Effectiveness of Carbonate Content on Removal of Cadmium from Contaminated Soil by Soil Washing Process

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Abstract

This study explained the effect of calcium carbonate on extraction of cadmium from contaminated soil with different extracting agent and surfactant (0.1 M EDTA, 1 M AA, and 1% SDS) (single or mixed extracting agents with surfactant, SDS).The extractedCadmium was more, when 0.1 M EDTAwas used at a pH above 5. Here, the extraction of cadmium from contaminated soil by 0.1 M EDTA decreased with the increase of calcium carbonate content for soil. The extraction of cadmium was moderately effective, when the concentration of acetic acid (AA) was 1.0 M. When the use of 1% SDS alone was ineffective for extraction of cadmium. But, the combination of 1% SDS with 1 M AA was highly effective in the extraction of cadmium. While, the addition 1% SDS to 0.1 M EDTA played only a slight role in the extraction process.

Keywords: Cadmium; Extraction of cadmium,Extracting agent EDTA, SDS, Heavy metal, Soil washing.

الخلاصة

هذه الدراسة وضحت، تأثيركاربونات الكالسيوم على انتزاع الكادميوم من التربة الملوثة مع مساعدات الانتزاع المختلفة و surfactant كمساعدات الانتزاع تستعمل لوحده او مموجه معsurfactant . الكادميوم الذي تم انتزاعه كان اكثر عندما استعمل 0.1مولاري من EDTA في حين كانت الاس الهيدروجيني اكبر من 5 . هنا، انتزاع الكادميوم من التربة الملوثة من قبل 0.1مولاري من EDTA نقصت بزيادة محتوى كاربونات الكالسيوم في التربة. انتزاع الكادميوم كان فعال باعتدالعندما كان تركيز حامض الخليك 1 مولاري. استعمال 1% SDS بمفرده غير فعال في انتزاع الكادميوم، لكن عندما تم مزجه مع 1 مولاري حامض الخليك كانت فالة جدا، في حين اضافة 1% SDS الى 0.1مولاري من EDTA لعب دور طفيف ومحدد في عملية الانتزاع.

الكلمات المفتاحية: الكادميوم، انتزاع الكادميوم، محاليل الانتزاع، غسل التربة، المعادن الثقيلة.

1- Introduction

Heavy metal contamination in soils is one of the world's major environmental problems, posing significant risks to human health as well as to ecosystem, because they cannot be biodegraded when releasing into environment (Chen *et.al*., 2004). Although, cadmium usually has an oxidation state of +2, it also exists in the +1 state. An element may be adsorbedon to metal hydrous oxides, silicates carbonates or soil organic matter, also in this case, the pH is the main factor controlling the adsorption reaction of this element to surface soil. In the solution, the element may be in the solvated form (solvation complex) or complexed with organic or inorganic ligands cadmium poisoning is an occupation hazard associated with industrial processes such as metal plating and the production of nickel- cadmium batteries, phosphate fertilizer, and rainwater.

The fields at different location around Kirkuk refinery in Iraqihave sufferedfrom cadmium and other heavy metals contamination. Ali (2013) investigated some contaminated Iraqi soils and found that the Cd^{+2}concentrationswere in the range 12.6 to 7.39 mg/kg for October and March, respectively, as shown in figure 1. Comparison of this range with the world allowable average 5 mg/kg then makes it clear that both values were higher. Another study in locations as Sultan (2010) was determined the concentrations of heavy metal in soil of the city Baghdad, the study showed that the concentrations of Cd, Ni, Co, Cu, and Pb in soil samples exceeded the permissible limits both locally and globally, then the results shown in Table (1), which indicates the presence of contamination with these elements in the soil of the city of Baghdad.

