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Comparison Between Washed and Unwashed Ninivite on the Removal Efficiency of Mercury from Aqueous Solutions

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ABSTRACT

Ninivite is a silica rich rock, which has a very high surface area, that may exceed ($800g/m^2$). Low grad ninivite is characterized by high absorption, adsorption ability and may act as an ion exchange to remove heavy metals. Efforts of applications under study are in the field of waste water treatment. Washing operation of ninivite with distilled water to reduce impurities; such as gypsum; and increasing silica ratio rendered it to be inefficient to removing mercury from its effluents. In the mean time the adsorptive materials such as alum and iron sulfate, are also washed out. It was found that the unwashed, raw, low grade, ninivite was outweighing washed one, using different concentrations of mercury(0-200mg/L) and at different pH values (1.6, 7.4, 9.5, and 10.6). Optimum removal efficiency of mercury concentrations of 75mg/L and 175 mg/L were at a pH of 9.5 and7.5 respectively.

مقارنة بين النينافايت المغْسول وغير المغسول على كفاءته في إزالة الزئبق من محاليله المائية

الملخص

النينافايت صخرة غنية بالسليكا، تمتلك مساحة سطحية عالية والتي من الممكن إن تزيد عن 800م^2/غم، تتميز الصخرة بقابليتها على ألامتصاص. التطبيقات الحالية تحت الدراسة هي باتجاه المطروحات حيث يمكن أن يعمل النينافايت كمبادل أيوني فضلاً عن ألامتصاص أو كلاهما لإزالة العناصر الثقيلة. إن غسل الصخرة بالماء المقطر لإزالة الشوائب مثل الجبس وزيادة نسبة السليكا لم يكن إيجابياً لإزالة الزئبق من مطروحاته. وفي الوقت نفسه فإن المواد ذات قابلية ألإمتزاز العالية مثل كبريتات الألمنيوم والحديد سيزال معظمها أيضا عند الغسل بالماء.

أظهرت الدراسة الحالية أن النينافايت الخام الواطئ النقاوة هو أفضل مما بعد الغسل باستخدام تراكيز متنوعة بين (0-200) ملغم/لتر، وعند دالات حامضية مختلفة منها (1.6 و 7.4 و 9.5 و 10.6). ولقد كانت ألإزالة المثلى للزئبق عند تركيز75ملغم/لتر و 175ملغم/لتر عند دالة حامضية 9.5 و7.5 على التوالي.

INTRODUCTION

Ninivite is a silica-rich rock discovered by Al-Naqib (Jassim *et al.*, 1987 and AL-Tayar *et al.*, 1994) in northern Iraq, Fig. (1). Occurrence of ninivite is in areas where H_2S emanation is going on, and the wet ground surface is characterized by a low pH value of 2.5-2.6 (Aswad *et al.*, 1995). It is closely associated with Alunite–Jarosite, during sulfuric acid–marl interaction. Disseminated carbonates dissolved preferentially and migrated in solution, and eventually precipitating gypsum according to the following reaction:

$$CaCO_3 + H_2SO_4 + 2H_2O \longrightarrow CaSO_4.\ 2H_2O + H_2CO_3$$

The chemical composition (as %) of ninivite using X-ray fluorescence (XRF) are: SiO_2 (55-95), Al_2O_3 (0.7-2.2), Fe_2O_3 (0.3-1.8), CaO (0.6-15.5), MgO (0.07-0.15), Na_2O (0.02-0.95), K_2O (0.04-1.08), P_2O_5 (0.01-0.55), Cl (0.6-1.3), SO_3 (0.1-15.5), loss on ignition (2.13-6.32), Jassim, and Al-Naqib (1989). There is also evidence that a significant loss of aluminum, iron, and calcium, concurrent with progressive enrichment of silica in various samples (1-4) has occurred, Table (1) (Aswad *et al.*, 1995). The physical properties of ninivite are given in Table (2) after Al-Naqib and Al-Dabbagh (1993). According to Al-Naqib and Mustafa, (1998) the surface area, is directly proportional to the silica content of ninivite and it may reach 800 m^2/g. Limited ratio of silica in a ninivite sample is accompanied by the an increase in the other components that are found in it thus resulting in a reduction of the surface area Al-Najjar (2000). The adsorption capacity of ninivite is limited in acidic solution Al-Naqib and Mustafa, (1998), while it is directly proportional to the surface area. In general, adsorption increases with high concentration of solutes, powdering of particles to fine powder, and the lower the molecular weight of solute. The resistant time is decreased as pH increases; it is very weak at pH 9.0 Al-Ubaidy, (2004) and Mustafa (2005).

