

The Use of Okra as a Coagulant and Coagulant Aids in the Removal of Heavy Metals of Solid Waste Leachates

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ABSTRACT

Coagulation-Flocculation processes play an important role in the treatment of water and wastewater. Aluminum sulfate (alum) and polyelectrolyte (polymer) are the common chemical coagulants which are used in this process. The produced leachate in waste disposal places is considered to be one of the highly contaminated resources from the physical, chemical, and biological point of view.

In Sulaimaniah, Tanjaro was found to be one of those solid waste landfill areas. Okra is used for the treatment of raw leachate samples that obtained directly from **Sulaimaniah – Iraq** solid waste sanitary landfill area. Fresh solid waste samples of the leachates were taken and tested for their heavy metals concentrations contents. It was found that the leachate contains a high amount of heavy metals of cadmium, chromium, copper, nickel, and zinc. By using conventional coagulants of alum, polymer and natural indigenous okra (as a primary coagulant or in combination with the other two primary coagulants) and by the jar testing, the best concentrations and pH values of the coagulants were determined. Analyzing the results, it was found that the optimal pH values were 6.65, 9.00 and 7.00 for alum, polymer and okra, respectively. In addition, the best dose of alum was 1400 mg/L in which a removal of heavy metals yielded 45-80 %, while the best dose of polymer was 500 mg/L in which a removal of 70-95% was achieved. For okra, the best dose was 500 mg/L in which a removal of heavy metals yielded 20-100%. It was found that okra has an efficient coagulation power with respect to alum and polymer in removing heavy metals elements in solid waste leachates.

Keywords: Coagulation , Natural Coagulants , solid waste Leachate, Okra, Heavy Metals.

إستخدام البامية كمخثرات و مساعد مخثرات في إزالة المعادن الثقيلة الملوثة من راشح النفايات الصلبة

الخلاصة

ان عمليات التخثير و التلييد تلعب دورا مهما في مراحل معالجة المياه و مياه الصرف الصحي و تعتبر استخدام مادتي الشب و البوليمر من المواد الكيميائية التقليدية التان تستخدمان في هكذا عمليات للتصفية . ان رواشح النفايات الصلبة نتيجة طرحها في مواقع الطمر الصحي تعتبر إحدى أهم الملوثات لمصادر المياه الطبيعية من وجهات النظر الفيزيائية والكيميائية والبايولوجية و وجدت منطقة التانجرو الواقعة في السليمانية من إحدى هذه المواقع . استخدمت في هذا البحث البامية في معالجة النماذج الماخوذة من راشح المخلفات الصلبة من منطقة تانجرو مباشرة . النماذج التي أخذت كانت جديدة و فحصت محتوى المعادن الثقيلة الملوثة فيهن حيث كانت قيمها عالية جدا من حيث الكاديوم , الكروميوم , النحاس , النيكل و الزنك . من ثم استخدمت المواد المخثرة التقليدية من الشب و البوليمر و مادة البامية (بمفردها تارة و مع إحدى المواد التقليدية تارة أخرى) و بإستخدام جهاز ال (Programmable Jar Tester) و لإيجاد أفضل قيمة للرقم الهيدروجيني (pH) و أفضل تركيز للمواد المخثرة و المقارنة بينهم . بعد تحليل النتائج, وجدت ان افضل قيمة للرقم الهيدروجيني كانت 6,65, 9,00 و 7,00 للشب , البوليمر و البامية على التوالي . كذلك افضل قيمة لتركيز المخثرات كانت 1400 ملغم /لتر للشب والتي ادت من 45الى 80 بالمائة إزالة للمعادن الثقيلة الملوثة و 500 ملغم / لتر للبوليمر والتي ادت من 70الى 95 بالمائة إزالة لنفس تلك المعادن في حين كانت 500 ملغم / لتر والتي ادت من 20الى 100 بالمائة إزالة لنفس تلك المعادن . وجدت ان البامية لها قدرة تخثيرية جيدة وعالية نسبة الى مثيلاتها من الشب و البوليمر من حيث إزالة المعادن الثقيلة الملوثة الموجودة في راشح المخلفات الصلبة .

