Removal of Cu^{2+}, Pb^{2+}, Cd^{2+} from Waste Waters by using Rich Carbonates Materials

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Abstract—The present work aims to assess the characterization of low cost Egyptian rich lime raw materials and their utilization for industrial waste water pre-treatment to remove the heavy metals from the industrial effluents. This is performed through the Characterization and evaluation of the carbonate rich materials used in this study using different techniques such as X-ray diffraction, FTIR spectroscopy, XRF, scanning electron microscopy and chemical analysis….etc. The uptake of Cu^{2+}, Pb^{2+}, Cd^{2+} from waste waters by using rich carbonates materials like clay from Sinai Peninsula (Abu Zenima area) and the second from (Gabal Hammam Feraun) and Lime stone sample was discussed.

Keywords— Cadmium, Copper, Lead, Removal, Waste Water.

I. INTRODUCTION

WATER is a vital necessity to life and constitutes the major part of all living organisms. It is extensively distributed in nature; occupying the greater part of the global surface .it forms about 70% of the human body weight and without it non-live a few days.

The heavy metals and other hazardous pollutants, which are found in industrial effluents, are harmful to sewers and to receiving water. Therefore, pre-treatment for the removal of these harmful substances is the key factor in handling the industrial waste water.

There are 35 metals that concern us because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Glanze 1996)[1]. Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may cause acute or chronic toxicity (poisoning). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's

disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. (International Occupational Safety and Health Information Centre 1999) [2].

Metals such as lead, zinc, copper, aluminium, cadmium and nickel are often described as "heavy metals" though some metals in low concentrations are essential in some organisms, high concentrations can cause sickness and death [3]. The insoluble metals can be absorbed by, inhaled or deposited on the food of primary consumers. Once taken in to the body of vertebrates, lead accumulates in the skeleton, while cadmium is stored in the kidneys [4].

Lead is number 2 on the ASTDR's "Top 20 List" Lead accounts for most of the cases of pediatric heavy metal poisoning (Roberts 1999) [5]. It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust. Target organs are the bones, brain, blood, kidneys, and thyroid gland (International Occupational Safety and Health Information Centre 1999) [2].

Cadmium is a byproduct of the mining and smelting of lead and zinc and is number 7 on ASTDR's "Top 20 list." It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. Target organs are the liver, placenta, kidneys, lungs, brain, and bones (Roberts 1999) [5].

In general clay minerals have been formed through the decomposition of igneous rocks such as granite which were themselves formed by solidification of molten materials from the interior of the earth[6] Granite is from the decomposition of feldspar, in the presence of air and water, over long periods of time that the kaolinite clay has been formed. All potash and part of the silica in feldspar have been dissolved away. The residue is combining with water to give the clay mineral kaolinite.

The structure of clay minerals is based on the combination or condensation of two kinds of layer structures. One layer, known as the silica layer, is composed of silicon and oxygen atoms, and a second layer, known as the gibbsite layer, is composed of aluminum atom and hydroxyl groups. In silica layer each silicon atom is surrounded by four oxygen atoms, the oxygen being at the corners of a regular tetrahedron as a whole carries as net charges of minus four. The tetrahedral join together, sharing oxygen and forming chains of sheets, in each tetrahedron three of the four oxygen atoms are shared with other, giving a continuous sheet. There of our oxygen in

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every tetrahedron are now valence satisfied, receiving one valency from each of two silicon to which they are linked. The fourth oxygen in each tetrahedron is joined to only one silicon atom, and so has one unsatisfied valency. Through these valencies unsatisfied oxygen that the silica layer can join via cations to similar structures.

Limestones [5] consist essentially of calcium carbonate, with which there is generally some magnesium carbonate, and siliceous matter such as quartz grains. The average of over 300 chemical analyses of lime stones showed 92 per cent of $CaCO_3$ and $MgCO_3$ together, and 5 per cent of SiO_2; the proportion of magnesium carbonate is small except in dolomite and dolomitic limestones.

El-Korashy [7] studied the divalent ions uptake of some transition metal cations by natural calcite. He found that, this uptake token place through re-crystallization (precipitation) and cation exchange mechanism between the metal ion and surface Ca^{2+}.the amount of this uptake (meq/g) has been found to increase with increase of metal ion concentrations and reaction time.

Lime in presence of inorganic additives as Na_2CO_3 was also used in heavy metals removal from acid mine drainage [8]. Removal of Cu^{2+}, Zn^{2+} and Pb^{2+} by adsorption onto fly ash and fly ash/lime mixing studied by *P. Ricou and coworker* [9]and they found that, in the first part of the study, isotherms at different pH were carried out at room temperature. Results show increasing removal with increasing pH. In the second part, experimental design methodology was used. The objectives were to determine the influential parameters among the seven studied for adsorption of copper, zinc and lead, then to study their interactions. Results indicate greater removal by using 100 g.l^{-1} of adsorbent with 20% mass of lime at pH 5. However, the preparation of the adsorbent must be modified to increase the role of lime in the removal mechanism.

