The Novel Use of Processed Ninivite-Kaolin Mixture
Part 1: Mercury Removal from Its Effluents

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ABSTRACT

The mixture of processed ninivite and kaolin has for the first time been used for the removal of mercury from its effluents after nitric acid digestion. Under optimum experimental conditions [shaking time, pH, temperature and quantity of processed ninivite and kaolin mixture, AS(N+K)], the removal efficiency has been found to be >95%. The process is believed to be economic and easily handled.

Keywords: ninivite and kaolin; AS(N+K); mercury removal; effluents.

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INTRODUCTION

Kaolin is known to have many different industrial chemical and environmental applications due to its specific chemical and physical properties (IPCS, 2005). For example, kaolin as clay has the ability to absorb heavy metals, many of which are health hazards and some of which have proven to be carcinogenic (Schwedt, 2001).

Ninivite is a silica rich rock (Jassim *et al.,* 1987; Al-Tayar *et al.,* 1994 ; Aswad *et al.*, 1995). It has been shown to be an effective material for the elimination of odors and spots, due to its excellent physical properties, concerning high porosity, permeability, surface area

(300-800) m^2/g (Al-Naqib and Mustafa, 1998). Accordingly, it is easy to say that their mixture as (N+K) is a unique raw material for heavy metal elimination due to their physical and chemical characteristics.   Table (1) shows the chemical composition of low- grade ninivite (N) and kaolin (K)**.**

Table 1: Chemical Composition * of Ninivite and Kaolin

Components %	Low-grade ninivite (N)	Kaolin(K)
SiO_2	56.50	47.93
TiO_2	N.D**	N.D**
Al_2O_3	1.11	35.78
Fe_2O_3	0.89	1.04
CaO	15.79	1.13
MgO	0.12	3.04
Na_2O	N.D**	0.01
K_2O	N.D**	0.02
P_2O_5	N.D**	0.03
SO_3^{-2}	17.30	0.25
Cl^{-1}	N.D**	0.51
L.O.I	8.25	10.43
Cd^{+2}	N.D**	N.D**
Pb^{+2}	N.D**	N.D**
Hg^{+2}	N.D**	N.D**

*(Jeffery and Hutchison, 1981),** N.D. = not detected.

Mercury is found in the earth's crust with an average content of 5 µg/kg. Top soil contains (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 air with a range of 2-10 $ng/10^3\ell$. In Europe, it is < 0.009-2.8 ng/ $10^3\ell$, while near volcanoes it is 18-250 $ng/10^3\ell$. In rain and drinking water, it is found in the range of 5-100 ng/ℓ (average of 25 ng/ℓ). In the hydrosphere, it is 0.1-280 ng/ℓ in fresh water and 10-220 ng/ℓ in sea water (WHO, 1997). Natural-occurring levels of mercury in ground water and surface water should be less than 500 ng/ℓ (Schumacher *et al.*, 1993). Mercury in water for human consumption should never exceed 1000 ng/ℓ (Reddy and Reddy, 2003). Limits of mercury in water should never exceed $2x10^4 ng/\ell$ (Lindeburg, 2001) in order to prevent kidney and nervous system disorders. Mercury has many industrial applications and uses, leaving polluted effluent (Snell, 1978).

The aim of the present article has been devoted to study local raw materials (ninivite+kaolin) as a possible way of decreasing mercury pollution of the environment especially surface waters, i.e, to the international recommended level ($2x10^3$ ng/ℓ). To the best of our knowledge this idea has not been used before to any extent.

EXPERIMENTAL

Chemicals and Solutions

Chemicals used are of the highest purity available. Mixed ninivite and kaolin have been used in order to identify their removal efficiency application of mercury (II) ions.