INTRODUCTION

Leachate from solid waste disposal area is considered as one of the highly contaminated resources from the physical, chemical, and biological point of view. The discharges of these leachates from sanitary landfill areas can lead to serious environmental problems, as they may percolate through to surface waters, soils and sub-soils with a very high concentration of heavy metals like cadmium, nickel, chromium, zinc and copper which cause extensive pollutions of ground and surface waters if they are not properly treated. Tanjaro in Sulaimaniah city (Northern of Iraq) is one of those sanitary landfill areas that discharging its leachate to upstream of Darbandikhan lake (south-east of Sulaimaniah). Darbandikhan Lake is the only water resource for most towns located downstream this lake such as; Darbandikhan, Kalar, Kifri, Diyala and other cities till Baghdad. Therefore, the incurred harm by these metals to the soil and water resources makes the importance of reducing their levels in leachate clear. Leachate treatment techniques can be classified as: combined treatment with domestic sewage, biological treatment and physic-chemical methods [Berrueta, 1996]. Although some of the pollutants in leachate can be removed by biological treatment, but heavy metals and non biodegradable parts of organic matter pass the biological processes. The coagulation / precipitation are the most common method of removing soluble metals. In precipitation reactions, chemicals are added to transform dissolved constituents to form insoluble precipitates. Precipitation can be used to remove most metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, zinc) and many anionic species (phosphates, sulfates, fluorides). So better removal

efficiencies can be achieved by using chemicals. In this study, the use of an alternative to those chemicals, such as okra, a natural indigenous material is used to avoid the formation of complex hydrocarbon materials in the produced sludge.

Table (1) The most important process for leachate treatment [Asadi,2008].

Activated Sludge	Organic compounds removal (biological)
Attached growth (trickling filter and RBC)	Organic material removal (biological)
Anaerobic Lagoons	Organic material removal (biological)
Neutralize	pH control
Precipitation	Heavy metals removal
Oxidation	Organic & inorganic compounds removal (chemical)
Ion exchange	Removal of soluble inorganic compounds (physico-chemical)
Ultra filtration	Bacteria removal
Reverse osmosis	Wastewater Dilution

As it is shown in Table (1), precipitation is a useful process to reduce the amount of heavy metals like lead, cadmium, zinc, and etc. To precipitate the heavy metals in leachate, the Jar test is used since by this test the best amount of coagulants in heavy metals precipitation can be determined. Using this test, the optimal pH level in heavy metal elimination process will be obtained. In the next step, all the beakers are adjusted to the optimal pH level and the coagulants like alum, polymer, and okra will be added. Computing the efficiency of elimination process, the amount of best material in heavy metals precipitation will be obtained.

EXPERIMENTAL WORK

Typical jar tests were run for this study using jar test apparatus is the PB-900™ programmable jar tester manufactured by Phipps and Bird Company / USA .

SOLUTIONS PREPARATION

All the solutions of alum and polymer coagulants and the okra suspensions preparations were prepared and used in the jar test runs daily and as in the followings :-

ALUM SOLUTION

Alum (which was brought from Sulaimaniah water treatment plant) was prepared by dissolving 10 g of the powdered alum into one liter of distilled water and stirred and mixed well to produce 1% solution strength. Thus each 1 ml of this solution is equivalent to 10 mg of alum.

POLYELECTROLYTE SOLUTION

Polyelectrolyte (also brought from Sulaimaniah water treatment plant) was prepared by dissolving 1 g of the powdered polyelectrolyte in one liter of distilled water and also mixed and stirred very well to produce a 0.1% strength solution. Thus each 1 ml of the solution is equivalent to 1mg of polyelectrolyte.

OKRA SOLUTION

The natural coagulants studied were all in the following manner (AlSamawi and Shokrola, 1996):-

- 1- The raw material coagulant was dried very well under the light of sun and cleaned of any fiber materials.
- 2- A 0.90 g of the powdered okra was weighed and mixed with 0.10 g of Soda Ash.
- 3- The powder was transferred to a flask and cleaned tap water was added to produce a 0.10 percent suspension.
- 4- After that the suspension was mixed by the means of magnetic stirrer for about 5 minutes to promote water extraction from flocculants.
- 5- Then it was filtered and set aside and it was ready to use.