Yoshitake Suzuki etal [10] studied mechanism and equilibrium relationships for the uptake of Cd^{2+}, Cu^{2+} and Pb^{2+} by coral sand from their nitrate aqueous solutions were studied. The maximum amounts of Pb^{2+} and Cd^{2+} uptaken by coral sand dried at 403 K were about 1.3 and 0.9 mol-kg^{-1}, respectively. That of Cu^{2+} was only about 1/100 that of Pb^{2+} at pH = 6.1-5.5.

The ability of bentonite clay to remove Pb (II) from aqueous solutions and from nitric acid, hydrochloric acid and perchloric acid solutions $(1.0^{-1} \times 10^{-5})$ has been studied [11] at different optimized conditions of concentrations, amount of adsorbent, temperature, concentration of electrolyte and pH. Maximum adsorption of Pb(II), i.e. >98% has been achieved in aqueous solutions, while 86% is achieved from 1.0×10-5 M HCl using 0.5 g of bentonite. [12]The adsorption decreases by increasing the concentration of electrolytes. Isotherm analysis of adsorption data obtained at 25°C, 30°C, 40°C and 50°C showed that the adsorption pattern of lead on bentonite followed the Langmuir isotherm and Freundlich isotherm, respectively.

II. MATERIAL AND METHODS

A. Materials

The raw material samples were taken from different places in Egypt. Two different clay samples the first were taken from Sinai Peninsula (Abu Zenima area) and the second from (Gabal Hammam Feraun). Lime stone sample were taken also from Gabal Etaa south east Suez city. Kaolines used were taken from. And the following table shows the detailed location of the raw materials. While figure 1 clarifies their occurrence on the map of Sinai and Gulf of Suez.

TABLE I
THE DETAILED LOCATION OF THE RAW MATERIALS

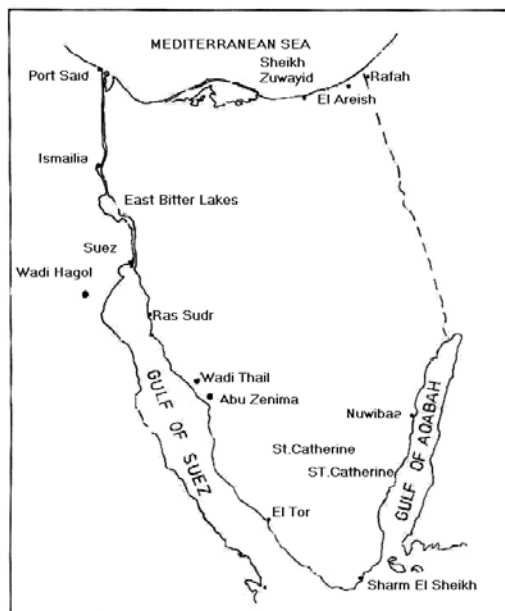| NO.	SAMPLE NAME	LOCALITY DESCRIPTION
1	CLAY 1	GABAL HAMMAM FERAUN, SINAI PENINSULA, EGYPT.
2	CLAY 2	SOUTH ABU ZENIMA CITY, GULF OF SUEZ, SINAI PENINSULA, EGYPT.
3	LIME STONE	GABAL ETAA, SOUTH EAST SUEZ CITY, EGYPT.
4	KAOLINITE	GABAL AL MARKHA, SOUTH ABU ZENIMA CITY, EGYPT.

Fig. 1 The Localities of the raw materials used in the present study

The metal salt solutions used in this study are BDH grads and were prepared by dissolving an accurate calculated weight of analytical grade salts in bi distilled water. Copper as Cu $SO_4.5H_2O$, Cadmium as $CdCl_2$ 2.5 H_2O and Lead as $Pb(NO_3)_2$, in distilled water to give the required concentration.

B. Methods

The transition metal cation reaction experiments were conducted following the standard procedure .A 50 mg of each sample was equilibrated for different periods in glass vials with 15 ml nitrate, sulphate or chloride solution of 100, 200,500 or 1000 mg /l of Cu^{2+}, Pb^{2+}, Cd^{2+}. Nitrate anions were used for Pb_{2+}, sulphate anions for Cu^{2+} and chloride anions were used for Cd^{2+} .After different periods of equilibration (1, 6, 12, 24 hours), the solution and the solid phases in the glass

vial were separated by centrifugation and apart of super latent solution was collected for chemical analysis. The pH of the equilibrium solution in the glass vials was immediately measured. The solid samples were then dried at 80°C for 2 hours in an oven. the solution were analyzed for Cu^{2+}, Pb^{2+}, Cd^{2+} by atomic absorption spectroscopy(AAS), and the amounts of M^{2+} uptake calculated.