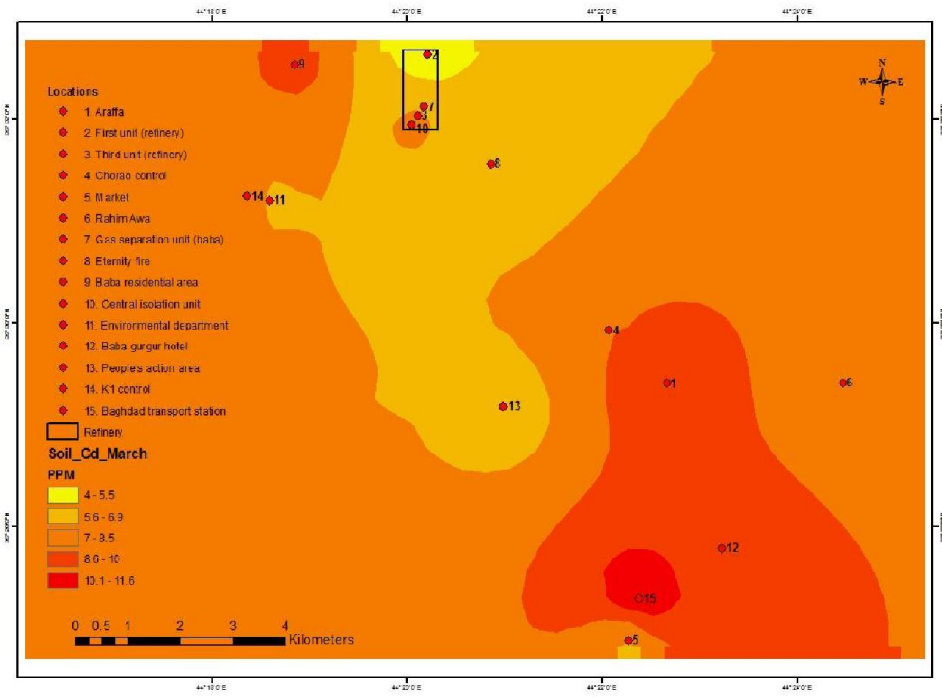

Figure.1:GIS Map showing Cadmium distribution in soil of the studied area in October2010 and March2011(Ali, 2013).

Station designation	**Name of station**	**Cadmium concentration (mg/kg)**
1	Cut check point	3
2	Achammaai	10
3	Al-Rasheed Hospital	2
4	Bab Alsharji	3
5	Al-Wazeeria	5
6	Al-Rashedia control check point	2
7	Al- Mahmudiyah check point	2
8	Al-Durah	2
9	Yarmouk	25
10	Abu Ghraib check point	5
11	Kadhimiya	2
12	Al-Taji check point	2
Average		5.25
Permissible limit (USEPA standards)*		1.6
Permissible limit (Dutch standards)*		0.8

Table 1: Concentration of cadmium in the soil samples of selected stations covered Baghdad city (Sultan, 2010).

*** Saleem *et.al.*, (2011).**

Methods for removing of heavy metal from contaminated soil involve either ex-situ or in-situ treatment systems. Ex-situ treatment included soil washing, which was considered one of the appropriate techniques on-site for removing heavy metals from contaminated soil. Since, heavy metals are mostly adsorbed on surface soil (fine-grained). For ex-situ treatment, when the selected soil is washed as technique for removal of metal ions from soil, then fine-grained soil is detached from the coarse-grained. Thereupon, Chemical extractionsare sometimes introduced in soil washing process to remove heavy metals from soil. These extractions can be: acids, surfactants electrolytes and chelating agents. Chelating agents, as ethylene-diaminetetraacetic acid (EDTA) form stable complexes within variety of heavy metals within a large scale pH.Some of laboratory studies were also determined that EDTA is more effective for removal of cadmium and it leadsto contaminated soils. Among factors, which wereeffective on the extraction of metal from contaminated soil were solubility of heavy metals, strength of EDTA, electrolytes, and processing condition (e.g. pH, and time). Extraction alsodepended on the modes of metal relation within the soil. Unfortunately, these also have disadvantages including persistent in the environment which has precluded their use in remediation of metal contaminated sites, as a cited by (Hsiao *et.al.*,,2007) and(Karthika *et.al.,* 2016), (i.e. Degree of removing of heavy metals from contaminated soil depends mainly on pH; buffering capacity of soil, which was resulting from presence of amount of carbonate in soil).

Another type of extractants was the use of either strong acids (HCl, HNO_3, etc.) or weak acids (acetic acid), there are advantages and disadvantages associated with the use strong acids and weak acid. The disadvantage of the strong acid is able to attack and degrade the soil crystalline structure along contact times. While, the advantage of weak acid was made less damaging to structure of soil and it was an alternative agents for the extraction of heavy metals from contaminated soil. Thus, metals dissolution by weak acids involves mobile metal fraction in the pore solution of soil. Recent studies by Oustan et al.(2011) was investigated the potential of two natural low molecular weight organic acids, oxalic acid (OA) and acetic acid (AA) to remove zinc-cadmium smelting plant area in Zanjan Province-Iran. A tests result explained that oxalic acid extracted greater Zn than Cd and the reverse occurred for acetic acid.

