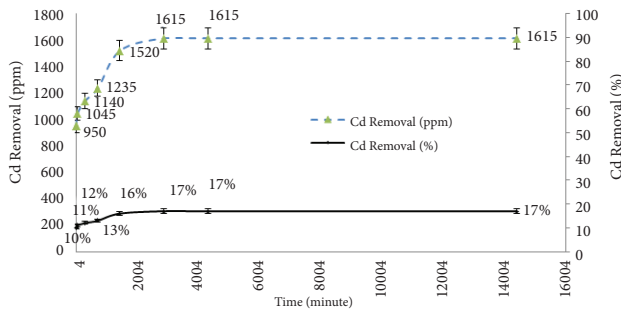
Figure 6. Removal of Cd by nanofluid at different Contact
Time (Concentration = 500 ppm, pH = 6.5, ratio of soil mass
(gr) to nanofluid volume (mL) = 1:10)

The results depicted that Cd removal increased considerably with increasing in contact time up to 24 hr (from 10% at 5 min to 16% at 1440 min). The difference was negligible between 24 hr and 48 hr (from 16% at 1440 min to 17% at 2880 min). Since a notable increment of removal was not observed after 48 hr, the 24 hr contact time was selected to continue.

As it is shown, initially, the rate of adsorption was rapid because of the adsorption of Cd onto the exterior surface. After that, adsorption occurred relatively slow due to the entrance of Cd into pores (interior surface). The initial faster rates of adsorption may also be related to the presence of more binding sites for adsorption and the slower adsorption rates at the end is due to the saturation of the binding sites. Similar conclusions have been proposed by Chowdhury *et al.* (Chowdhury *et al.* 2011).

2.1.4. Effect of the ratio of the mass of the soil to the volume of the nanofluid

To study the effect of ratio of the soil mass (gr) to volume of the nanofluid (mL), 1.5 g of soils were washed with different ratio of mass of soil to the volume of nanofluid,1:2, 1:5, 1:10, 1:20, 1:50,1:100, and 1:150 at pH = 6.5 for 24 hr. The results are shown in Figure 7. According to these experiments, increasing the ratio of nanofluid volume to the soil mass can improve the removal of cadmium up to 100% which occurred at the ratio of 1:150 (mass soil (gr) to volume of nanofluid (mL)).

With increasing the ratio of nanofluid volume to the soil mass, a higher amount of Cd was removed because of the increase in the dosage of adsorbent. This is due to an increase in the surface area of the adsorbent, which in turn increases the number of binding sites (Chakravarty *et al.* 2010). Similar result had also achieved by Nasiri *et al.* (2013) who assessed the effect of concentration of nanoparticle NZVI on Cd removal from each fraction of soil. Accordingly, with increasing the nanoparticles concentration, the Cd removal increased in different fractions of the contaminated soil.

According to these tests, the comparison between samples used as control and samples washed with nanofluid depicted that nanofluid could remove 100% of cadmium from the soil. Cadmium extraction from contaminated soil by this method is considerably effective in contrast to the available literature. For example, by Thermally Responsive Elastin (ELPEC20) Biopolymers biopolymer in soil washing experiments, up to 62% removal was achieved (Lao *et al.* 2007), the efficiency of cadmium removal from the soil using acetic acid was 70.6% (Gzar *et al.* 2014), and 85% reduction of cadmium concentration was achieved by combination of electrokinetic remediation and soil washing technology (Giannis, Gidarakos 2005).

2.2. Sequential Extraction Tests

After investigation on the effect of different parameters on the removal of cadmium using iron oxide nanofluid, and optimizing the removal conditions, the tendency of iron (III) oxide nanoparticle to remove cadmium from each fraction of the soil was studied using the SSE techniques proposed by Yong in 1993 (Yong *et al.* 1993). For this purpose 1.5 g of the soil was washed with distilled water as control and the nanofluid at the following conditions: nanofluid concentration = 500 ppm, pH = 6.5, contact time = 24 hr, and ratio of soil mass (gr) to nanofluid volume (mL) = 1:100. According to the optimized test at the ratio of soil mass (gr) to nanofluid volume (mL) = 1:150 Cd^{2+} was completely removed from all fractions of soil, thus it is not possible to determine the order of tendency of nanoparticle, for removal of Cd^{2+} under this condition. Therefore, SSE test was done at the ratio of soil mass (gr) to nanofluid volume less than the optimized amount of this parameter. All the tests were in triplicate.
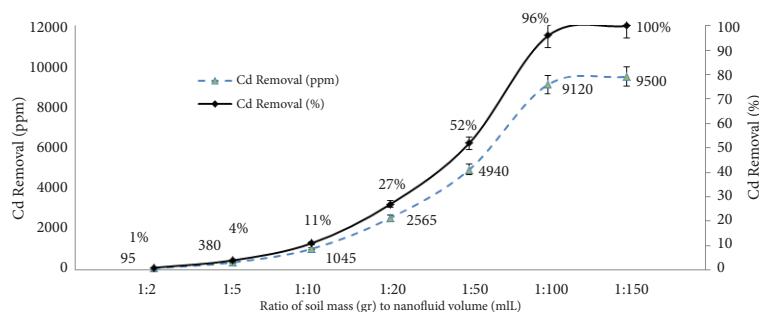