On the other hand mercury is found in the earth's crust with an average of 0.005 mg/kg WHO, (1997). Also due to volcanic activity mercury concentration may raise up to 5.5µg/L in the ground water WHO, (1997). It is found on top soil in a range of (10-500 µg/kg) depending on clay content of soil, pH value, % ratio of organic matter, nature of water drainage and aeration, biological activity, % of $CaCO_3$, and concentration of other ions Abdul Al-Noor, (2000). Mercury is found in rain and drinking water in the range of 5-100 ng/L and increase in the hydrosphere, to 0.0001-2.8 µg/L in fresh water and 0.01-0.22 µg/L in sea water WHO, (1997). Naturally-occurring levels of mercury in ground and surface water are less than 0.5µg/L. Mercury guideline in water for human consumption should never exceed 1µg/L, WHO, (1997), and Ready and Ready (2003). Pregnant women should avoid eating fish containing even lower levels of mercury, Lindeburg(2001)and Stanitki *et al.*, (2000).

Mercury has many industrial applications and uses, leaving polluted effluents. Its main sources are chlorine and caustic soda industry, electrical appliances, control instruments, laboratory apparatus, dental amalgams, fungicide, antiseptics, preservatives, pharmaceu-ticals, electrodes, reagents, explosives manufacture, photography, paper, fertilizers, paint, fluorescent lamps, textile, smelting....etc, WHO (1997), Lindeburg (2001), Stanitki *et al.*, (2000) and Allen *et al.* (1998). In Iraq, a mercury fungicide accident, took place in the winter of 1971-72, leaving over 6000 patients and over 50 deaths WHO, (1997).

The aim of the work is to examine washed and unwashed ninivite as local raw mineral materials to remove mercury from various effluents.

MATERIALS AND METHODS

1. Preparation of solutions:

- Mercuric nitrate stock solution (1g/L), was prepared by dissolving 1.6182g of pure analar $Hg(NO_3)_2$ in distilled water containing few drops of concentrated HNO_3 then kept in a poly ethylene bottle.
- Potassium iodide solution (2.5%): was prepared by dissolving 2.5g in 100 mL distilled water.
- Methyl violet reagent solution (0.01%): was prepared dissolving 0.01 g methyl violet in 100mL ethanol.
- Saturated lime solution was used for pH adjustment.

2. Mercury determination:

Acidify 3.0 mL of mercuric nitrate solution to pH 1.4 by hydrochloric acid, then add 1.3 mL of 0.01% methyl violet solution, followed by 0.5 mL of 2.5% potassium iodide solution, the final volume should be 5.0mL using distilled water. The blue colored solution formed is measured against the corresponding reagent blank at 400nm, Snell (1978). Different concentration had been used of them (66.7, 133.4, 200.0, 266.7 and 333.0 mg/L), in order to get a final concentration of Hg equivalent to 40.0, 80.0,120.0, 160.0 and 200.0 mg/L. These concentrations had been tested at different pH values of 1.6, 7.4, 9.5 and 10.6. Determination conditions of the used materials (washed and unwashed ninivite) were; of a particle size ≤ 0.3mm. Tests were run at room temperature, with a mixing time of 10 minutes and a speed of 300 cycle/minute. These parameters were considered in accordance with the work of Mustafa, (2005).

RESULTS AND DISCUSSION

As ninivite possessing a relatively high surface area Al-Ubaidy, (2004), it is expected that it will acquire a high adsorption capacity; actually low grade ninivite may also have ion exchange capacity. Heating to ≥ 600^oC, and salting by 10% brine solution will improve these characteristics Mustafa, (2005). Washing of ninivite may remove soluble materials that may reduce the ability for adsorption, Table (3). In the mean time the removed materials may change the ninivite texture. By all means parameters like pH, temperature and dissolution of impurities, can play an important role in the characterization of adsorption, absorption and ion exchange ability of ninivite Mustafa, (2005).

Removal of mercury at low pH value of 1.6 is more or less limited, because, at such pH mercury is found as free ion, which may exchange with ions in the structure of ninivite, Table (4), i.e. there is no chance for adsorption and/or absorption. Increasing the pH with lime solution to 7.4, 9.5 and 10.6 Tables (5, 6, and 7) shows a significant removal efficiency mainly at pH of 7.4 and 9.5, this agrees with the results of Mustafa, (2005).

Tables (4-7) show higher removal efficiency of mercury for unwashed low grade ninivite (Fig.1), than the washed one with significant difference except at pH 7.4. These results can be confirmed by the Figures (2-5) as the curves of the unwashed media were above those of the washed media.

