Studies on the Recovery of Cu (II) and U (VI) on Highly Adsorptive Modified Magnetic Amine Resins from Dolostone Leachate Solution

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Abstract

Magnetic chelating resin containing amine moiety was obtained by polymerization of chloromethyl styrene with both 5 % and 10% divinylbenzene as a crosslinking agent in the presence of Fe_3O_4 as magnetite particles, the yield was treated with malononitrile followed by reaction with hydrazine hydrate in the presence of absolute ethanol to get hydrazenyl amine polymer. The obtained resins were investigated by FT-IR, elemental analysis and SEM. The use of magnetite particles was used for increasing the surface of chelating active sites and easy collection from solution. The obtained resins were evaluated toward the uptake of Cu (II) and U (VI) from their aqueous synthetic solutions followed by application on acid leachate of dolostone ore materials from southwestern Sinai. Contact time, pH and initial concentration of the metal ions were investigated as factors affecting the uptake behavior. The modified resins display higher uptake capacity compared to the metal oxide-free resin also high regenerated efficiency.

Keywords: Magnetic resin; Uranium; Dolostone; Waste.

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1. Introduction

Magnetic amine resins represent an important class in the solid phase separation. Bimolecular separation, water and wastewater treatment, desalination, color imaging and information storage are some uses of these resins. Synthesis and uses of magnetic resins became more attractive to researchers for separation of radioactive and heavy metal ions from their aqueous waste [1-6].

Different techniques have been employed such as solvent extraction, precipitation, co-precipitation, sorption and ion exchange [7]. Chelate-forming resins play an important role in ion exchangers for various metal ions in different environmental and industrial areas [8-12]. These resins show greater selectivity compared to the conventional types of ion exchangers [13-15]. Besides, they show good physical and chemical properties such as porosity, high surface area, durability and purity. Many chelating resins with different functionalities like quaternary amine [16, 17], sulfonamides [18], Schiff base [18- 21], sulfonic acid [22, 23], hydroxamic acid [24] and amidoxime [25, 26] have been emphasized for interaction with metal ions.

Copper and uranium are well known heavy toxic metals that pose a serious when discharged into industrial wastewater. The present work is the studying of selective adsorption properties of synthesized resins toward copper (II) and uranium (VI) before application on natural liquor from acid leaching on dolostone ore material from Allouga locality.

2. Experimental

2.1 Materials

Chloromethylstyrene (CMS) and hydrazine hydrate 99.9% were obtained from Fluka, Japan. Divinylbenzene (DVB, 55%), uranyl nitrate hexahydrated (source of uranium) and sodium hydride, potassium per-sulfate (KPS) were obtained from Sigma-Aldrich, England. All other chemicals were analytical grade and used as received.

2.2 Measurements

Fourier transform infrared spectra (FTIR) were measured on JASCO 460 plus FT–IR spectroscopy model in the 400–4000 cm^{-1} region. Uranium concentration was measured using ICP-MS. Copper was analyzed using atomic absorption technique (Perkin-Elmer, Waltham, MA, USA, AAnalyst100).

2.3 Preparation of cross-linked magnetic resin

Magnetite (Fe_3O_4) particles were prepared by co-precipitating Fe^{2+} and Fe^{3+} ions by ammonia solution and treating under hydrothermal conditions [27]. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3 M iron ions. Chemical precipitation was achieved at 25 ^{o}C under vigorous stirring by addition of NH_4OH solution (29.6 wt.%). During the reaction process, the pH was maintained at about 10. The precipitates were heated at 80 ^{o}C for 30 min, washed several times with water and ethanol, and then finally dried in a vacuum oven at 70 ^{o}C.

The water/oil (W/O) emulsion cross-linking technique was used for the preparation of magnetic chloromethyl styrene-divinyl benzene resin. In a typical procedure, 9.5 g chloromethyl styrene, 0.5 g divinyl benzene for 5% MAR (CM1) and 9 g chloromethyl styrene with 1.0 g divinyl benzene for 10% MAR (CM2) was taken in a three-necked round-bottom flask, and the mixture was sonicated for 10 minutes. Another mixture of 0.5 g of KPS (initiator) and 73 ml of 1% polyvinyl alcohol was added followed by 24.5 ml of methylbenzoate and dioctyl phthalate. Polymerization was performed under nitrogen at 75◦C for 10 hours. The final product of the cross-linked magnetic resin was collected using a magnetic and rinsed with ethanol and deionized water for three times. The resin was then dried in an oven at 60 ^{o}C for 24 h and kept in a vacuum desiccator for further analysis and use.