In-situ (on-site) remediation systems all are the groundwater pump-and treat, bioremediation and chemical extraction involved in-situ soil washing.It is not advisable for removing heavy metals from fine-grained soil, because of high CEC and the low soil permeability (Wuana *et.al.,*2010). The present study examined the influence of different percentage of calcium carbonate content coupled with different extracting agents, for application of these extracting solutions to enhance electro-kinetic technology. Therefore, the aim of this study to investigate:

(i) The extractability of cadmium in contaminated soil by single extraction (AA, EDTA, and SDS), and mixed extraction (AA+SDS, EDTA+SDS).
(ii) To assess the possibility of removing heavy metals at different carbonate content from contaminated soil.

2- Materials and Method

2.1 Soil

Kaolin was deemed as the perfect soil for this study as it represents lower CEC (cation exchange capacity), which leads to a lower capacity in comparison to other clay minerals. Average particle size of 2.5 μm and specific surface of 20 m^2/g. X-ray fluorescence analyses revealed the presence of 36% SiO_2, 55% Al_2O_3 and 0.5% TiO_2,

where pH was 7.3. In this study a set of samples were prepared by adding for different percentage of calcite (laboratory added calcite). Initial concentration of calcite in kaolinite sample was 0.9%. Therefore, the total calcite content in a set of samples prepared were 5%, 20%, and 45%, respectively.

2.2 Soil Contaminated

To simulate the kaolin's cadmium contamination, a solution of $Cd(NO_3)_2.4H_2O$ (which are manufactured by Scharlau Company/European union) was prepared and added to the specimen to obtain representative cadmium concentration of 250 mg/kg and initial moisture content equals to 40% by weight, 0.68 g of $Cd(NO_3)_2.4H_2O$ dissolves in 400 ml of distilled water and this solution was added to 1 kg of dry soil. In the meantime, the soil specimen was kept as wet through period 3 day in order to ensure completeness and even exposure of every soil particle to contamination. Then, soil of specimen was dried.

Initially parameters were examined: pH in a 1:5 (soil/distilled water), the carbonate content of soil was determined with titration (Pansu, 2003).

2.3 Soil Washing Experiments

Batch extraction experiments were conducted using extraction solution (chelating agent as 0.1 M EDTA (because of the increase of EDTA dose, only a small portion was effectively transformed into metal-chelant complexes, while the excess remained in free form), involves organic acid as acetic acid, 1M AA and surfactant as 1 % SDS) at a soil to solution ratio of 1:8 or, specifically, five grams of the soil with 40 ml of extracting solution in polyethylene tube. Here are some test that mix between chelating agent or organic acids with surfactant was as follows: by adding 20 ml of chelating agent(EDTA) or organic acid (Acetic Acid) solutions at concentration of 0.1 M and 1 M, respectively, with 20 ml of 1% of surfactants (SDS) according to the procedure reported by (chang *et.al.,* 2005). Four series of tests (series-1, series-2, and series-3) were performed with different factors such as: the main factor in the experiments was amount of calcite where percentages of different prepared soilwere addedto mixture of soil and solutions pH, as listed in table.2. Series-1 was included the tests (P-1 to P-6) that studies the removal of cadmium from contaminated soil by using extracting solutions like 1 M AA, 0.1 M AA+1% SDS, 1% SDS, and DW, respectively. While, series-2 was included the tests (P-7 to P-11), these tests were carried out by using extracting agents (EDTA) and surfactant (SDS) for removing the cadmium from contaminated soil. Finally, series-3 included the tests (P-12 to P-16) was repeated using organic acid (AA), and extracting agents (EDTA) with surfactant (SDS). Then, solutions pHwere maintaining around value of 3, 5, and 7.5, respectively. All testswere adjusted by using 1 M HNO_3 or 1 M $NaOH_2$. Subsequently, these tubes wereshaken in orbital shaker (model: LSI1) at 180 rpm for 6 hr. After this mixture was shaken for a few minutes and the solid-solution mixture was centrifuged at 2000 rpm for 10 min. The sample was filtered on the paper No.42 and save it in polyether container; and the concentration of cadmiumin the solution was determined by Atomic Absorbance Spectrophotometry (AAS). Percent of each metal removed was calculated using an equation similar to the one used by Reddy and Chinthamereddy (2000) and is shown below:

$$\text{Percentage metal removal} = (C_l V_l / C_s m_s) * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where C_l and C_s are the concentrations of metal in supernatant (in mg/L) and soil (mg/kg), respectively; $V_l$is the volume of supernatant (in L) and m_s is the dry mass of the soil (in kg).

Table.2: Illustrating factors for operation experiments affect soil washing process.