These figures also show strong cubic relationships between the concentrations of mercury and the removal efficiency, for different pHs, as the coefficient of determination ranged between 0.633 to 0.999. These relationships were not directly linear as they contain peaks, as shown in Figures (2-5). The peak values differ according to pH values. For pHs 1.6, 9.5 and 10.6, the peak removal was obtained with initial mercury concentration of about 75mg/L; while for pH 7.4, the peak removal occurred at mercury concentration of 175 mg/L.

In the mean time the unwashed ninivite outweighed washed ninivite in its removal efficiency. By all means adsorption and/or ion exchange seem to be the way of mercury removal by ninivite.

To compare the present work with other recently published results Mustafa (2005), Table (8), reflect that very simple conditions of room temperature, short analysis time, with minimum amount of material (2g/L) had been applied. This shows a 35% and 22% removal efficiency of mercury of initial concentration of 75mg/L and 175 mg/L the unwashed low grade ninivite at a pH of 9.5 and 7.4.

CONCLUSION

1. Minimum size particle is necessary for treatment in spite of the physical properties of ninivite, and the pH control to around 9.5 is essential for obtaining optimum Hg removal.
2. Initial concentration of mercury of about 75mg/L must be treated at one of the pHs 1.6, 9.5 or 10.6, and the optimum pH is 9.5, while higher mercury concentrations of ≥ 175 mg/L must be treated at a pH of about 7.4, (i.e. around neutral media).

RECOMMENDATIONS

1. As heating may expel impurities and expand the ninivite layers and constituents, this will help in increasing the surface area, so heating to ≥ 600°C, may also leave free edges and added activity.
2. Salting with 10% brine solution, may help creating some new functional groups, by occupying free edges positions and/or displacing some divalent ions like residual Ca and Mg. This will improve the ion exchange capacity of ninivite rock.

Table 1: Chemical Analysis of Ninivite, of Different Origins.

Minerals Types	% Components Sample No.			
	1	2	3	4
SiO_2	25.06	50.14	85.86	95.70
TiO_2	-	-	-	0.59
Al_2O_3	0.28	0.38	0.30	0.22
Fe_2O_3	0.18	0.19	0.12	0.08
CaO	24.10	16.96	4.20	0.98
MgO	-	-	-	0.02
Na_2O	-	-	-	-
K_2O	-	-	-	-
P_2O_5	-	-	-	-
SO_3	33.98	19.00	3.40	0.07
Cl	-	-	-	-
Loss on ignition	15.93	11.81	4.46	2.20

* Samples from Humeira, South Mosul city, Fig. (1), (Aswad *et al.*, 1995).

Table 2: Physical Properties of Ninivite.

Physical properties	Range	Average
Porosity (%)	62.1-76.07	70.5
Density (g/cm^3)	0.67-0.78	0.74
Surface area (m^2/g)	300-800	700
Water absorption (%)	93.4-104.7	95.2
Permeability (cm/sec)	$6.9x10^{-5}$–$6.07x10^{-5}$	6.8×10^{-5}

* after Al-Naqib and Al-Dabbagh (1993).

Table 3: Chemical analyses of washed and unwashed ninivite

Composition / Treatment Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	Cl	L.O.I
W.L	64.83	0.07	0.08	14.21	3.1	N.D	N.D	12.0	N.D	0.2	3.36
L	56.21	1.05	0.32	16.14	5.67	0.03	0.01	15.88	N.D	0.3	3.66

W= Washed by distilled water with minimum and constant conductivity of filtrate,
L= low grade ninivite, (contains minimum to medium silica content)

Table 4: Comparison of Mercury Removal Efficiency between washed and unwashed low grade ninivite at 1.6 pH (solution as it is)

Concentration of Mercury mg/L	Blank	Unwashed low grade ninivite	Washed low grade ninivite
40	0.239	0.198	0.235
80	0.352	0.219	0.288
120	0.394	0.300	0.360
160	0.442	0.370	0.417
200	0.483	0.403	0.459
Average (120)	0.382	0.298	352
%Removal efficiency (mean ± SD)		22.33 ± 9.19	7.82 ± 6.30
p. value	p<0.05 (significant)		

Table 5: Comparison of Mercury Removal Efficiency between washed and unwashed low grade ninivite (treatment run at a pH 7.4)

Concentration of Mercury mg/L	Blank	Unwashed low grade ninivite	Washed low grade ninivite
40	0.226	0.186	0.196
80	0.255	0.245	0.260
120	0.319	0.304	0.320
160	0.399	0.318	0.350
200	0.406	0.336	0.377
Average (120)	0.323	0.278	301
%Removal efficiency (mean ± SD)		12.77±7.8	7.14±5.65
p. value	>0.05 (not significant)		