Reaction of the magnetic crosslinked resin with malononitrile in the presence of sodium hydride in DMF at 60 ^{o}C for 1 h to produce magnetite polychloromethyl styrene divinylbenzene malononitrile (MPAN) in which it was treated under refluxing temperature with hydrazine hydrate 99.9% on 16 ml absolute ethanol for 5 h to yield yellow precipitate of magnetic polychloromethyl styrene hydrazinyl amine (MCHA) that filtered off, washed with ethanol and dried at 50 ^{o}C for 4 h (Figure 1).
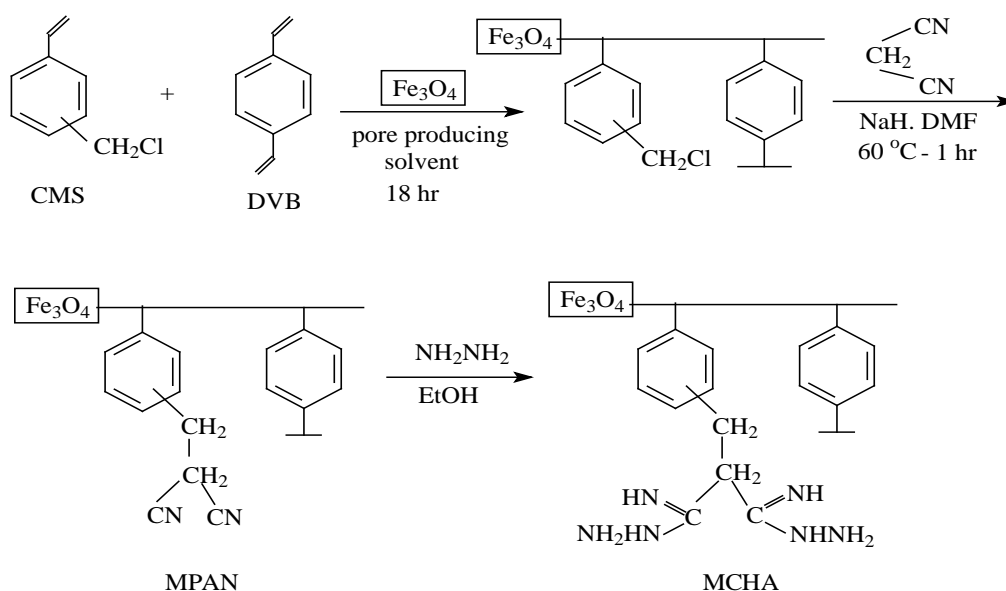
Figure 1: Synthesis of magnetic polyhydrazinyl amine based on chloromethyl styrene resin with 5 % divinyl benzene (GCHA).

2.4 Metal adsorption–desorption experiments

2.4.1 Effect of pH

Solution of 50 – 500 ppm of the metal salt under study was prepared in acidified distilled water. Uptake experiments were performed at controlled pH by shaking 0.1 g resin with 1000 ml metal ion solution for 3 h at 25 ^{o}C and 200 rpm. Using of sulfuric acid and sodium hydroxide for pH adjustment.

2.4.2 Effect of contact time

The experiments were conducted by shaking 0.1 g MCHA with 1000 ml (100 ppm) metal ion solution at pH 5.0. The contents of the flask were shacked on a shaker at 200 rpm and 25 ^{o}C. Five milliliters of samples were taken at time intervals for the analysis of residual metal concentration in solution.

2.4.3 Effects of temperature on the uptake

Effects of temperature were determined by mixing resin with solution and shaking for 3 h at pH 5 while varying the temperature to 25 ^{o}C, 30 ^{o}C, 40 ^{o}C and 50 ^{o}C.

After mixing, the aqueous phase was separated from the solid phase by magnetic rod. The amount of metal ions in the supernatant was determined by the following equation.

$$qe = [(C0 - Cf) V]/W$$

Where C0 and Cf are the initial and final concentrations (mg/L) of metal ion in the aqueous solution, respectively, V is the volume of metal ion solution (L), and W is the weight of MCHA resin (g).