Series	Experiment designation	Extraction solution	pH
Series-1 (kaolin+5% carbonate)	P-1	1% SDS	3, 5, and 7.5
	P-2	0.1 M EDTA	
	P-3	0.1M EDTA+1% SDS	
	P-4	1M AA	
	P-5	1M AA+1% SDS	
	P-6	D.W	
Series-2 (kaolin+20% carbonate)	P-7	1% SDS	3, 5, and 7.5
	P-8	0.1 M EDTA	
	P-9	0.1M EDTA+1% SDS	
	P-10	1M AA	
	P-11	1M AA+1% SDS	
Series-3 (kaolin+45% carbonate)	P-12	1% SDS	3, 5, and 7.5
	P-13	0.1 M EDTA	
	P-14	0.1M EDTA+1% SDS	
	P-15	1M AA	
	P-16	1M AA+1% SDS	

3. Results and Discussion

3.1 Effect of pHand surfactant with chelating agents on extraction of cadmium

Figure 1 (a&b) illustrated the cadmium concentration extractable at 1% SDS mixed with 1 M AA or 0.1 M EDTA within range the pH of the soil-solution mixture ranged between 3 to 7.5, while contaminated soil with initial concentration of cadmium was equal to 250 mg/kg. As shown in figure 1 (a) cadmium concentration extractable was gradually increased from 80 to 170 mg/kg as performed in test of P-5, where 1% SDS+1 M AA was used as an extraction solution . In other words, higher amount of extracted cadmium from contaminated soil was obtained at pH the soil-solution mixture 7.5 as compared to others values of pH in this study. While, the lower amount of cadmium concentration extractable occurred when 1 M AA was applied as chelating agents in the test of P-4 as compared with cadmium concentration extractable at the addition of 1% SDS to 1 M AA. The results prove that the cadmium concentration extractable for test P-1 (when was using 1% SDS as washing solution) decreased from 47.5 to 37.5 mg/kg within the tests of series-1 at 5% carbonate content.Figure 1 (b) showed that, the results of cadmium concentration extractable when 0.1 M EDTAwas used as chelating agents with and without 1 % SDS as surfactant was very effective in mobilizing of Cd^{+2} in the tests of series-1 at 5% carbonate content, because of ability of EDTA for mobilization of cadmium from the carbonate-bound fraction (i.e., making the precipitate soluble and reactive with heavy metals),.These results were obtained at the pH of soil-solution mixture higher than 5. Whereas, when the pH of soil- solution mixture is below 5, EDTA becomes less soluble and precipitates as cited by Mohanty and Mahindrak (2011).