Table 6: Comparison of Mercury Removal Efficiency between washed and unwashed low grade ninivite (treatment run at a pH 9.5)

Concentration of Mercury mg/L	Blank	Unwashed low grade ninivite	Washed low grade ninivite
40	0.237	0.177	0.210
80	0.312	0.205	0.263
120	0.337	0.256	0.278
160	0.375	0.291	0.340
200	0.398	0.321	0.367
Average (120)	0.332	0.250	292
%Removal efficiency (mean ± SD)		25.08±5.61	12.35±4.15
p. value	P<0.01 (significant)		

Table 7: Comparison of Mercury Removal Efficiency between washed and unwashed low grade ninivite (treatment run at a pH 10.6)

Concentration of Mercury mg/L	**Blank**	**Unwashed low grade ninivite**	**Washed low grade ninivite**
40	0.217	0.197	0.215
80	0.290	0.220	0.278
120	0.315	0.246	0.288
160	0.350	0.306	0.340
200	0.385	0.350	0.369
Average (120)	0.311	264	298
%Removal efficiency (mean ± SD)		15.38±7.15	4.13±2.81
p. value	<0.05 (significant)		

Table 8: Comparison between different heavy metals removal processes.

Metal (II) ions	**Removal by**	**Removal mechanism**	**Experimental Conditions**				**% Removal**	**Reference**
			pH	Time	Temp.^{o}C	Qt/L		
Hg(1)	Quartz (SiO_2) and Gibbsite [$Al(OH)_3$]	Adsorption	7.7-9.5	1-48h	20-25	4	Not mentioned	Sarkar *et al*., (1999)
Cd(1)	S(K+L)	Ion exchange & adsorption	11.5	10 min	20-25	2	>85	
Hg(1)	AS(K+L) or A(K+L)	Mainly adsorption	9.5	10 min	20-25	2	>95	Mustafa 2005
Pb(1)	S(K+L)	Adsorption & ion exchange	7.0	10 min	20-25	2	>90	
Hg	Photo catalysis	Precipitation	9.0 11.0	-	0 40	-	Not mentioned	Malati (2002)
Cd Pb Hg	$ZrPO_4$ grafted in silica gel surface	Adsorption	4.5	15min	20-25	4	Not mentioned	Nagata *et al*., (2001)
Pb(2) Cd(3) Hg(4)	Polystyrene-supported chelating polymer resin	Ion exchange chelating or adsorption or both	10 6 10	1 h 1h 1h	25-30	27-133	50-60	Ready and Ready (2003)
Hg	Un W (75)*	Mainly adsorption	9.4***	10 min	20-25	2	35	Present work
	W (75)*						15	
	Un W(175)**		7.4***				20	
	W (175)**						10	

1. mainly as nitrate, 2. dose = 10-13 mg/g, 3. dose = 2-5 mg/g, 4. dose = 8-12 mg/g.

A= heating the material to about 600^{o}C for 2 hr, S= salting with 10% brine solution for 2hr.

AS= heating after salting, K= Kaolin, L= low grad Ninivite, Un W= Unwashed low grade ninivite, W = Washed low grade ninivite, * = concentration of mercury is 75mg/L, ** = concentration of mercury is 175mg/L, *** = optimum pH.