Mercury stock solution (1000 mg/ℓ): This solution is prepared by dissolving 1.6182 g of mercuric nitrate (BDH) in distilled water containing few drops of concentrated nitric acid and diluting the volume to 1000 ml in a volumetric flask. This solution is then transferred to a polyethylene bottle (Snell, 1978)**.**

Mercury working solution (100 mg/ℓ): This solution is prepared by diluting 100 ml of the above stock solution to 1 ℓ with distilled water in a 1000-ml volumetric flask. Less concentrated solutions are prepared by appropriate dilution of the standard mercuric solution.

Potassium iodide solution (2.5%): It is prepared by dissolving 2.5 g of potassium iodide (BDH) in distilled water, then diluting it with distilled water to 100 ml in a volumetric flask.

Methyl violet reagent solution (0.01%):   This solution is prepared by dissolving 0.01 g methyl violet (BDH) in ethyl alcohol, then diluting to 100 ml in a volumetric flask, with the same solvent.

Saturated lime solution: This solution is prepared by dissolving uncounted quantity of lime (quick lime), with distilled water shake several times and left for clarification then filtered clear saturated solution of lime. Actually water dissolves only normally burned calcium oxide (CaO), this solution is prepared weekly. Lime solution should be clear, filtration is necessary when it is turbid.

Apparatus

Absorbance measurements are performed using CECIL, Ce1021, 1000 series and Apel PD-303S digital spectrophotometers, with 1-cm silica or plastic cells. Shaker KS10 (Edmund Bühler, Germany) for shaking samples. Heater and magnetic stirrer, HMO 15 (Thermo Lab Industries, Jordan) for dissolution purposes. Memmert oven (supplied by KARL KOLB, Germany), for drying of samples. Electric Muffle Furnace OSK 9540 Mk-15(Ogawa Seki company, Japan) for activation of ninivite and kaolin mixtures. PW 9421 pH meter (Philips, England), for pH measurement of samples. ASTM 11-70, sieving set (U.S.A.), British standard test sieve (Slough, England), OSK 7341 standard sieve (Ogawa Seki Company, Japan). Flame photometer ANA-10KL (Ogawa Seki company LTD Japan) for sodium and potassium measurement.

Mercury Determination

Mercury is determined spectrophotometrically by the following procedure. To 3.0 ml of the acidified (to pH 1.4 by hydrochloric acid) mercuric solution, covering the concentration range (2-30 mg/ℓ and 40-200mg/ℓ),1.3 ml of 0.01% methyl violet solution and 0.5 ml of 2.5% potassium iodide solution are added. The final volume should be 5 ml (using distilled water), the concentration is equivalent to 1.2-18, 24-120 mg/ℓ. The blue coloured solution formed is measured spectrophotometrically against the corresponding reagent blank (Snell, 1978).

RESULTS AND DISCUSSION

The various parameters affecting and related to the removal efficiency of mercury by the local mineral raw materials, ninivite and kaolin, have been examined and optimum conditions have been sought.

Preliminary investigations

The preliminary experiments (Mustafa, 2005) have pointed out that ninivite (N) and kaolin (K) show good removal capability to mercury (II) ions from its solution. This observation leads to study the optimum conditions for such removal. These include amount of raw materials used (N+K), pH, temperature, and time of treatment. These parameters are all considered at a mixing speed of 300 cycle/minute.

Amount of local mineral raw materials

The study has started with, 1 g-amount of local raw material. According to the above mentioned composition of both low grade ninivite and kaolin, Table (1), a mixture of 1:1 by weight (N+K), (as the most effective for the removal of heavy metal ions had been used (Mustafa, 2005). Volume of 50 ml of mercury solution of different concentrations is treated, considering the parameters mentioned above. Then the following experiments had been run according to the above mentioned parameters, (amount of mixture, pH, temp. and time).

Effect of pH

In general the holding capacity of the used raw materials (N+K), depends on two factors: (i) the state of the mineral raw material and (ii) the chemical form of the metal ion. Both factors seem clearly to be pH dependent (Crear, 2001).Therefore, the effect of pH on mercury removal by the mixed mineral raw materials has been investigated (Table 2).