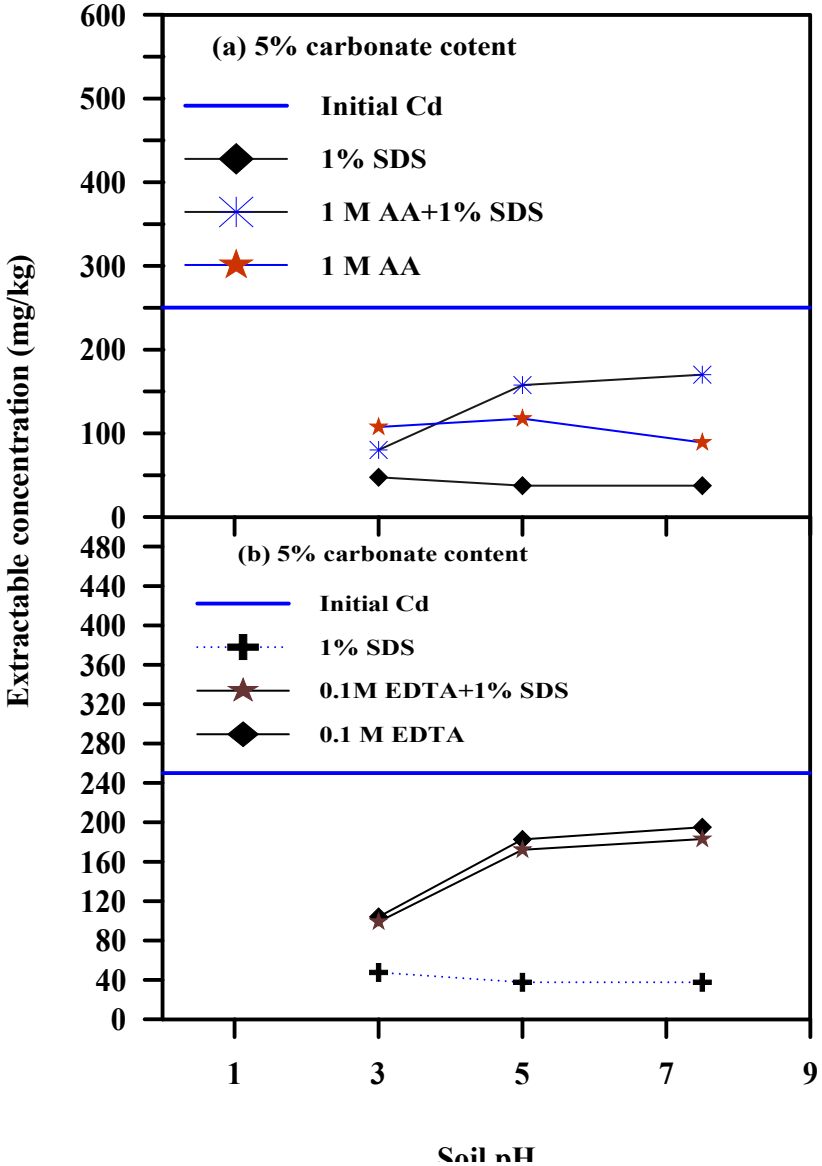

Figure 1: Effect of pH on extractable concentration cadmium by using (a) SDS and AA, (b) SDS and EDTA.

3.2 Effect of carbonate content with extracting solution on extraction of cadmium

Figure 2 shows that, effects of extracting solutions (0.1 M EDTA, 1% SDS, 1 M AA, and DW) on desorption of cadmium from contaminated soil within carbonate content 5% were studied for all at pH values 3, 5, and 7.5. As it can be seen in this figure, the highest cadmium concentration extractable by using 0.1 M EDTA with soil/solution ratio 1:8 for 6 hr. the extraction of solution observedof about 195 mg/kg at the pH value of 0.1 M EDTA was7.5. Also, the results elucidated ability of 0.1 M EDTA for extracting greater amount of cadmium from contaminated soil due to EDTA possesses a high complexation capacity and most of heavy metal migrating from carbonate-bound fraction to residual fraction (Heidari *et.al.,* 2015),this results in low carbonate content. While, the result of tests with using 0.1 M EDTA+1% SDS, showed limited enhancement in cadmium extraction when compared with cases that use 0.1 M EDTA alone, similar results have also been reported by Olusegun and Oluwafemi (2012). The sorption of surfactants (SDS) should also be considered because the amount of the adsorbed surfactant may reduce it solubilization ability and

cause secondary contamination (Giannis *et.al.,* 2007). It was signified from the results of test P-4 and P-5 (using 1 M AA and 1 M AA+1% SDS as extracting solution, respectively),that the extraction concentration of cadmium obtained was117.5 mg/kg (for test P-4 at pH value 5) and 170 mg/kg (for tests P-5 at pH value of 7.5). This indicated that the extraction strength of acetic acid increased when it is mixed with proportion of 1% SDS of the soil under study with low carbonate content (5%). On the basis of tests which reported in table 2, where series-1 was included the test P-6 was conducted by using distilled water as an extracting solution that serves as a baseline. Thereupon, DW was unable to efficiently extract cadmium from soil in spite of the existence of low calcium carbonates content.

As Figure 3 shows,the effects of extracting the solutions (0.1 M EDTA, 1% SDS, and 1 M AA) on desorption of cadmium from contaminated soil within calcium carbonate content 20% were studied for all pH values 3, 5, and 7.5. As it can be seen from the figure, extractable cadmium concentration were obtained in tests P-7, P-8, P-9, P-10, and P-11 were conducted by using 1% SDS, 0.1 M EDTA, 0.1 M EDTA+1% SDS, 1 M AA, and 1 M AA+1% SDS respectively, as extracting solution. The plateau of extractable cadmium concentration was 32.5,145, 132.5, 87.5, 107.5, respectively, corresponding to pH values for each solution of extraction 3, 7.5, 7.5, 3, and 5 respectively. It seems that, superior extraction of cadmium occurred by using 0.1 M EDTA as compared with others from solutions of extraction.