HEAVY METAL ELEMENTS DETERMINATION

To perform the experiments, the leachate samples were brought to the laboratory in sufficient quantities from the waste disposal place (Sulaimaniah Solid Waste Disposal-Site). The experiments and tests performed on values of the heavy metal element concentrations (Zn , Ni , Cu , Cr , and Cd) in the solid waste leachate by the means of AAnalyst 200 atomic absorptions device . Also, the conductivity, total dissolved salts TDS and temperatures were measured for all the leachate samples before and after the processes of coagulation and flocculation and during the time periods of taking samples for the settling velocity tests. These measurements were obtained by the use of the Oakton® pH/CON 510 series benchtop, NOVA-TECH International, USA. The samples were taken to the laboratory in 20 liter plastic bottles. Parameters such as initial pH of the samples, heavy metal concentrations (Nickel, Cadmium, Chromium, Zinc and Copper) solid concentrations such as TDS were determined according to standard methods of examination of water and wastewater [AWWA, 1998].

LEACHATE SAMPLING

The raw leachate samples were obtained directly from Sulaimaniah solid waste sanitary landfill which is located in Tanjaro 10 km south west of the city center (35°29'14.25"N, 45°26'08.09" E, and 691 m above mean sea level with altitude accuracy of 19.5 m).The location of the area where fresh solid waste is deposited is shown in Figure (1).

COAGULATION AND FLOCCULATION TESTS

The jar test apparatus is the PB-900™ programmable jar tester manufactured by Phipps and Bird Company / USA. It was used in the experiments. The experimental

process consisted of three subsequent stages : the initial rapid mixing stage took place for 3 minutes at 120 rpm , the following slow mixing stage for 15 minutes at 20 rpm , while the final settling step lasted for another 45 minutes [Eckenfelder, 1989].



Figure (1) Location of the Sulaimaniah solid waste landfill area.

Leachate samples were collected from the sanitary landfill of Tanjaro-Sulaimaniah. The first phase of the experimental scheme focused on the analysis of heavy metals content of the leachate wastewater. The results of these tests are shown in table (2).

Table (2) Composition of the investigated solid waste leachate

Constituents	Tested samples		Standard values*	
	Mean +SD	Range	Concentration Range	Typical Concentration Range
pH	6.51±0.06	6.47-6.57	3.70-8.80	5.00-7.00
TDS mg/L	15633±2914	12,300-17,700	584-44,900	1,000-20,000
Conductivity μS/cm	33,600±2,100	31,300-33,600	1,400-17,100	2,000-8,000
Cadmium (Cd) mg/L	2.4±1.9	1.02-3.70	0.03-17.00	0.00-0.10
Chromium (Cr) mg/L	0.9±0.1	0.82-1.02	0.02-18.00	0.05-1.00
Copper (Cu) mg/L	0.5±0.1	0.343-0.59	0.005-9.90	0.02-1.00
Zinc (Zn) mg/L	16.8±5.9	10.08-21.20	0.06-370	0.50-30.00
Nickel (Ni) mg/L	6.2±0.2	5.97-6.42	0.02-79.00	0.10-1.00

*Based on data collected by U.S. army corps of engineers, construction engineering research laboratory technical manual 5-814-5, sanitary landfill, 15 January 1994. From table (2), the followings can be noted in comparison to the general characteristics of leachate wastewater in the U.S.A. as reported by the department of the USA Army in their technical manual 5-814-5 on sanitary landfills of 1994:-

- 1- The pH value of the leachate wastewater was found to be within the reported range of pH values of leachate wastewater in U.S.
- 2- The total dissolved solids content (TDS) was found to be with the range of values for such parameter, however the values observed were close to the higher limit of the range of values. These values indicated that the leachate may be classified as fresh or raw according to references [Tchobanoglous, 2002].
Similar high values of TDS were reported by Zazouli and Yousefi (2008) and Asadi (2008) for leachate wastewater from sanitary landfills in Iran.
- 3- Conductivity values for Tanjaro sanitary landfill leachate are found to be much higher than those reported by the Technical Manual for leachate conductivity in U.S. This is in agreement with the finding for TDS values.
- 4- Concentration values for heavy metal cadmium (Cd) were found to be high in comparison with values for concentration of (Cd) in leachate wastewater in the U.S. In addition, such high values exhibited high variation in comparison with the solid wastes buried in this landfill.