The raw materials were thoroughly investigated using X-ray diffraction (XRD) The phase's composition of materials and the solid after reaction with transition metal solutions were identified by (XRD) technique. Using cobalt target (λ=1.791 Å) and a Nickel filter. A Philips X-ray diffract meter was used in the present study at 40 KV and 20 mA. The selected scanning speed was 1°/min. and the sample was used to fill the aluminium mould of the diffract meter with an average thickness of about 1.0 mm. the phases were identified by correlation with the corresponding standard X-ray cards (ASTM)., X-ray florescence (XRF) The samples is irradiated by primary X-radiation from an X-Ray tube .Atoms and anions of the various elements in the sample are there by excited and emit their characteristic radiation. The fluorescence radiation from excited sample is dispersed on special crystals according to Bragg's law (n λ=2dsin θ).The resolved characteristic radiation of every element is analyzed individually and measured by appropriate detectors. The intensity of the characteristic radiation is thereby a direct measure of the chemical composition of corresponding element. and infrared spectroscopy (FTIR) that KBr disc technique was used through the infrared spectroscopic study in the present work. About 3 mg of the sample was thoroughly mixed with 197 mg KBr (A.R spectroscopy) and pressed under vacuum to form a transparent disc with a diameter of 10 mm and a thickness of 1 mm. another disc of the pure KBr using 200 mg sample was similarly prepared and used as a blank. At first the pure KBr disc was scanned using computerized Perkin Elmer 1430 Ratio Recording Infrared Spectrophotometer Instrument in the wave number range 200-4000 cm-1. Each sample under investigation was put in the path of IR beam and scanned through three minutes.

The concentrations of Cu^{2+}, Pb^{2+} and Cd^{2+} in solutions, after reaction, were measured by using Perkin-Elmer set model 2380 atomic absorption spectrophotometer transmission. The instrument was adjusted and the wavelength that gives the maximum absorption for the given element (λmax) was selected. The absorption or emission of a number of standard curves was plotted. The tested solution was diluted to the linear range and its absorption or emission value and the standard curve, the concentrations were determined.

The solid material Samples after treatment with heavy metal solutions scanned by A Philips XL30 attached to EDX unit, with accelerating voltage up to 30 KV, magnification 10 X up to 40,000 X, and resolution for W. (3.5 nm) was used.

The morphology and microstructure of some selected row material after heavy metal uptake process were studied by using scanning electron microscopy (SEM) technique. The powdered samples were suspended in ethyl alcohol and left to settle on disc, after drying, each coated with thin film of carbon using a vacuum evaporator with cathodic rays, to prevent or minimize the accumulation of the electric charges of the incident electron beam on the sample surface. A Philips XL30 attached to EDX unit, with accelerating voltage up to 30 KV, magnification 10 X up to 40,000 X, and resolution for W. (3.5 nm) was used.

The concentration of Cu^{2+}, Pb^{2+} and Cd^{2+} in solutions , after reaction, were measured by using Perkin-Elmer set model 2380 atomic absorption spectrophotometer transmission . The instrument was adjusted and the wavelength that gives the maximum absorption for the given element (λmax) was selected. The absorption or emission of a number of standard curves was plotted. The tested solution was diluted to the linear range and its absorption or emission value and the standard curve, the concentrations were determined.

III. RESULTS AND DISCUSSION

The constitution of the raw materials under the study was achieved through the study of their chemical composition by chemical analysis.

A. XRF of the raw materials:

The x-ray fluorescence (XRF) gives the composition of the raw material .as the given data in the following tables II,III.

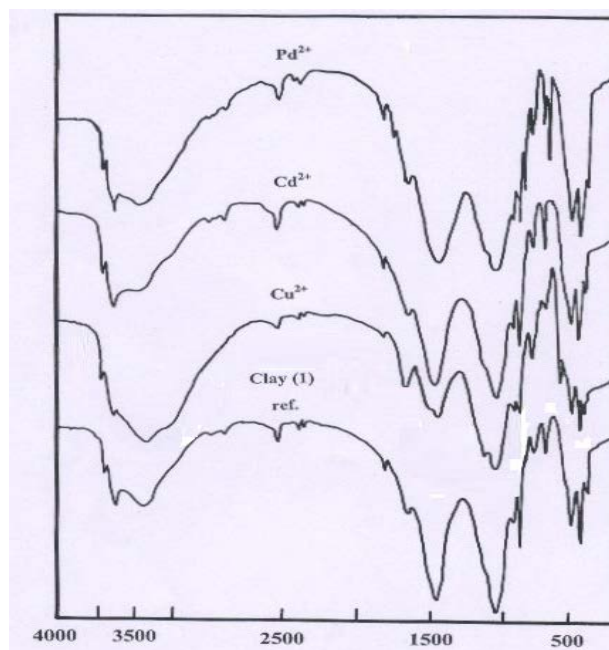#### B. FTIR spectra of the raw materials:

Fig. 2 IR of clay I after and before sorption of metal ions

C. FTIR spectra of the raw materials:

The FTIR spectroscopy is one of the most powerful techniques available for mineral analysis and phase identification. The FTIR spectra of the raw materials were shown in the figures (2, 3 and 4). These figures shows that a medium sharp band appears in the clay samples at 3620-3700 cm-1 which is assignment to valency vibration band of hydroxyl group in clay minerals, medium broad band appear

at 3430 cm-1 can be assignment to the OH- valency vibration of water absorbed to the surface.
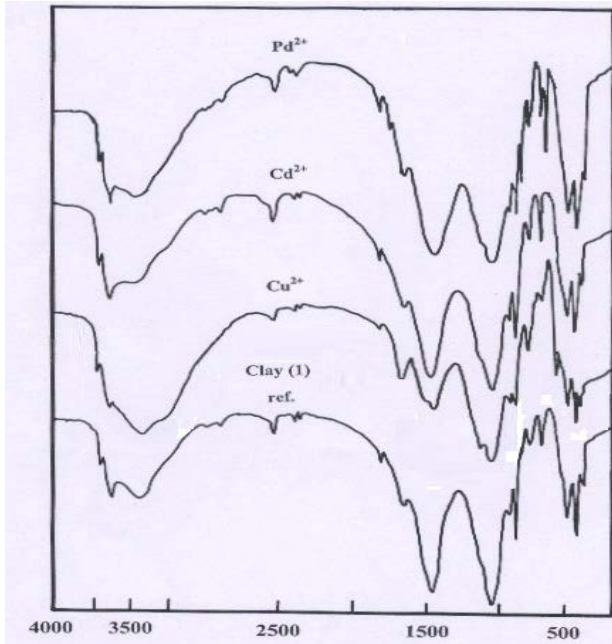

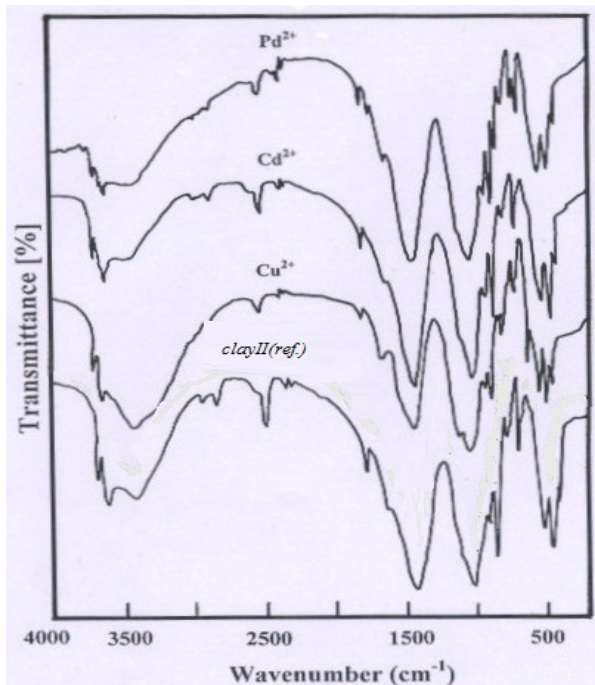Fig. 2 IR of clay I after and before sorption of metal ions

Fig. 3 IR of clay II after and before sorption of metal ions

Weak sharp bands at (1799&2515cm-1) , other very strong broad band at (1430 cm-1) , strong sharp band at (874 cm-1) and medium sharp band at (711 cm-1) are adsorption bands typical of carbonates. Medium strong band appear at 914 cm-1 indicates a deformation vibration of Al-OH group of clay minerals. Symmetrical valency vibration bands of Si-O bonds appear at (797&1033cm-1). Triple strong sharp bands (426&469&527 cm-1) indicate to bending vibration of Si-O-Si in silicate& quartz.
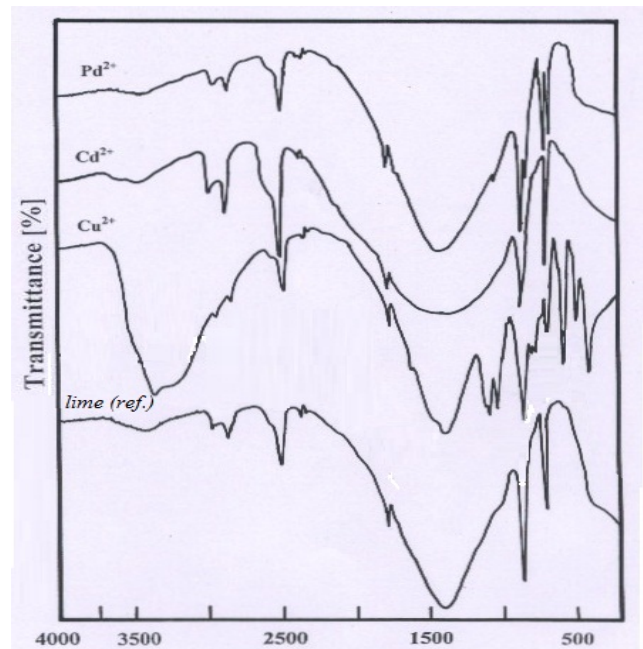