2.4.4 Elution of adsorbed metal ions

Batch desorption experiments were carried out using, 0.5M HNO_3, 1M EDTA-1M NH_4OH, 1M thiourea, and 0.3 M HNO_3-1.0 M thiourea. The adsorbed precious metal ions on MCHA were washed several times with deionized water. Addition of 30 ml of the eluent for each 1 g resin and then the bottles were shaken at 25 ^{o}C for 2h. The concentration of precious metal ion released from the MCHA into aqueous phase was analyzed.

2.4.5 Reuses of synthesized polymer

To investigate the reusability of the adsorbents, the MCHA after desorption was reused for other adsorption experiment and the process was repeated for five times.

## 3. Results and discussions

3.1 Characterization of synthesized resin

3.1.1 IR spectra and SEM photos

The amine chelating resins were obtained from nitrile groups through the treatment by hydrazine hydrate. This behavior was confirmed from IR measurements of the resins as in Figure (2). For chloromethyl styrene divinyl benzene resins (Figure 2a) it shows the identified peaks for C-H aromatic of benzene ring at 3077 and peak at 1950 for C-H aliphatic. For MPAN (Figure 2b) it shows band at 2240 Cm-1 for CN stretching, peaks at 2980 – 2956 Cm-1 for C-H aliphatic stretch and that at 3050 for C-H aromatic of benzene ring, the peak at 1080 Cm-1 for C-N stretch. On the other hand, the spectra of the amino-resins (Figure 2c) are characterized by υNH at 3440

Cm-1 and a new peak at 1640 Cm-1 for C=N. Also SEM photos were appeared in Figure (3) and show the coated polymer on magnetite particles
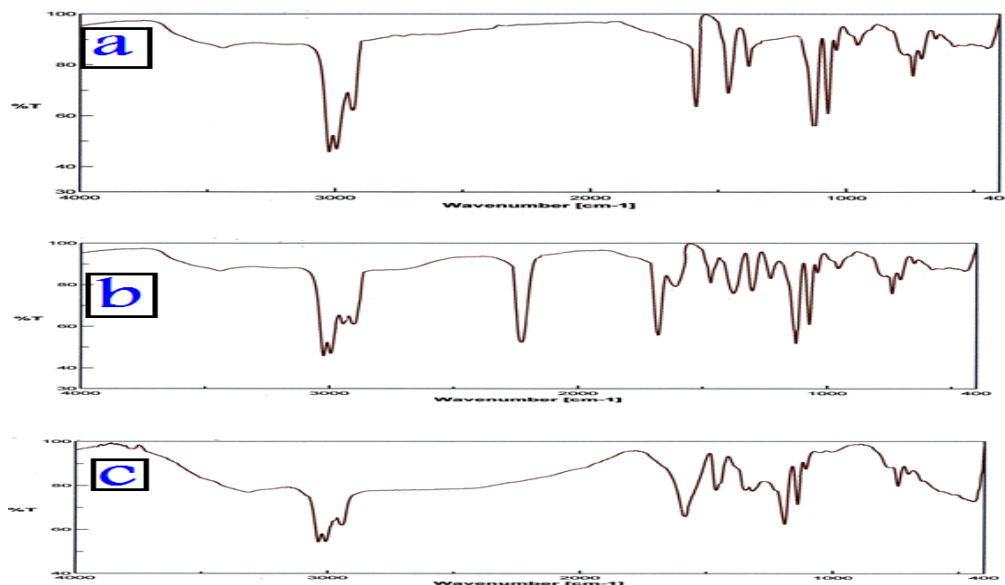
Figure 2: FTIR spectra of (a) polychloromethylstyrene-DVB, (b) poly malononitrile derivative (c) polyhydrazenyl amine derivative
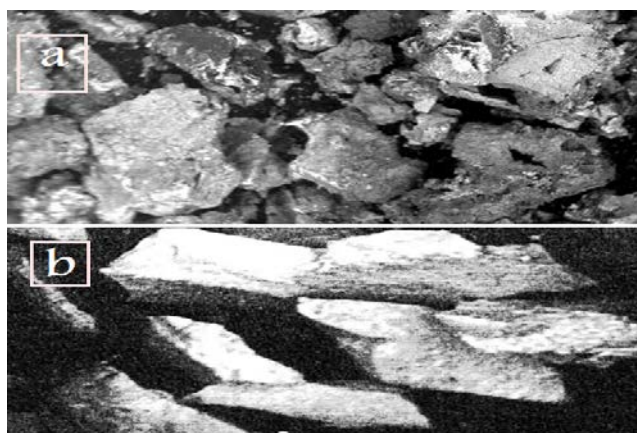
Figure 3: SEM photos of coated polymer on magnetite particles a) polychloromethyl styrene divinyl benzene b) MCHA