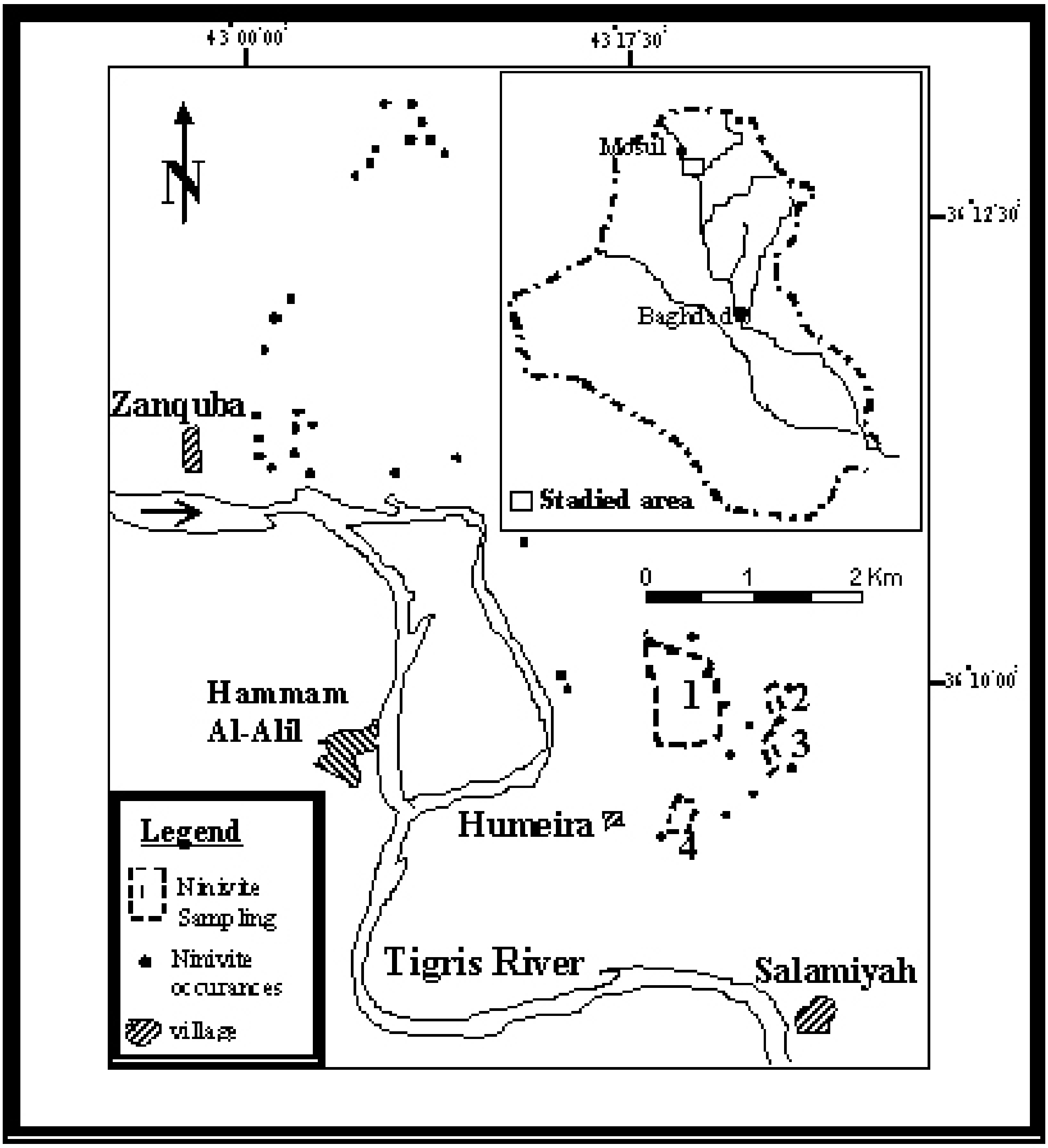

Fig. 1: After Jassim and Al-Naqib (1989)

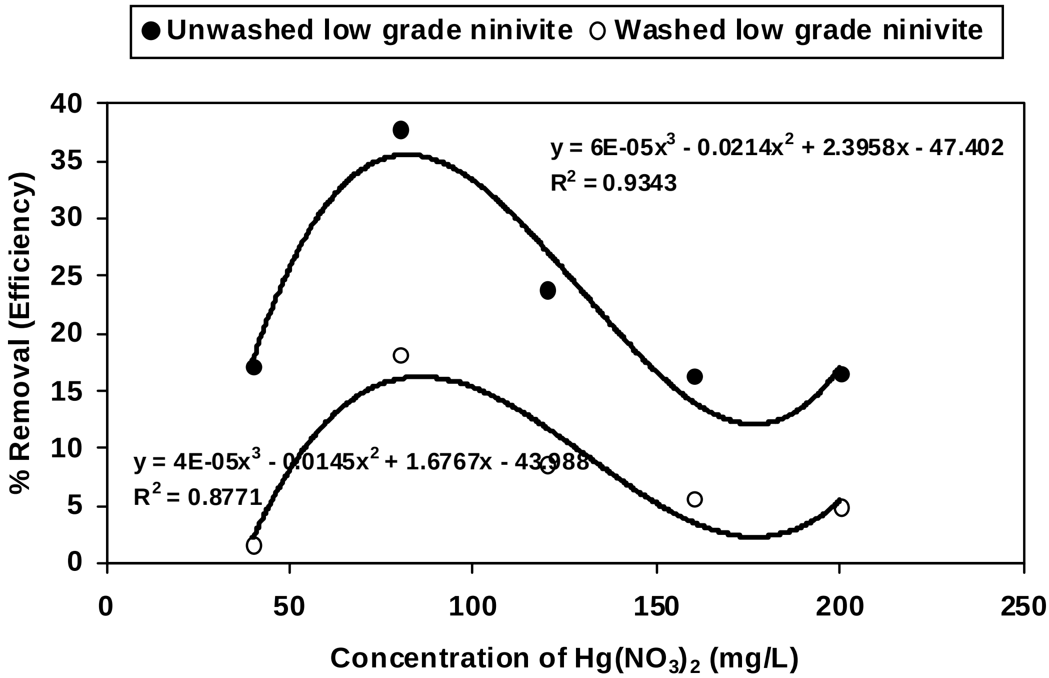

Fig. 2: Comparison of Removal Efficiency Between Unwashed and Washed Low Grade Ninivite at a pH of 1.6.