Table 2**:** Removal efficiency of mercury from solution at different pH

pH of Hg (II) solution	Residual Mercury (II) ions, mg/ℓ		
	a	b	c
5.4 (as it is)	5.1	9.6	13.1
7.0	4.3	9.8	12.8
8.5	4.1	9.8	11.3
9.5	1.6	3.0	3.8
11.5	2.6	9.6	13.6

A 50 ml volume shaken at 300 cycle/min. at room temp. for 1hr.Initial Hg (II) concentrations (mg/ℓ): a = 6, b = 12, c = 18 and 0.1 g of (N+K).

The removal efficiency shown in Table (2) tends to increase as the pH of the metal solution increases (up to 9.5 pH). This is attributed to the formation of some hydroxo compounds which may precipitate or adsorb on the surface of the mineral raw materials (Crear, 2001). The subsequent experiments are performed using the (N+K) mixed mineral raw material and its new forms after processing, (i) activation by heating to 600°C to give A(N+K), (ii) by salting (to induce forming exchangeable ions), using brine solution of 4% to produce S(N+K), or by both to produce AS(N+K). Since it relatively shows the more promising removal efficiency at pH~9.5, which is comparable to that in the literature

(pH 10) **(**Reddy and Reddy, 2003**).** So this pH should be considered in all further experiments.

Evaluation of treatment materials amount

       The effect of the amount of (N+K) on the holding capacity for mercury (II) ions from the solution has next been investigated. The experimental results are given in Table (3).

Table 3**:** Evaluation of (N+K)(1) and A(N+K)(2) amounts on mercury (II)ion (6 mg/l) removal.

wt. of mixture, g	0.25		0.5		0.75		1.00		1.5		2.00	
	1	2	1	2	1	2	1	2	1	2	1	2
Residual Hg^{2+}, mg/l	1.3	0.67	1.4	0.67	1.3	0.67	1.17	0.61	1.20	0.61	1.15	0.61

       The results depicted in the above table show that lower amounts of both (N+K) and A(N+K) are more efficient. This might be explained as follows: The extent of adsorption of soluble complexes of mercury (II) ions will increase (Sarkar *et al.,* 1999) as compared with the less available surfaces at higher amounts of (N+K), probably due to agglomeration. For the subsequent experiments, 0.25g of the mixed (N+K) and A(N+K) are used.

Effect of mixing time

       Using the optimum amounts of (N+K) and A(N+K) found in the preceding section, time of mixing is next evaluated and the experimental data are given in Table (4).

Table 4**:** Removal efficiency of (N+K) (1) and A(N+K) (2) mixtures at different times.

Time, minutes	15		30		45		60		90		120	
	1	2	1	2	1	2	1	2	1	2	1	2
Residual Hg^{2+}, mg/l	1.31	0.65	1.22	0.65	1.22	0.65	1.22	0.65	1.22	0.65	1.22	0.65

Note: using 0.25 g mixture, initial concentration of Hg (II) ions = 6 mg//ℓ.

       The above table shows clearly that optimum time is only 15 minutes. Using aluminum silicate as holder for mercury (II) ions, at least 1-hr time is required (Reddy and Reddy, 2003). From this point of view, mixed raw materials are superior to aluminosilicate, which requires longer times in their removal of mercury (II) ions from solution.

Effect of temperature

       To evaluate the optimum temperature during the mixing of mineral raw materials and solutions of mercury (II) ion, a range of temperature (20- 50) ^{o} C is examined. The results are given in Table (5).

Table 5: The removal efficiency at different temperatures.

Temperature, ^{o}C	20		30		40		50	
	1	2	1	2	1	2	1	2
Residual Hg^{2+}* mg/l	1.22	0.65	1.14	0.65	2.34	0.65	6.0	5.43

*Initial concentration of Hg (II) = 6 mg/ℓ, (1): using 0.25g (N+K) mixture, (2): using 0.25 g A((N+K) mixture, at pH=9.5.