Fig. 4 IR of lime stone after and before sorption of metal ions.

The FTIR -spectra shows strong absorption bands found at 1423,875,711 cm^{-1} ,in addition to weak bands at 2514and 1799 cm^{-1} .These bands are characteristic for pure limestone $CaCO_3$[13].

D. XRD of the raw materials:

The X-ray diffraction patterns of the raw materials under investigation are shown in figures (6, 7, and 8). From these figures it is clear that the investigated clay samples consist of montmorillonite – illite – kaolinite mixtures, with appreciable calcite (CaCO3) and quartz (SiO_2) minerals. It clear that the investigated sample is pure calcite which agreed with ASTM card no. 5-0586 and gives strong bands at (d values = 2.09 & 2.277 & 3.04Å) and medium bands at (d values = 2.49 & 3.88Å).

The carbonate phase consisted of aggregating of subhedral crystals on examination by SEM (Fig. 5a), while EDAX detected a radiation peaks of Ca, C and oxygen only (Fig. 5b).

E. Reaction With Metal Ion Solution:

1. Reaction With Cu^{2+} Solutions:

The amounts of Cu^{2+} ions uptake by the solid materials (meq./100g) as function of time and Cu^{2+} concentration are demonstrated in Table IV. From these data the following conclusion could be drown:

In general, the Cu^{2+} uptake from solutions by the solid raw materials is increased with the increase of the initial concentration of Cu^{2+} solutions. At 100 ppm of Cu^{2+}, limestone has the lowest capacity of uptake compared with clays. This trend was reversed at 200ppm concentration; moreover the capacity of clay II was higher than clay I. At 500&1000ppm of Cu^{2+} the uptake of Cu^{2+} by lime stone is in between clay I&II and at 1000ppm there is no sharp increase of Cu^{2+} uptake by the solids with increasing of reaction time. This means that the uptake of Cu^{2+} from solution by the solids take place mainly through recrystallization (precipitation) of

Cu^{2+} as langite phase.The uptake reactions of raw materials with Cu^{2+} shows new absorption peaks on their XRD.
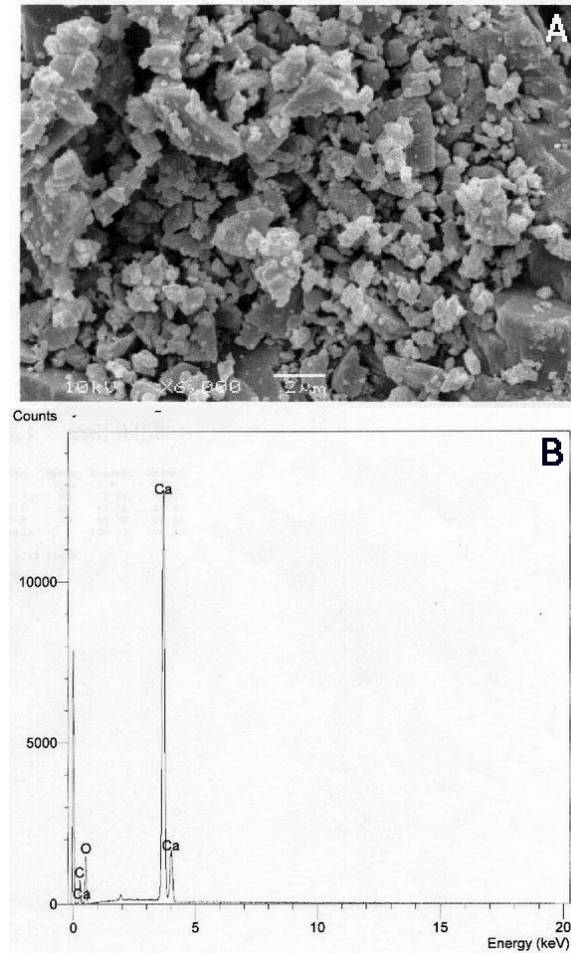