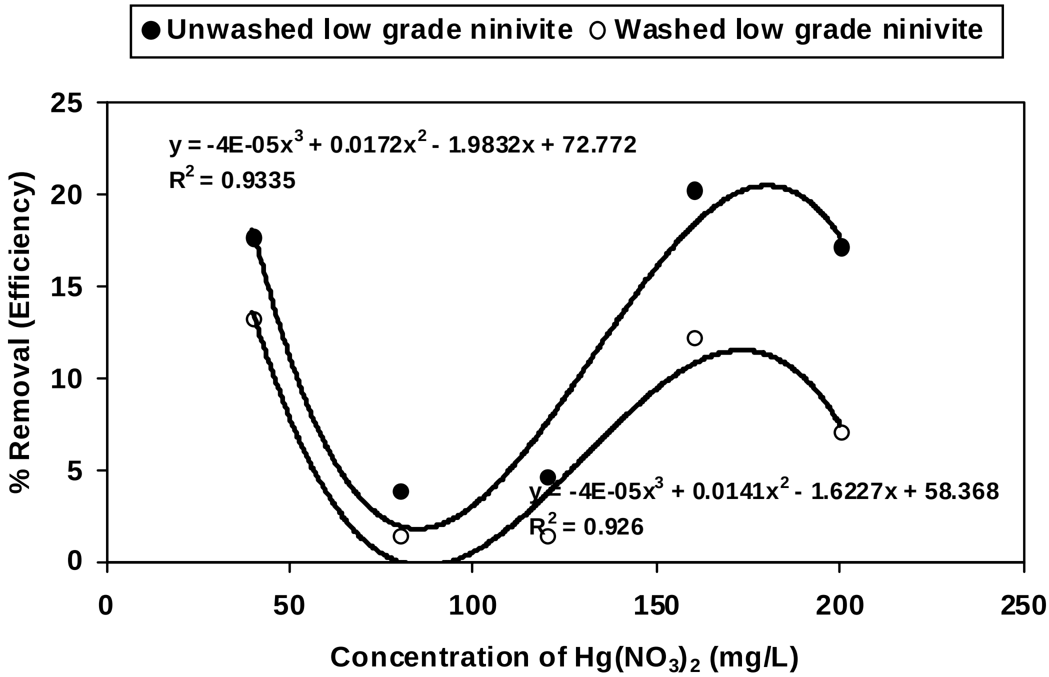

Fig. 3: Comparison of Removal Efficiency Between Unwashed and Washed Low Grade Ninivite at a pH of 7.5.