The results in Table (5) show clearly that room temperature 20 ^{o} C is optimal, and it should be considered from the economic point of view. Higher temperatures seem to favor desorption.

Effect of Processed Treatment Materials
The next experiments were run using high concentrations of mercury (II) solution of (24, 48, 72, 96, 120 Hg/, mg/l). Raw materials processed are, (N+K), A(N+K), S(N+K) and AS(N+K) (A means heat activation, S means salted and AS means activation after salting) have been tested to find their removal efficiency compared with charcoal as a typical adsorbent and Dowex-50X resin as a strong cation exchanger, respectively. Table (6) shows the efficiency of the types of mixtures.

Table 6: Removal efficiency of different types of mixture and standards.

Hg (II) mg/ℓ	Residual Hg (II) ions concentration, mg/ℓ					
	AS(N+K)	S(N+K)	A(N+K)	(N+K)	Charcoal	Dowex-50X
24	9.8	11.7	12.2	16.4	2.81	5.6
48	11.7	12.2	11.7	16.4	2.75	6.6
72	11.7	13.1	13.1	16.8	3.75	5.6
96	11.7	13.1	12.2	18.75	2.81	3.75
120	12.2	16.4	13.1	21.1	3.28	3.75

Wt. of treatment materials 0.25g, room temp. pH=9.5, particle size=0.3-1.2, time=15min, speed of mixing 300cycle /min.

The above results in Table (6) show that AS(N+K) mixture gives the highest removal efficiency (excluding charcoal and Dowex-50X). Application of the above facts on a chromatographic column had failed, due to compaction of ninivite and kaolin, where ninivite may expand due to water imbibitions, so water cannot further pass through, while kaolin particle is passing through the column bed and found as turbidity.

Effect of amount of processed (N+K)
According to Table (7), the effect of the amount of processed (N+K) [A(N+K), S(N+K) and AS(N+K)] on the removal efficiency towards mercury (II) ions from the solution has been carried out. The new results (using particle size <0.3 mm) after the failure of the original particle size are represented in Table (7).

Table 7: Removal efficiency of A(N+K) and AS(N+K) mixtures at different times.

g. wt. of mixture	0.05		0.10		0.20		0.25		0.50	
	1	2	1	2	1	2	1	2	1	2
Residual Hg^{2+}* mg/l	12.2	**11.7**	3.28	2.81	3.28	2.81	10.78	2.81	10.78	2.81

*Initial concentration of Hg (II) = 60 mg/ℓ, particle size<0.3mm, at room temp., time=15 min, pH9.5, mixing speed 300 cycle/min.

The above table reflects clearly that the removal efficiency for mercury ion becomes independent of weight in the range of 0.1- 0.5 g. A 0.1 g seems to be promising amount for the processed mixtures [mainly for AS(N+K) (2)] , so it is selected for the subsequent work.

Effect of time
The removal efficiency of A(N+K) and AS(N+K) mixture at different periods of time, using a particle size passing 0.3 mm and a concentration of 60 mg Hg/ℓ is shown in Table (8).

Table 8: The Removal efficiency of A(N+K) (1) and AS(N+K) (2) mixtures at different periods of time.

Time in minutes	5.0		10.0		20.0		25.0		30.0	
	1	2	1	2	1	2	1	2	1	2
Residual* Hg^{2+} mg/l	12.18	11.72	3.75	2.81	3.28	3.28	3.75	3.28	4.03	3.28

*Initial concentration of Hg (II) = 60 mg/ℓ, (1): using 0.1 g A(N+K), (2): using 0.1 g, AS(N+K). particle size <0.3mm, at room temp., pH = 9.5. mixing speed 300 cycle /min.

Results in Table (8) show that a 10-minute time seems to be optimal.