- 5- Chromium (Cr) concentrations in the leachate from Tanjaro sanitary landfill were found to be rather high in comparison to that for leachate wastewater from U.S. sanitary landfills.
- 6- Copper (Cu) and zinc (Zn) concentration values were found to be within the range values of such heavy metal concentrations in leachate from American sanitary landfills.
- 7- The heavy metal nickel (Ni) concentrations in leachate from Tanjaro sanitary landfill were found to be much higher than values of concentrations of Ni in leachate from American sanitary landfills.

The presence of Cadmium (Cd) and Nickel (Ni) in high concentrations in leachate wastewater of the Tanjaro sanitary landfill needs a forensic study to be conducted to determine the source of such concentrations. Elimination of or treatment of such concentrations at its origin would be more practical and feasible. The composition of the investigated leachates from the above results is shown in the Table (2). Taking into account the high concentration of the heavy metals, the pH values of 6.51 ± 0.06 and the high content of the TDS (15633 ± 2914) mg/L the leachate was classified as raw or fresh leachate [Tchobanoglous, 2002]. So, this leachate displayed high concentration of contaminants. Similar heavy metal concentration levels have also been reported by Asadi (2008). The chemical composition of the leachate showed that an important content of heavy metals concentration can exhibit considerable temporal variation. The variations of leachate characteristics were attributed to variations in the composition of the deposited solid wastes, moisture and decomposition type. From Table(2); it can be deduced that the fresh leachate correspond to the acidic phase of decomposition.

In addition, the comparison of the average values of heavy metal concentrations in the leachate with the guidelines from USEPA according to water irrigation and agricultural standards shows that the concentration of heavy metals in leachate exceeds the maximum values allowed. The minimum and maximum concentrations of heavy metals were 0.5 ± 0.1 mg/L and 16.8 ± 5.9 mg/L related to Cu and Zn, respectively. This result indicated that sources of Zn in solid wastes are more than Cu and the others.

BEST PH VALUES

Samples of collected leachate wastewater were placed in beakers and subjected repeatedly to a standard jar test using the following coagulants

- i- Alum [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$] at a dose 1400 mg/L.
- ii- Polyelectrolyte [Cationic Ferrocril ® 8766 T]. Its molecular weight is $5-6 \times 10^6$ and its medium cationic at a dose of 500 mg/L.
- iii- Okra with a dry solid content giving a dose of 500 mg/L.

Each beaker in the set of the standard jar test apparatus had its pH adjusted to a different value. Figures (2) to (4) show the results of the coagulation- flocculation and settling results for the different heavy metals. From these figures, the best value of the pH for the removal of each heavy metal with one of the three coagulants was possible to determine. The study of all figures indicated that the best pH for all three coagulants was possible to assume to be 7.00 when each was used as a primary coagulant.