The results shown in Figure 4 indicate that when 0.1 SDS solutions at pH 3 achieved about 16 mg/kg of cadmium extracted from contaminated soil within series-3 (calcium carbonate content 45%). However, when 0.1 M EDTA at pH 5 occurred it increases in the amount of extractable cadmium concentration to 83 mg/kg, as compared with others for extracting of solution. This solution proved to be more effective in the removal of cadmium from a contaminated soil. This may be attributed to the fact that EDTA which form effective complex with Cd^{+2} (in particular under acidic circumstances, because cadmium is attached strongly to calcium carbonate) resulting low mobilization of Cd^{+2} from the soil as compared to case when the calcium carbonate content is low (such as 5% carbonate content). Whereas, 0.1 M EDTA and 1% SDS were mixed as extractant solution, the cadmium concentration extractable was lower than it is when 0.1 M EDTA was used as a lone extracting solution. This mixture is not effective for cadmium extracting since only 78 mg/kg at pH 5 was observed. Then, a 1 M AA at pH 3 could extract about 61 mg/kg of cadmium from contaminated soil as shown in figure. Meanwhile, the combination of 1 M AA and 1% SDS was employed. There was more increase in the amount of cadmium extracted (74 mg/kg at a mild acidic condition) than it is the case when 1 M AA was used as extracting solution. Here, it was notable that, the combination 1% SDS with 1 M AA would be highly effective for extraction of cadmium at appreciated amounts as it is shown in Table 3.

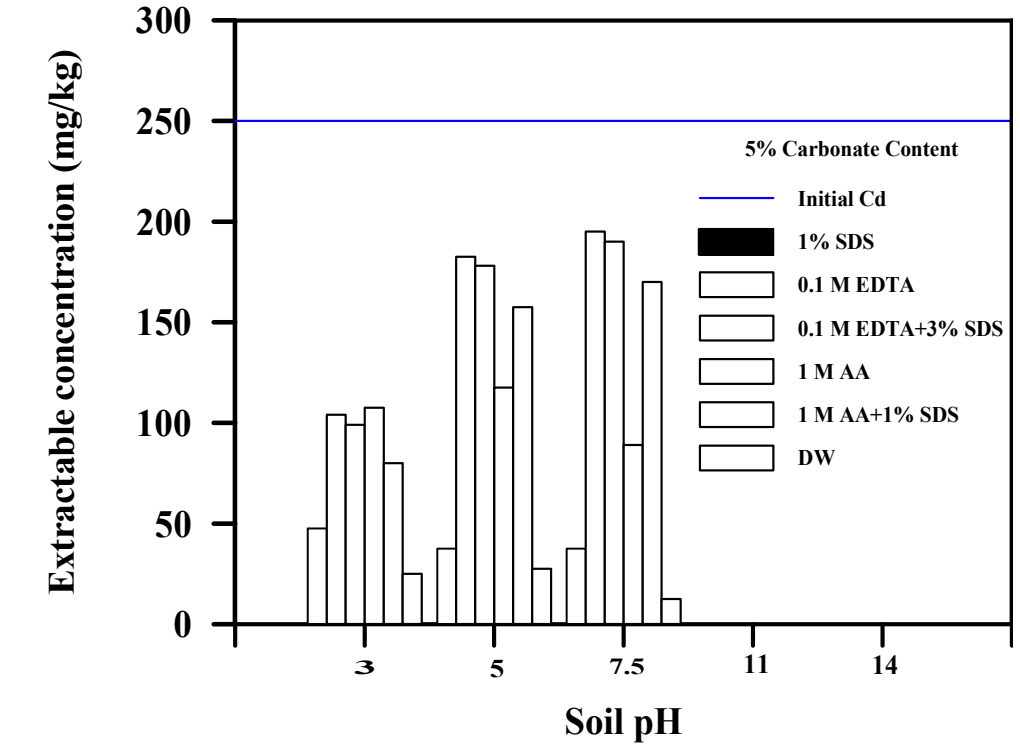

Figure2: Cadmium concentrations extractable from soil, it contains 5 % calcium carbonate as function of pH with using 0.1 M EDTA, 1%SDS, and 1 M AA.