Effect of temperature
The effect of temperature of the solution of mercury (II) ions has been studied from its removal point of view. The results are depicted in Table (9).

Table 9: The Removal efficiency of A(N+K)(1) and AS(N+K)(2) mixtures at different temperatures, (initial concentration 60 mg Hg/ℓ).

Temperature, °C	20		30		40		50	
	1	2	1	2	1	2	1	2
Residual Hg^{2+}, mg/l	4.22	3.28	7.03	6.56	13.1	11.72	32.8	19.7

1= A(N+K), 2=(ASN+K), using 0.1g of mixture, particle size <0.3mm, time=10minute pH = 9.5. mixing speed 300cycle /min.

High temperatures caused a decline in adsorption; room temperature (20-25°C) seems to be optimum for the removal of mercury (II) ions. Accordingly, it is recommended in subsequent work.

From the above results in Tables No.7, 8, and 9, it is easy to say that the new optimal conditions of the removal efficiency of mercury should be 0.1 g for all types of processed mixtures, room temperature, 10 minute time, pH 9.5, in addition to the new particle size of passing through 0.3 mm.

Evaluation of processed raw materials

Under the above-established optimum experimental conditions, the different possible processed mineral raw materials have been compared for their efficiency in removing Hg (II) ion from solutions having different concentrations. The results are shown in Table (10).

Table 10: Removal efficiency of different mixtures, under optimum conditions.

Hg, mg/ℓ	Residual Hg^{+2} ions concentration, mg/ℓ					
	AS (N+K)	S(N+K)	A(N+K)	(N+K)	Charcoal	Dowex-50X
24	2.4	2.81	2.81	6.56	2.34	4.22
48	2.72	2.81	2.81	7.03	2.81	4.22
72	2.81	3.75	3.75	7.03	4.22	6.1
96	2.81	3.75	3.75	7.5	4.22	4.22
120	2.81	5.63	2.63	9.38	5.63	6.56

The results above reflect clearly that the mixture of AS(N+K) has given the highest removal efficiency for mercury (II). This is attributed to increased surface area (by heat treatment) and generation of actively ionic groups (by salt treatment). The amount of 0.1g of AS(N+K) has been recommended for use due to its highest removal efficiency because particle size reduction leads to larger surface area. The above ratio (0.1 g/50 ml solution) is equivalent to 2 g/ℓ or $2kg/m^3$.

Field-Work Application

Direct measurement of mercury in samples collected from field is not feasible. Therefore, a preconcentration step by evaporation (in the presence of 10 ml concentrated nitric acid per each 500 ml sample) is performed (Kebbekus and Mirta,1998; Allen, Garrison, and Luther III, 1998; Meeravali and Kumar, 2000**)**. The sample of 500 ml is reduced by evaporation to 50 ml). The results for mercury in different channels within Mosul city are represented in Fig (1) and Table (11).

Table 11: Results of Hg (II) concentration in (mg/ℓ) from different channels within Mosul city

Treatments	Al-Khosar	Aqab[a]	Al-Seeb	Danfilly[b]
Filtration only	2.0	2.9	1.5	7.5
Liming + Filtration	N.D	2.0	N.D	2.9
Liming, (N+K) + filtration	N.D	N.D	N.D	N.D
Liming, A(N+K) + filtration	N.D	N.D	N.D	N.D
Liming, S(N+K) + filtration	N.D	N.D	N.D	N.D
Liming, AS(N+K)+ filtration	N.D	N.D	N.D	N.D

a and b=serving the right and left banks industrial zones.