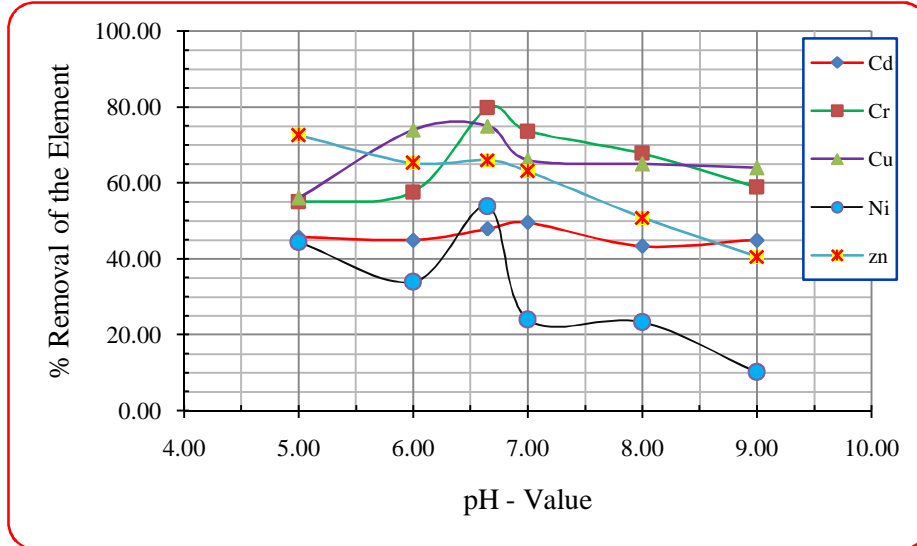


Figure (2) The effect of pH values on the removal of total investigated heavy metals with initial dose of 1400 ppm Al₂(SO₄)₃.18H₂O.

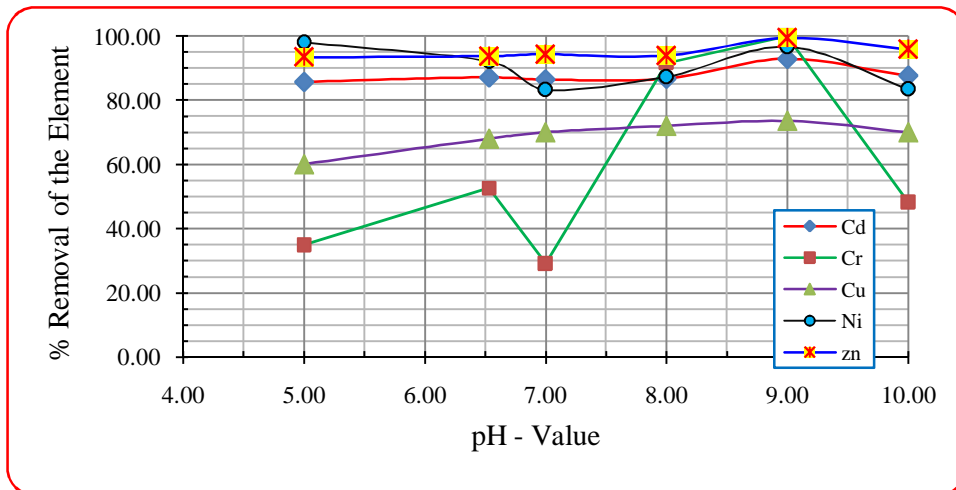


Figure (3) The effect of pH values on the removal of total investigated heavy metals with initial dose of 500 mg/l polymer.

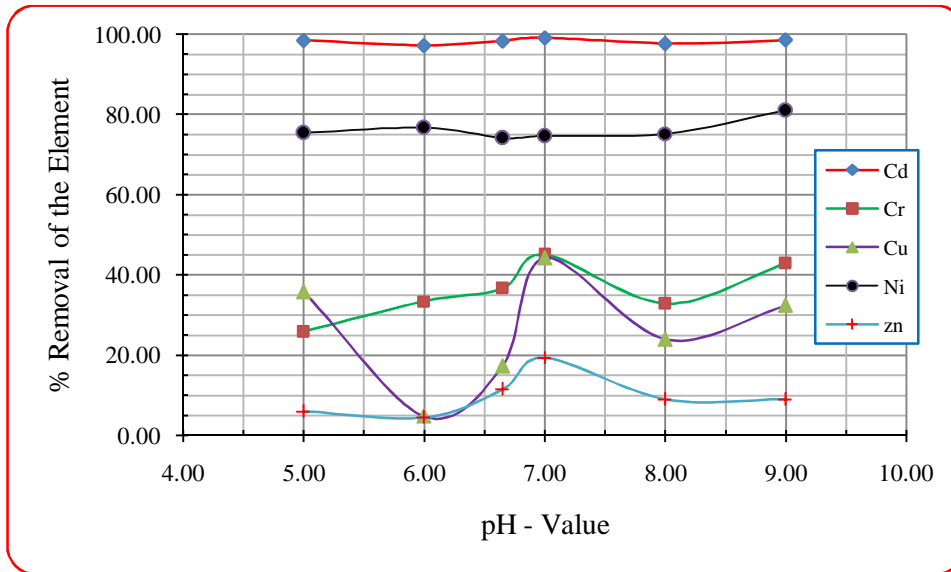


Figure (4) The effect of pH values on the removal of total investigated heavy metals with initial dose of 500 ppm okra.