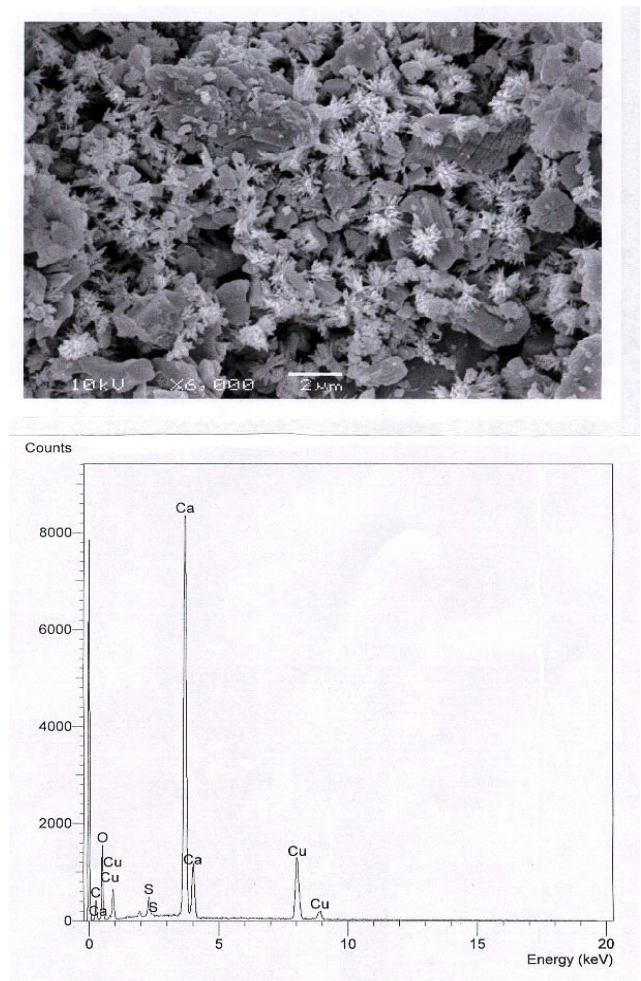Fig. 5 (A&B): SEM of the investigated limestone with EDAX

Fig. 9 microstructure + EDAX of lime stone after Cu^{2+} uptake

Both detect the formation of langite phase $(Cu_4SO_4(OH)_6 .H_2O)$.FTIR spectra Figs.(2,3) shed light on the uptake reaction of the raw materials with the Cu^{2+} metal ion ,new absorption bands were present clearly in the raw material's bands at 2405 (broad) , 1651 ,1116 ,1060 ,816, 792, 600, 432 cm^{-1} these new bands due to the presence of hydrated copper sulphate hydroxide(langite phase)[13]. The examined microstructure of limestone reacted with 1000 ppm of Cu^{2+} for 24hr Fig.(9) detect the formation of langite phase $(Cu_4SO_4(OH)_6 .H_2O)$.

2. Reaction With Pb^{2+} Solutions:

The amounts of Pb^{2+} ions uptake by solid materials (meq./100g) as a function of time and Pb^{2+} ion solution concentration are demonstrated in Table IV .

The Pb^{2+} ions uptake from solution by solid raw materials is increased with the initial concentration of the lead ions and time of the reactions. At 100 and 200 ppm concentrations of Pb^{2+}, the complete removal of lead (100%) from solution was achieved after 1 hr of reaction time by both clay I and limestone. This trend is also confirmed by using clay II but after 6 hr at 100ppm Pb^{2+} and after 24 hr reaction time when 200 ppm of Pb^{2+} is used. At 500ppm of Pb^{2+} concentration the uptake increases with increasing the time of reaction and became 100% after 6 hr by clay II. The order of this uptake has been found as in the following sequence: clayII > clayI > limestone, and in the order: limestone ≥ clay I > clay II when 1000 ppm of Pb^{2+} is used.

TABLE II
XRF ANALYSIS OF CLAY SAMPLES

Clay samples	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	SO$_3$	K$_2$O	Na$_2$O	Cl	Total	S.R.	A.R.	CaCO$_3$
Clay I	21.04	33.68	8.92	4.23	2.71	0.16	0.96	1.81	1.64	75.46	2.50	1.97	37.57
Clay II	25.75	29.49	9.72	3.39	1.78	0.41	1.51	1.12	1.05	74.22	2.25	2.87	46.01

TABLE III
XRF ANALYSIS OF LIME STONE

CaO	SiO₂	Al₂O₃	Fe₂O₃	MgO	SO₃	K₂O	Na₂O	Cl	TiO₂	P₂O₅	Mn₂O₃	CaCO₃
54.77	0.27	0.17	0.03	0.62	0.06	0.03	0.02	0.04	0.01	.010	0.09	97.08

TABLE IV
MEQ./100 G UPTAKE OF IONS AS A FUNCTION IN INITIAL CONCENTRATION (PPM) AT DIFFERENT REACTION TIMES

meq./100 g uptake of Cu²⁺ as a function in initial concentration (ppm) at different reaction times:

Time (hr.)	100 ppm			200ppm			500ppm			1000ppm		
	clay1	clay2	limestone	clay1	clay2	limestone	clay1	clay2	limestone	Clay 1	Clay2	limestone
1 h	68.73	68.13	29.30	117.14	155.78	149.40	237.90	214.60	162.32	336.01	798.42	710.19
6 h	69.92	72.31	44.83	156.57	169.72	185.25	240.29	240.97	274.94	363.49	883.26	778.11
12 h	79.73	78.88	50.81	177.29	177.48	188.83	262.40	306.61	319.75	367.08	904.76	886.17
24 h	89.04	88.24	80.92	181.07	188.83	188.83	312.58	409.96	385.47	471.03	913.43	913.48

meq./100 g uptake of Pb²⁺ as a function in initial concentration (ppm) at different reaction times

Time (hr.)	100 ppm			200ppm			500ppm			1000ppm		
	clay1	clay2	limestone	clay1	clay2	limestone	clay1	clay2	limestone	Clay 1	Clay2	limestone
1 h	28.96	15.35	28.96	57.91	56.12	57.91	130.86	100.77	110.91	252.45	163.03	238.61
6 h	28.96	28.96	28.96	57.91	56.58	57.91	138.41	144.79	115.83	261.73	168.53	260.62
12 h	28.96	28.96	28.96	57.91	56.58	57.91	138.11	144.79	115.83	270.99	173.75	284.94
24 h	28.96	28.96	28.96	57.91	57.92	57.91	140.15	144.79	135.23	270.99	236.00	284.94

meq./100 g uptake of Cd²⁺ as a function i in initial concentration (ppm) at different reaction times:

Time (hr.)	100 ppm			200ppm			500ppm			1000ppm		
	clay1	clay2	limestone	clay1	clay2	limestone	clay1	clay2	limestone	Clay 1	Clay2	limestone
1 h	*28.95*	22.84	11.85	30.03	27.37	18.82	136.83	129.30	135.60	407.27	395.18	390.29
6 h	*30.28*	25.04	13.69	31.90	29.81	22.13	145.38	134.38	136.22	407.33	402.51	391.51
12 h	*34.44*	27.37	15.16	33.48	31.65	24.93	163.69	135.73	138.66	407.39	403.73	393.35
24 h	*35.63*	28.47	17.35	37.39	35.56	29.20	164.57	140.19	139.27	412.36	404.59	395.18

The uptake of Pb²⁺ from solution is mainly due to the recrystallization of lead from solutions as Cerussite phase (PbCO₃) as cleared from XRD pattern Figs.(6,7,8). This reaction possibly took place by dissolution of carbonates in clays or limestone raw materials by acidic nature of Pb²⁺ solution. These results agreed with the data published in [7].

FTIR spectra Figs (2,3,4) shed light on the uptake reaction of the raw materials with the Pb²⁺ metal ion. New absorption bands were clearly observed in the raw material's bands at 1728,837,695 and 678 cm⁻¹ .These new bands could be due to the presence of lead as Cerussite phase.

The examined microstructure of clay II reacted with 1000 ppm of Pb²⁺ for 24hr Fig.(10) show the precipitation of lead in the form of hexagonal crystals of Cerussite (PbCO3).

3. Reaction with Cd²⁺ solutions:

The amounts of Cd2+ ions uptake by solid materials (meq./100g) as a function of time and Cd2+ concentration are demonstrated in Table IV . From these data the following conclusions could be drawn:

From the data obtained, it is generally obvious that the Cd²⁺ ions uptake is increased with increase of the reaction time and the initial concentration. The maximum uptake percent obtained was about 77 % from 1000ppm cadmium solution by the solid clay I (412 meq. Cd²⁺ /100g of solid). In all cases, the amount of Cd²⁺ uptake by the solid materials was found in the following order: clay I>clay II> limestone.
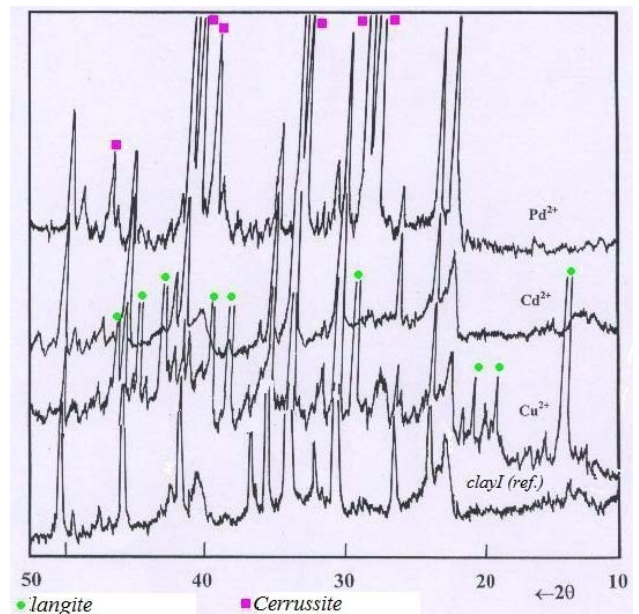