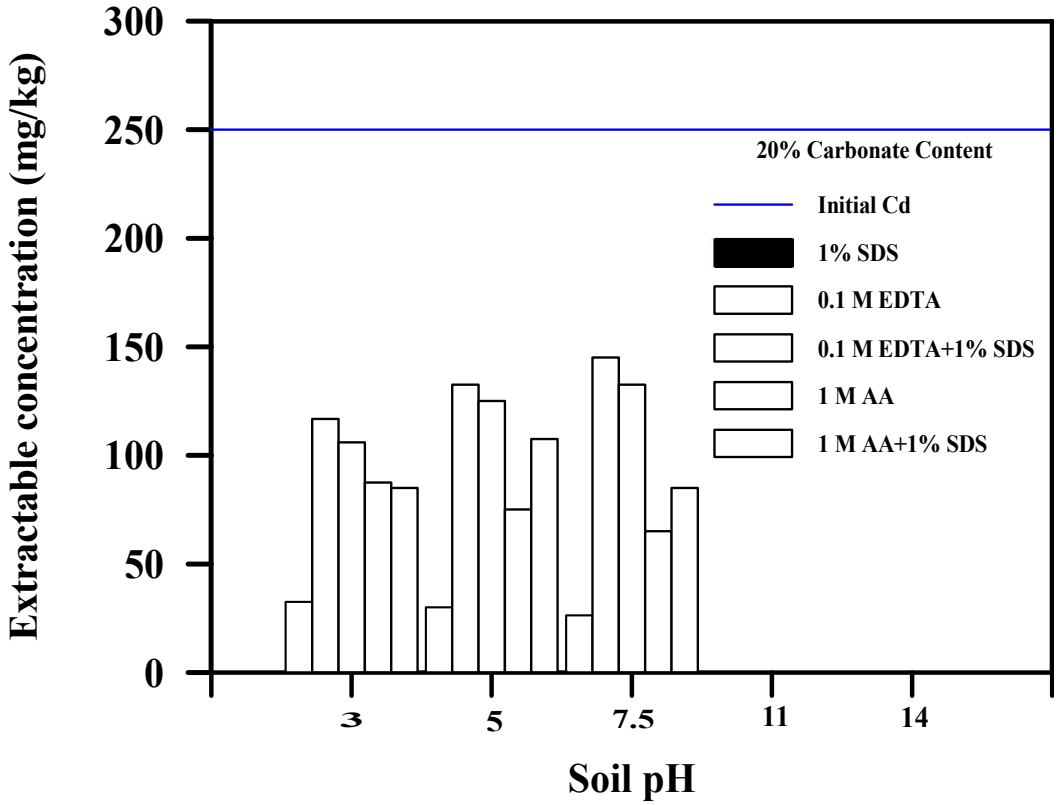

Figure 3: Cadmium concentrations extractable from soil, it contains 20 % calcium carbonate as function of pH with using 0.1 M EDTA, 1%SDS, and 1 M AA.

Table 3: Cadmium concentration extractable from soil in this study.

Extractants	pH	Cadmium concentration extractable (mg/kg) at difference percentage for calcium carbonate content		
		5%	20%	45%
Single extracting 1 M AA	3	107.5	87.5	61
	5	117.5	75	59
	7.5	89	65	53
Mixed extracting 1 M AA+1% SDS	3	80	85	63
	5	157.5	107.5	74
	7.5	170	85	69

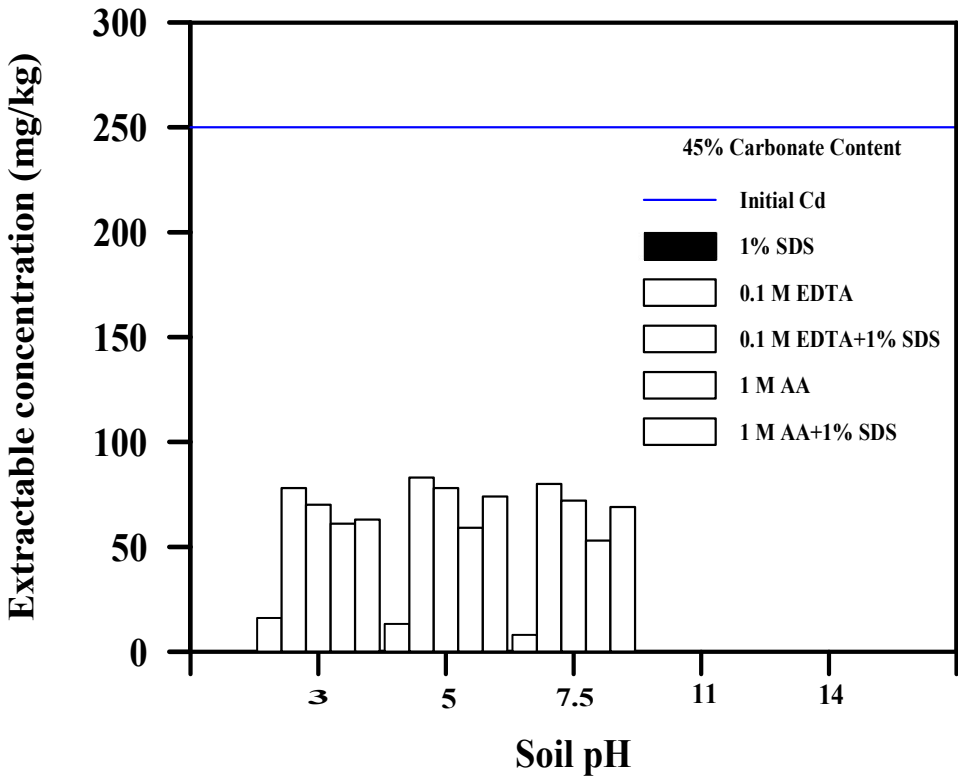

Figure 4: Cadmium concentrations extractable from soil, it contains 45 % calcium carbonate as function of pH with using 0.1 M EDTA, 1%SDS, and 1 M AA.