The concentration of the amine active sites in the obtained resins was estimated using the volumetric method [28]. A 20 ml of 1 N HCl solution was added to 0.1 g resin and conditioned for 15 h on a shaker. The residual concentration of HCl was measured through titration against 0.5 N NaOH. The number of moles of HCl that interacted with the N atoms was determined and consequently the active sites concentration was calculated. The concentration of active sites is 13.1 and 12.7 mmol/g of MCHA1 and MCHA2 respectively that indicate as crosslinking agent increased active site is consequently decreased. This decrease in the concentration of the amino group is closely related to the decrease in the ratio of chloromethyl styrene monomers and so hydrazyl amine (which later transforms into the amino resin) and the skeletal structure of each resin as shown in Table 1.

Table 1: The concentration and other textural properties of amino group on resins with different cross-linking ratios.

Resin	Density (g/ml)	Porosity (%)	Total pore area (m^2/g)	Concentration of amino group (mmol/g)
MCHA1	0.51	33.56	44.43	13.1
MCHA2	0.39	41.76	35.77	12.7

3.2 Physical measurements

The data of the physical properties for the resins obtained were present in Table 1. The density was found to follow the order, MCHA1 > MCHA2. This indicates that as the cross-linking degree increases, the resin formed becomes less dense and expected to be more porous that increases in the same direction. On the other hand, the values of the total pore area and the average pore diameter change irregularly with the change in the ratio of cross-linking agent. So, while resin MCHA2 gave large average pore diameter and low total pore area, resin MCHA1 showed low pore diameter and high pore area. Moreover, resin MCHA1 showed higher pore area and lower pore diameter compared to MCHA2.

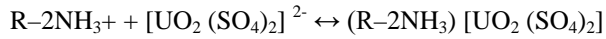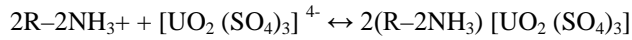### 3.3 Studies on the uptake of metal ions using batch technique

3.3.1 Effect of the contact time

The effect of the agitation time on the degree of extraction of Cu^{2+} and U^{6+} on MCHA1 and MCHA2 resins was studied in Figure 4. From this Figure it seen that high adsorption rates are observed at the beginning of adsorption process and then saturation values (i.e. adsorption equilibrium) are gradually reached within 60 min also it was shown that greater than 50% of adsorbed metal ions were performed within 20 min, it is seen that, the maximum uptake follows the order U^{6+} MCHA1 > U^{6+} MCHA2 > Cu^{2+} MCHA1 > Cu^{2+} MCHA2 for at all-time intervals. The uptake capacities of MCHA1 for both U (VI) and Cu (II) is as follow 410, 360 respectively and that for MCHA2 is 380, 335 respectively.
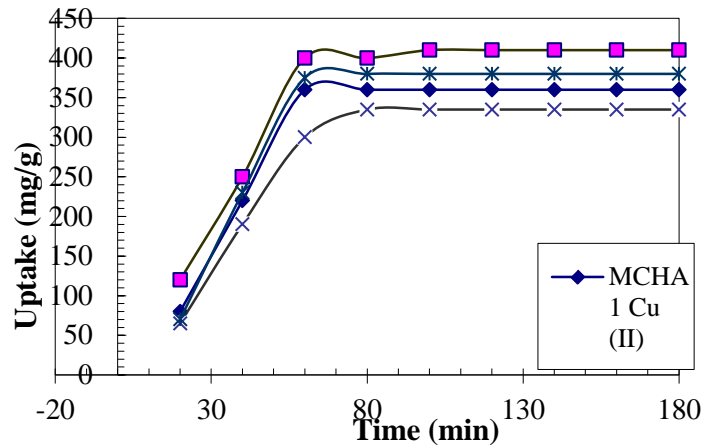
3.3.2 Effect of pH on the uptake