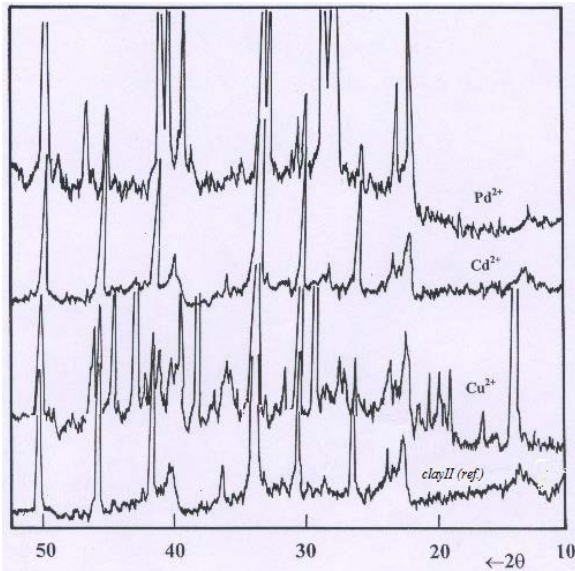Fig. 6 XRD of clay I after and before sorption of metal ions

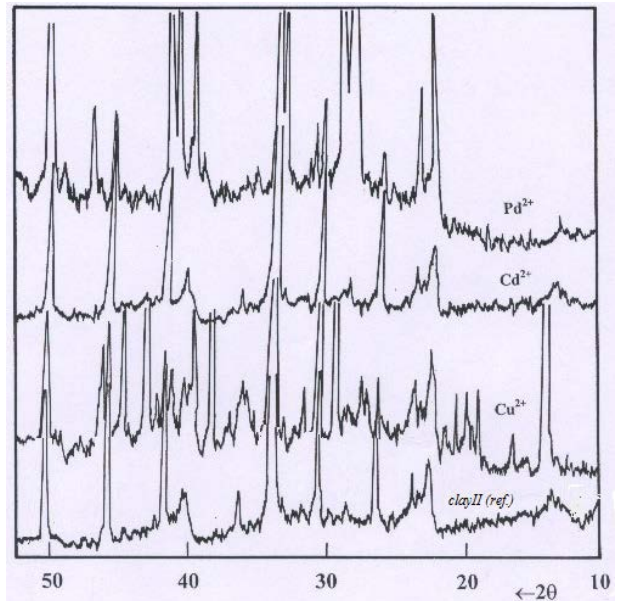Fig. 7 XRD of clay II after and before sorption of metal ions

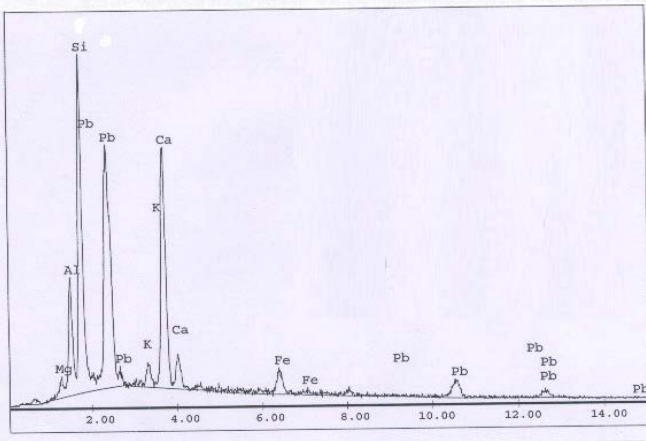Fig. 8 XRD of limestone after and before sorption of metal ions

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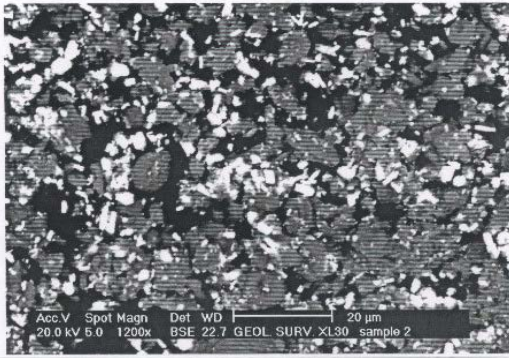[1] Glanze WD C.V. Mosby, St. Louis, MO, U.S.A. (1996),
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Fig. 10 microstructure + EDAX of clayII after Pb^{2+} uptake