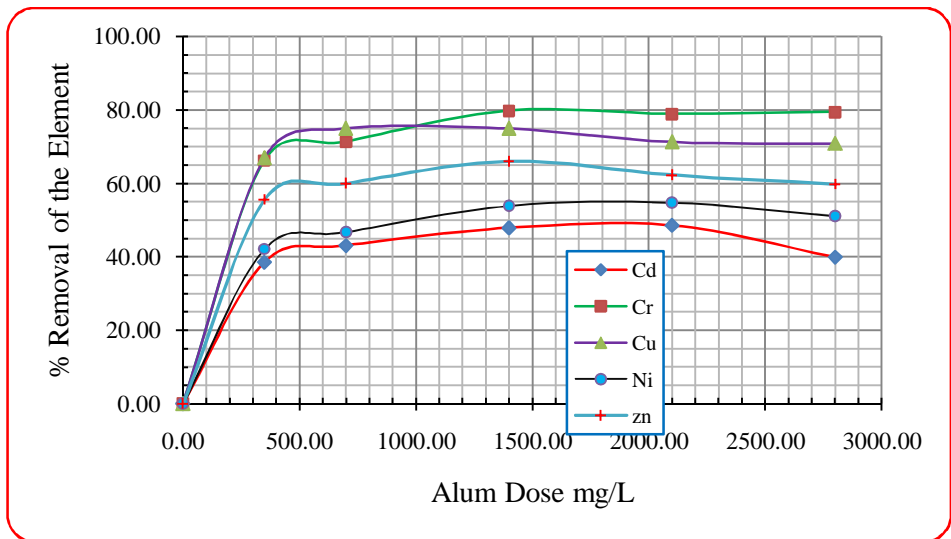


Figure (5) The effect of Alum coagulant dosages at best pH of 6.65 on the heavy metals removal efficiencies of investigated leachate.

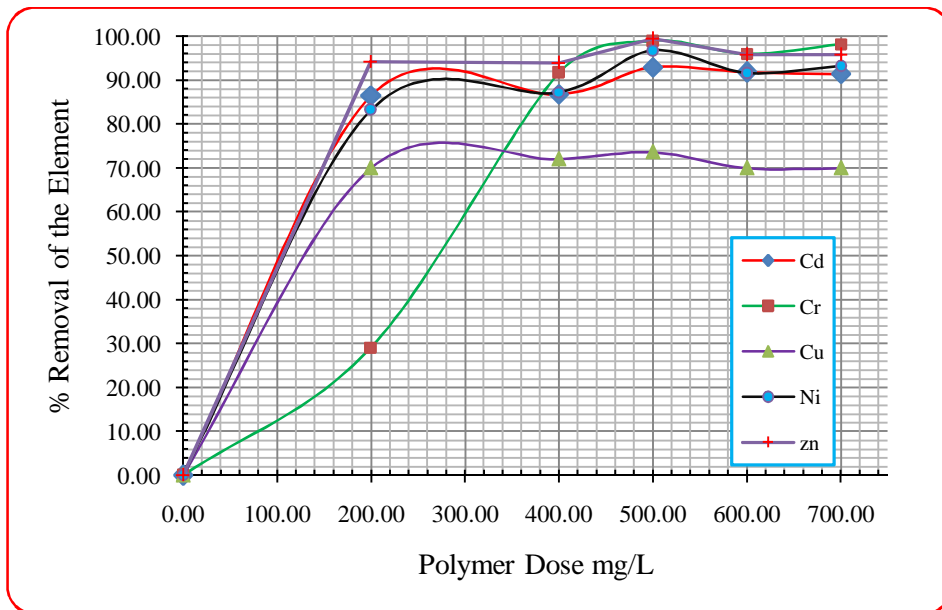


Figure (6) The effect of Polymer coagulant dosages at best pH of 9.0 on the heavy metals removal efficiencies of investigated leachate.