The above table shows that filtration after liming was fair enough to hold mercury from combined sewerage system (Al-Khosar and Al-Seeb), while Aqab and Danfilly need further treatments, probably due to the nature of industrial effluents passing through. Also, it has been found out that (N+K) and other processed materials are promising. This can be due to coprecipitation of different inorganic ions.
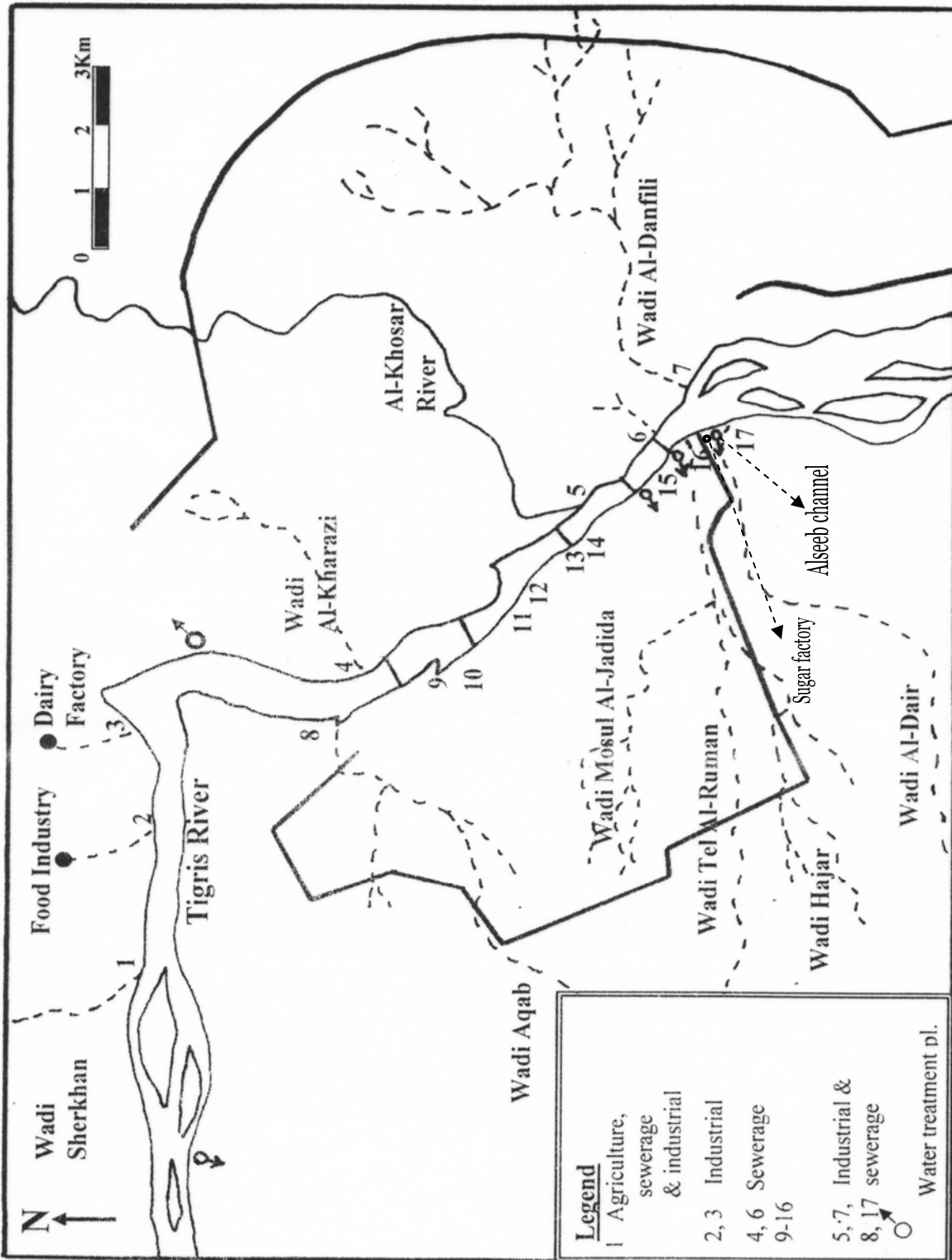

Fig (1): Point source pollution of different wades and outfall discharge to Tigris river within Capital Mosul City.