Figure 7. Removal of Cd by nanofluid with different Ratio of soil mass (gr) to volume of nanofluid (mL)
(Concentration = 500 ppm, pH = 6.5, Contact time = 24 hr)

Selective sequential extraction results on control samples showed that Cd removal didn't occur by washing the soil with distilled water. According to the results, shown in Figure 8, the accumulation of Cd in soil fractions was 55% (5225 ppm) in carbonates, 30% (2850 ppm) in oxides and hydroxides, 7.5% (712.5 ppm) in residual fraction, 5.5% (522.5 ppm) in exchangeable, and 2% (190 ppm) in organic matter.

Selective sequential extraction also showed that 96% (9120 ppm) of Cd content was removed from soil by nanofluid (soluble fraction). According to the results (Figure 9), Cadmium was completely removed from exchangeable fraction (522.5 ppm). The rates of removal from other fractions were 97.8% (5108.7 ppm) from carbonates, 95,3% (2717.3 ppm) from oxides and hydroxides, 94.1% (178.8 ppm) from organic matter, and 82.4% (587.3 ppm) from residual fraction.

Removal from the soil fractions using iron oxide nanofluid in this study occurred as follows:

- Exchangeable: The highest removal (100%) occurred in this fraction where cadmium completely removed. Cd content in this part changed from 5.5% (522.5 ppm) to 0%;
- Carbonate: 97.8% (5108.7 ppm) of Cd removed from carbonate phase, and Cd content changed from 55% (5225 ppm) to 1.2% (116.3 ppm);
- Oxides and Hydroxides: Cd removal occurred in this fraction with the mass fraction of 95.3%

(2717.33 ppm) and Cd content changed from 30% (2850 ppm) to 1.4% (132.67 ppm);
- Organic matter: 94.1% (178.8 ppm) Cd removed from this fraction of soil. In this phase, Cd content decreased from 2% (190 ppm) to 0.12% (11.18 ppm);
- Residual: Cd removed from this part of soil with the removal rate of 82.4% (587.3 ppm). Cd content in this fraction decreased from 7.5% (712 ppm) to 1.32% (125.3 ppm).

Conclusions

The soil treatment procedure and Cd^{2+} removal from contaminated soil were affected by different parameters. According to the findings at this study, nano Fe_3O_4 stabilized with PAA could remove up to 100% of cadmium from the soil at the following optimized conditions: nanofluid concentration = 500 ppm, pH = 6.5, contact time = 24 hr, and the ratio of mass of soil (gr) to volume of the nanofluid (mL) = 1:150.

The results of the SSE tests on the soil samples which washed with distilled water and the nanofluid depicted that the partitioning of cadmium in different fractions of the contaminated soil before washing tests were carbonates, oxides and hydroxides, residual fraction, exchangeable, and organic matter respectively. The tendency of nano Fe_3O_4 to adsorb cadmium from different fractions of the soil and its removal rate from each fraction were in the following order:

Exchangeable (100%) > Carbonate (97.8%) > Oxides and hydroxides (95.3%) > Organic Matter (94.1%) > Residual (82.4%)

Therefore, it could be concluded that iron (III) oxide nanoparticle stabilized with polyacrylic acid could be used as an effective adsorbent to remove cadmium from contaminated soil.
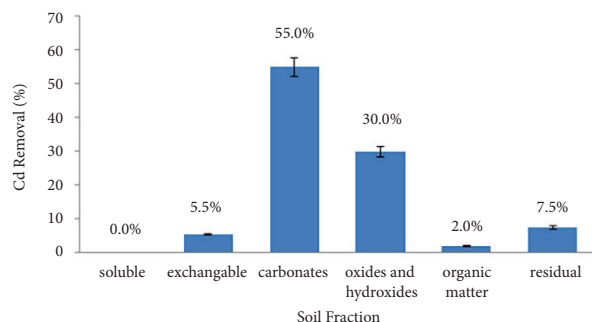

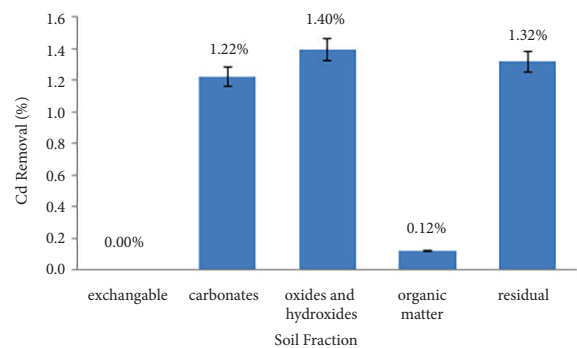Figure 8. Sequential extraction of cadmium from contaminated soil

Figure 9. Sequential extraction of cadmium from contaminated soil after washing with nanofluid (Concentration = 500 ppm, pH = 6.5, Contact time = 24 hr, ratio of soil mass (gr) to nanofluid volume (mL) = 1:100)

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