4. Conclusion

This study explained effect of calcium carbonate on extraction of cadmium from contaminated soil with (0.1 M EDTA, 1 M AA, and 1% SDS) single or mixed extracting agents with surfactant (SDS). High extraction of cadmium occurred with 0.1 M EDTA at a pH above of 5. Here, the extraction of cadmium from contaminated soil by 0.1 M EDTA decreased with it was increaseof calcium carbonate content of soil. The extraction of cadmium was moderately effective when 1 M AA was employed. When 1% SDS alonewas used, it was ineffective for extraction of cadmium. But, the combination of 1% SDS with 1 M AA was highly effective in the extraction of cadmium. While, the addition of 1% SDS to 0.1 M EDTA played only a slight role in the extraction process.

References

Ali L. A. A. (2013) "Environmental impact assessment of Kirkuk Oil Refinery" Ph. D Thesis, University of Baghdad, College of Science, Department of Geology.

Chang S. H., Wang K. S., Kuo C. Y., Chang C. Y., and Chou C. T., (2005) "Remediation of metal contaminated soil by an integrated soil washing electrolysis process", Soil& Sediment Contamination, 14:559-569.

Chen Y., Shen Z., Li X. (2004) "The use of vetiver grass (vetiveriazizanioides) in the phytoremediation of soils contaminated with heavy metals" Applied Geochemistry, Vol.19:1553-1565, October.

Giannis A., Gidarakos E., and Skouta A.(2007), "application of sodium dodecyl sulfate and humic acid as surfactants on electrokinetic remediation of cadmium –contaminated soil", Desalination, N.211, P:249 – 260.

Heidari S., Oustan S., Neyshabouri M. R., and Reyhanitabar A., (2015) "Mobilization of heavy metals from contaminated calcareous soil using organic acids", Malaysian Journal of Soil Science, Vol. 19:141

Hsiao K. H., Chang Y. P., and Hseu Z. Y. (2007) " Time effect on chemical fractions of cadmium and lead with EDTA extraction in contaminated soil", J. Envirom. Eng. Manage, 17(6), 441-447.

Karthika N., Jananee K., Murugaiyan V., (2016)" Remediation of contaminated soil using soil washing- a review", Int. Journal of Engineering Research and Application, Vol.6, Issue 1 (part-2),P:13-18.

MohantyB. ,andMahindrakar A. B., (2011) "Removal of heavy metal by screening followed by soil washing from contaminated soil", International Journal of Technology and Engineering System (IJTES), Vol.2, No.3, Jan.-March.

Olusegun A. O.&Oluwafemi A. S. (2012) "Evaluation of chelating agents for the removal of heavy metals from contaminated soil", Global Journal of Bio-Science & Biotechnology, Vol.1, (2):152-156.

Oustan S., Heidari S., Neyshabouri M. R., Reyhanitabar A., Bybordi A. (2011) " Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelatings agents", International Conference on Environmental Science and Engineering, IPCBEE, Vol. 8, Singapore.

Pansu M. (2003) "Handbook of Soil Analysis mineralogical, Organic and Inorganic Methods", Springer Berlin Heidelberg New York.

ReddyK.R., and Chinthamreddy S. (2000)“Comparison of extractants for removing heavy metals from contaminated clayey soils” Soil Sediment Contaminat., Vol.9:pp.449-462.

Salman K. H. (2007) "Study in the environmental situation for Al- Basra Governorate" Ph.D Thesis, college of Science, Baghdad University.

Sultan, M.A., (2010) "Evaluation of soil pollution by heavy metals in Baghdad city using GIS". 1St International Conference Applied Geological Congress, Islamic Azad University, Iran, 852-863.

WuanaR. A.; OkieimenF. E.;.ImborvunguJ. A., (2010),"Removal of heavy metals from a contaminated soil using organic chelating acids", Int. J. Environ. Sci. Tech., 7 (3), P:485-496.