The most dependent factor affecting the metal ion complexation with polymeric ligands is the pH of the medium. Uranium and copper precipitation occurs above pH 6.5, which also depends on the concentration of metal ions in the medium. Therefore, in the present study the uptake studies were carried out prior the precipitation limit of each metal ion by changing the pH range between 1.5 and 6.0. The effect of pH on the adsorption of these resins is also shown in Figure 5. The Cu (II) exhibited a low affinity in acidic conditions (pH ≤ 2.0); due to protonation of amine groups at low pH values a somewhat higher affinity at pH 6.0 may be attributed to the presence of free lone pair of electrons on the nitrogen atom suitable for coordination with the

metal ion to give the corresponding resin-metal complex. At pH < 2, no appreciable uptake was detected for Cu^{2+} but it was relatively high for U^{6+} due to formation of tetra and divalent complex of uranyl sulfate [29] that can be attached to ammonium group on resin to form tetra (di) valent amine complex as in below equations

$$2R–2NH_3+ + [UO_2 (SO_4)_3]^{4-} \leftrightarrow 2(R–2NH_3) [UO_2 (SO_4)_3]$$

$$R–2NH_3+ + [UO_2 (SO_4)_2]^{2-} \leftrightarrow (R–2NH_3) [UO_2 (SO_4)_2]$$

The effect of concentration of the investigated metal ions on their uptake by (MCHA1 and MCHA2) resin is given in Figure. 5 in which the loading capacity at lower pH for U (VI) is higher than four times at pH 1 and 2 than Cu (II) and for pH 3 it is twice higher in the uptake, where as for other pHs it is higher by 50 to 100 ppm for other that it was 15, 122, 157, 270, 390, 410 for MCHA1 in U VI loading and 5, 35, 70,190 350 and 360 for MCHA1 in Cu (II) loading. For MCHA2 U (VI) loading it is 10, 90, 100, 200, 370, 380 and for Cu (II) it is 4, 33, 45, 170, 295, 335 at pH from 1-6 respectively as in Figure 5.


Figure 4: Effect of the contact time on the uptake of Cu (II) and U (VI) by MCHA1 and MCHA2 resins with initial concentration 100 ppm and neutral pH.
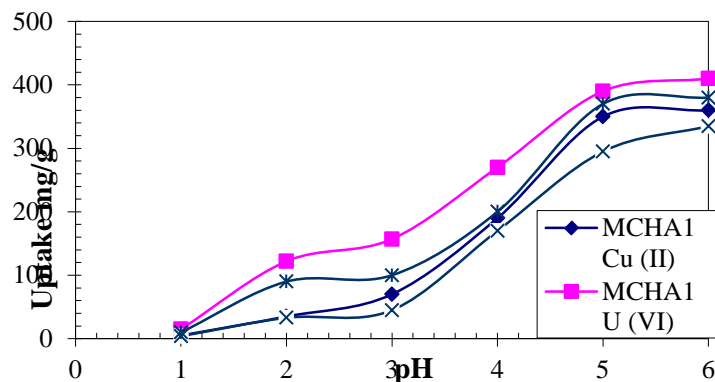

Figure 5: Effect of PH on the uptake of Cu (II) and U (VI) by MCHA1 and MCHA2 resins with initial concentration of 100 ppm, 28 oC and contact time 3 h.