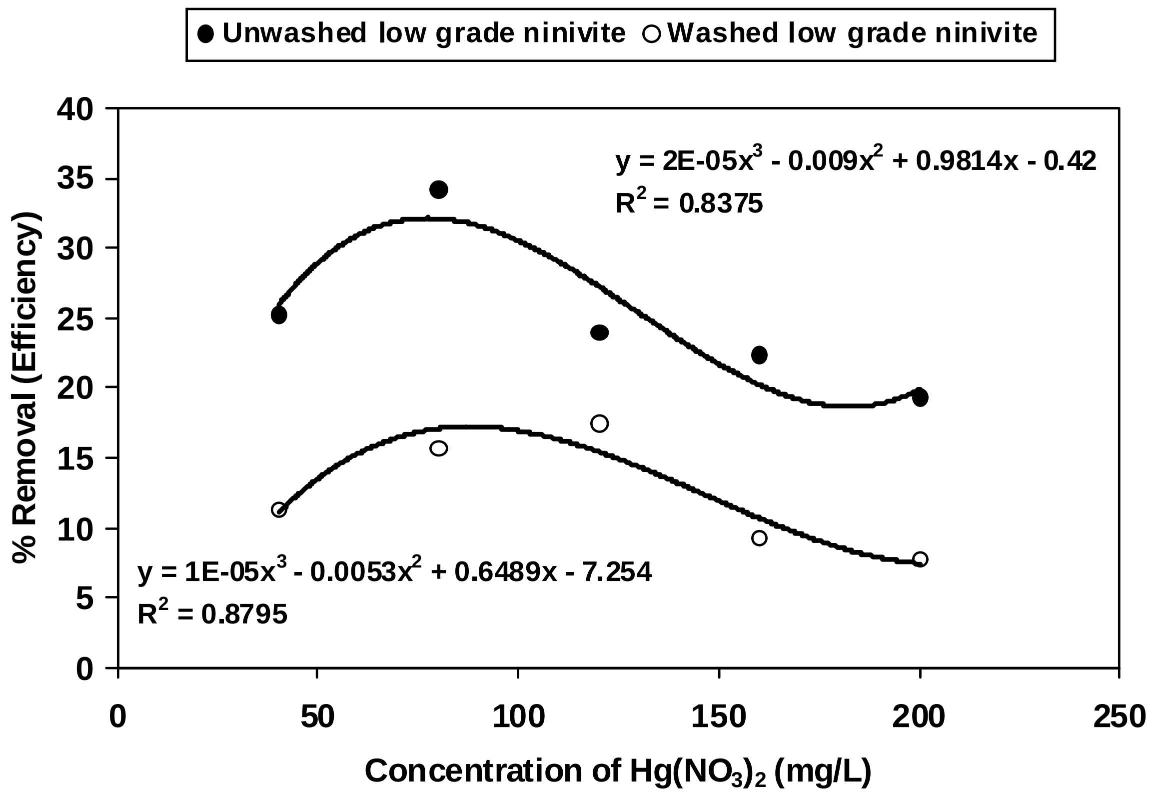

Fig 4: Comparison of Removal Efficiency Between Unwashed and Washed Low Grade Ninivite at a pH of 9.5.

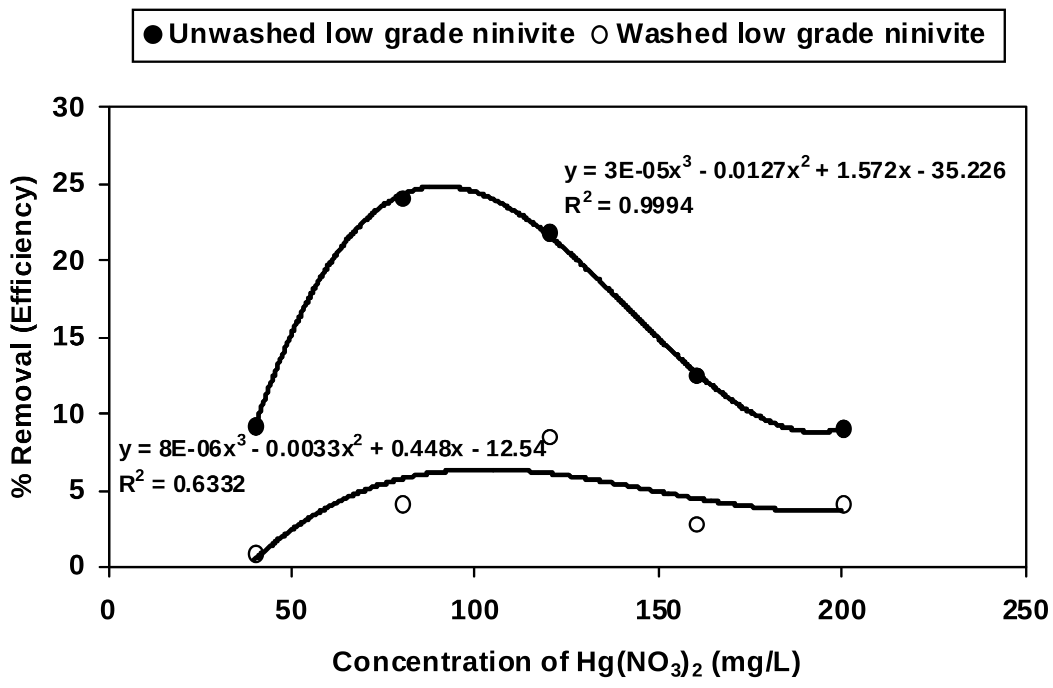

Fig. 5: Comparison of Removal Efficiency Between Unwashed and Washed Low Grade Ninivite at a pH of 10.6.

REFERENCES

Abdul Al-Noor, A., 2000, Environmental Pollution, Soil and Plant, Dar Al-Nasher Lel-Jamiate, Cairo, Egypt, pp.57-59, 63-64, 67-69, (Arabic).

Allen, H.E.; Garrison, A.W. and Luther III, G.W., 1998, Metals in Surface Waters, Ann Arbor Press, U.S.A., pp.44, 46, 52.

Al-Tayar, T.A; Mustafa, M.H., and AL-Naqib, S.Q, 1994, Pollution of Tigris River Water by the Seepage of Natural Acid Water at Zanquba South Mosul city, Scientific Journal of Water Resources, 2(1), pp.33-36.