Hydrolysis products of mercury as $HgOH^+$ and $Hg(OH)_2$, leading to the conclusion that these aqueous species may preferentially adsorbed by mineral surfaces, (Malati, 2002) and (Nagata *et al.,* 2001).

This phenomenon could happen in spite of the mercury solution being clear at high pH. Since it relatively shows the more promising removal efficiency at pH~9.5, which is comparable to that in the literature (pH 10). Reddy and Reddy (2003)**,** who stated that the uptake of mercury (II) ions is directly proportional with the increase of pH, and pH 10 is an optimum plateau value of their uptake using polystyrene–supported chelating polymer resins. To further confirm the mechanism of the removal of Hg (II) ions, a set of experiments has been carried out. Various amounts of charcoal (typical adsorbent) and Dowex-50X (typical strong cation exchanger) have been prepared and the removal efficiency of each mixture is established. The removal of each mixture is compared with the mineral raw materials studied. The results are given in Table (12).

Table 12: Evaluation of the removal efficiency of 80 mg Hg/ℓ at a pH 9.5 using a mixture of different ratios of charcoal and resin in comparison with K, L, their mixtures and processed materials.

No.	Treatment material	Residual Hg, mg/ℓ	%Removal
1.	0.01 g carbon + 0.09 g resin	75	6.3
2.	0.02 g carbon + 0.08 g resin	73	8.8
3.	0.03 g carbon + 0.07 g resin	71	11
4.	0.04 g carbon + 0.06 g resin	70	13
5.	0.05 g carbon + 0.05 g resin	60	25
6.	0.06 g carbon + 0.04 g resin	50	38
7.	0.07 g carbon + 0.03 g resin	40	50
8.	0.08 g carbon + 0.02 g resin	36	55
9.	0.09 g carbon + 0.01 g resin	33	59
10.	Activated carbon	3	96
11.	Resin Dowex-50	70	13
12.	Kaolin (K)	78	3
13.	Low grade ninivite (L)	60	25
14.	AS(K+L)	3	96
15.	S(K+L)	30	63
16.	A(K+L)	12	85
17.	(K+L)	40	50

Weight of materials from 10 to 17 is 0.1g.

Above all the evaluation of the removal efficiency of Hg is shown in Table (12), where it was clear that adsorption is outweigh the exchanging ability.
Comparison of the present work with other methods is shown in Table (13).

Table 13: Comparison between methods used in the removal of mercury ions.

Metal(ll) ions*	Removal by	Removal mechanism	Experimental Conditions				% Removal	Reference
			pH	Time	Temp., ºC	Quantity, g/l		
Hg	Quartz (SiO$_2$) & Gibbsite [Al(OH)$_3$]	Adsorption	7.7-9.5	One 48hrs	20-25	4	Not mentioned	Sarkar *et al*., (1999)
Hg	AS(K+L) or A(K+L)	Mainly adsorption	9.5	10 min.	20-25	2	>95	Present work
Hg	Photo catalysis	Precipitation	9.0 11.0	-	0 40	-	Not mentioned	Malati (2002)
Hg	ZrPO$_4$ grafted in silica gel surface	Adsorption	4.5	15 min.	20-25	4	Not mentioned	Nagata *et al*., (2001)
Hg	Polystyrene-supported chelating polymer resin	Ion exchange, chelating or adsorption or both	10	1hr	25-30	27-133	50-60%	Reddy and Reddy (2003)

* Mainly as nitrate with a dose of 8-12 mg/g.

The result in the above table establishes that the present mode of mercury removal is superior to previous methods since it is characterized by simplicity, rapidity and economy.

CONCLUSION

In the present investigation, it has been found that mercury (II) ion removal from solutions by the mineral raw mixed materials is by the adsorption phenomenon. Therefore, the mixed raw materials prove successful (96%) in removing mercury (II) ions from its effluents. This would promote the use of such materials for further treatment of river water for domestic purposes.

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