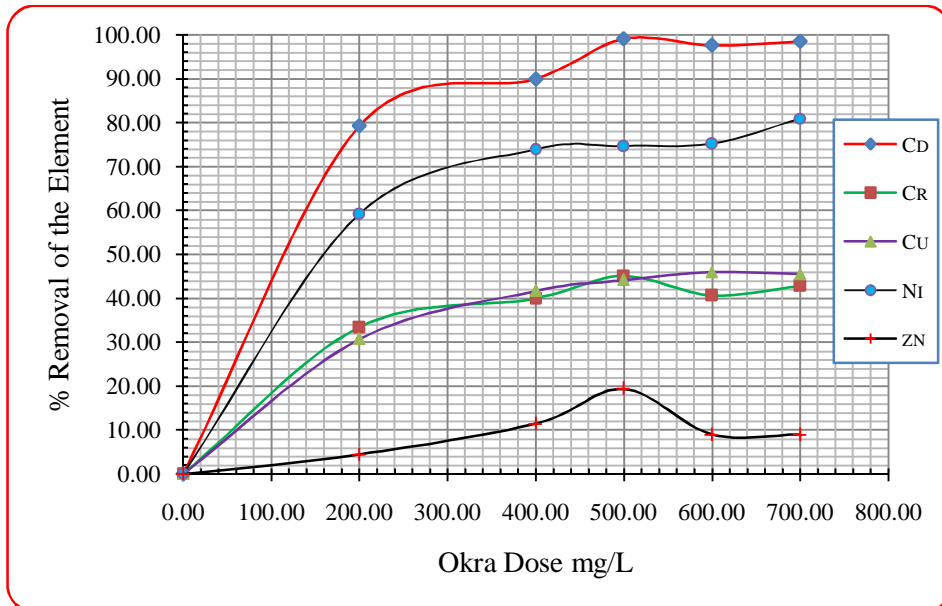


Figure (7) The effect of okra coagulant dosages at best pH of 7.0 on the heavy metals removal efficiencies of investigated leachate.

CONCLUSIONS AND DISCUSSIONS

- 1- The comparison of the characteristics of Tanjaro solid waste leachates to the general characteristics of leachate wastewater in the U.S.A. as reported by (USA Army,1994) shows the followings :
 - a. pH values were within the reported range.
 - b. Observed TDS values were close to the higher limit of the range of values.
 - c. Conductivity values are found to be much higher than those reported by the Technical Manual.
 - d. Concentration values for heavy metal cadmium (Cd) were found to higher than the upper limit.
 - e. Chromium (Cr) concentrations in the leachate from Tanjaro sanitary landfill were found to be rather high.
 - f. Copper (Cu) and zinc (Zn) concentration values were found to be within the acceptable range.
 - g. The heavy metal nickel (Ni) concentrations in leachate from Tanjaro sanitary landfill were found to be much higher.
- 2- By analyzing the results of using coagulants in heavy metal removal from leachate wastewater, it was found that the optimal pH values were 6.65, 9.00 and 7.00 for alum, polymer and okra, respectively.
- 3- As it can be seen in Figures (5), (6) and (7), the optimal coagulant dose for the investigated leachate heavy metals concentration removal for $Al_2(SO_4)_3.18H_2O$ was 1400 mg/L, polymer was 500 mg/L, and okra was 500 mg/L.
- 4- The relative abundance of heavy metals after treating fresh investigated leachate of Tanjaro landfill with alum followed the order: Cd>Ni>Zn >Cu>Cr, while after treating with polymer it was Cu> Ni> Cd>Cr > Zn; and after the treating with okra it was Zn > Cr > Cu > Ni > Cd.
- 5- The following table(3) shows the effective treatment power of the used coagulants alum, polymer and okra with respect to heavy metals removal.
- 6-

Table(3)Effective power of the coagulant with the heavy metal removal .

Heavy Metal Element	Best Coagulant Choice		
	Alum	Polymer	Okra
Cd)
Cr)	
Cu)		
Zn)	
Ni)	

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