Al-Najjar, Q.A.A., 2000, An Investigation of Using Locally Ninivite Rocks in Water Treatment, M.Sc Thesis, Civil Engineering Department/ Environment, College of Engineering, The University of Mosul, pp.42, 64, 75-77 (Arabic).

Al-Naqib, S.Q., and Al-Dabbagh, 1993, Some Physical Geotechnical Properties of the New Rock Type Ninivite, Proc. of the 26th Annual Conf. of the Engineering Group Geol. Soc. Leeds, UK., Sept. 9-13, Bulkema, pp.29-34.

Al-Naqib, S.Q., and Mustafa, M.H., 1998, Preparation of New Material from Montmorillonite-Smectite, to Eliminate Odors and Spots, Iraqi patent No. 2710, Central System for Measurement and Quality Control, Baghdad, pp.11- 23, (Arabic).

Al-Ubaidy, N.H.T., 2004, Ninivite Silica Rocks Doping with Chromium Oxide Gel, Physical and Structural Characterization and Application in Solid Phase Extraction Technique to Separate Virgin Iraqi Olive Oil, Ph.D Thesis, College of Education University of Mosul, pp.55-56, (Arabic).

Aswad, K.J.; Amin, M.A., and Al-Naqib, S.Q., 1995, Marl-H_2S Interaction Under Surfacial Oxidizing Conditions, DIRASAT (Pure and Applied Sciences), 22 B (6), pp. 58-1542.

Jassim, S.Z., and Al-Naqib, S.Q., 1989, Ninivite; A New Form of Porocelenite and the Associated Alunite and Jarosite Minerals. A Suite Related To Sulfuric Acid Seepages South of Mosul, Northern Iraq, Journ. Geol. Soc. Iraq, 22 (1), pp.112-122.

Jassim, S.Z.; AL-Naqib, S.Q., and Dawood, Y., 1987, Occurrences of Porocelenite in Nineveh Governorate, Salamia Area, S.O. M. Library, Baghdad, pp.13-15 (Arabic).

Jeffery, P.G., and Hutchison, D., 1981**,** Chemical Methods of Rock Analysis, Pergamon Press, New York, pp.22, 30-42.

Lindeburg, M.R. PE, 2001, Civil Engineering Reference Manual for the PE Exam, 8th Edition, Professional Publications, Inc, Belmont, CA, U.S.A., pp.25-4, 6, 32-2 www.pp12pass.com.

Malati, M.A., 2002, Removal of Toxic Metals from Water and Recovery of Precious Metals by Photocatalysis, pp.1-12. www. sachtleben.de/m/pdf/0162e072.

Mustafa, M.H., 2005, The Use of Mixed Ninivite and Kaolin for the Removal of Cd, Hg, and Pb from Their Waste Water, PhD thesis in the field of Environmental Analytical Chemistry, Chemistry Department, Science College, The University of Mosul.

Nagata, N.; Kubota, L.T.; Bueno, M.I.M.S., and Peralta-Zamora, P.G., 2001, Adsorption Parameters of Cd (11), Pb (11), and Hg (11) on Zirconium (1v) Phosphate Chemically Grafted onto Silica gel Surface, Journal Article, Journal of Colloidal and Interface Science; U.S.A., 200, pp.121-125.

Reddy, A.R., and Reddy, K.H., 2003, Heavy Metal Ion Uptake Properties of Polystyrene-Supported Chelating Polymer Resins, Proc. Indian Acad. Sci (Chem. Sci.), June, 115(3), pp.156-159.

Sarkar, D.; Essington, M.E., and Essington, K.C., Misra, 1999, Adsorption of Mercury (II) by Variable Charge Surface of Quartz and Gibbsite, Soil Science Society of America Journal, DIVISONS-2-SOIL CHEMISTRY,U.S.A., 63, pp.1627-51. messington@utk.edu.

Snell, F.D., 1978, Photometric and Fluorometric Methods of Analysis Metals, Part1, A Wiley-Interscience Publication, U.S.A., 514p.

Stanitski, C.L.; Edunanks, L.P.; Middlecamp, C.H., and Stratton, W.J., 2000, Chemistry in Context, Applying Chemistry to Society, 3rd Ed., Mc-Graw Hill, UK., 206, pp.214-217.

WHO, 1997, International Program on Chemical Safety, Guidelines for Drinking–Water Quality 2nd, Ed., Health Criteria and Other Supporting Information, Eastern Mediterranean Regional Office, (CEHA) 2, pp. 4, 16-18, 20-22, 24-27.