The effect of concentration of the Cu^{2+} and U^{6+} on their uptake by (MCHA1 and MCHA2 resins at different temperature) is given in Figure 6. From this Figure it was noticed that, as the temperature increases the uptake gradually increase due to increase the pore size and so the diffusion of metal ions adsorbed easily inside it. From these reason, the uptake of MCHA1 and MCHA2 resins toward U^{6+} is 450, 400 respectively at 30 °C, 490, 420 respectively at 40 °C and 500, 440 respectively at 50 °C, and 520, 505 respectively at 60 °C, where as for Cu^{2+} loading capacity it is 418, 365 respectively at 30 °C, 430, 375 respectively at 40 °C, 440, 383 respectively at 50 °C and 470, 353 respectively at 60 °C.
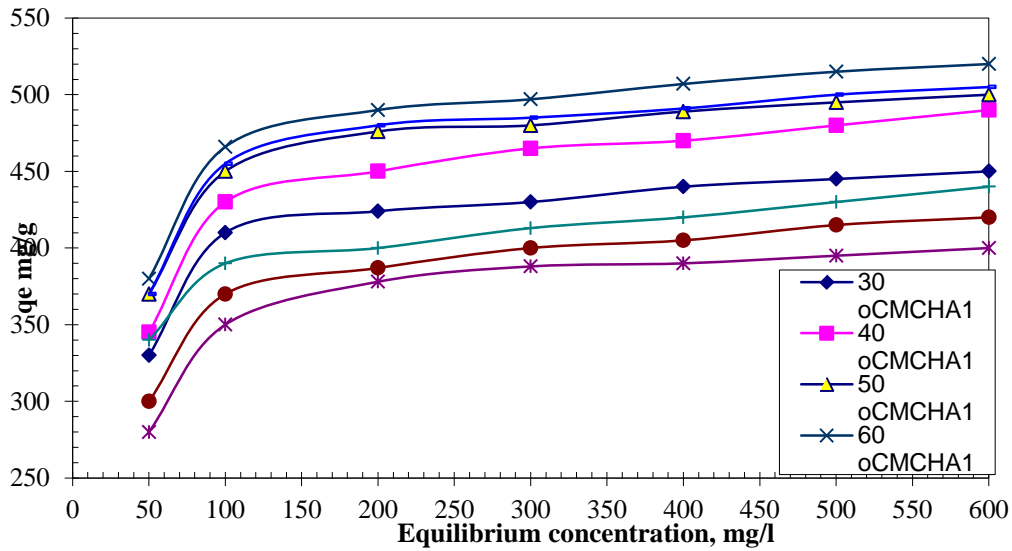
(a)
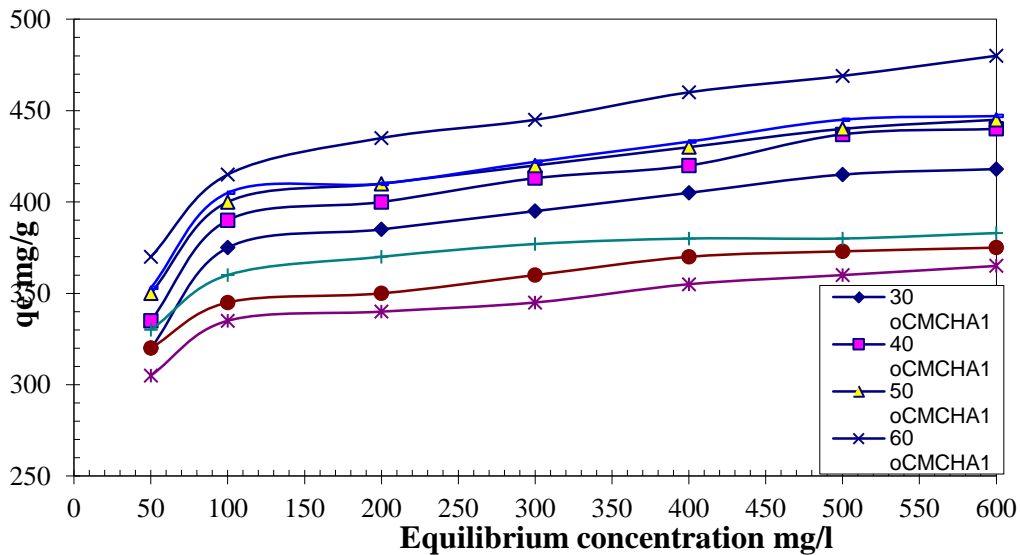
(b)

Figure 6: Adsorption isotherms of (a) U $^{6+}$ and (b) Cu^{2+} on MCHA1 and MCHA2 resin, natural pH as a function of temperature and contact time 4 h.

3.3.3 Elution of adsorbed ions

Beside the selectivity in adsorption by pH adjustment, there is a selectivity in elution step that is appear in the using of 0.1 M EDTA that elute above 95 % of adsorbed Cu^{2+} and below 25% of U^{6+} this results was expected that mentioned in the previous research [30] that is the results are shown in Table 2. It is seen that the ratio of elution efficiency for Cu^{2+} against U^{6+} is higher in the case of 0.1 M EDTA and 1M EDTA: 1M NH_4OH than other eluents.

Table 2: Desorption ratio of Cu (II) and U (VI) metal ions for various eluents.

Conc. of	Desorption efficiency (%)	
	Cu (II)	U (VI)
0.1 M EDTA	95.6	20.7
1M EDTA: 1M NH_4OH	97.3	34
1 M thiourea	93.5	40.4
0.3M HNO_3–1.0 M thiourea.	98.8	91.9
0.5M HNO_3	98.8	97.7

3.3.4 Resin regeneration

Reuses of resins for further loadings and compare to the first one is known as regeneration and calculated by the following eq.

$$\text{Efficiency of regeneration } = \frac{\text{Total adsorption capacity in the second run}}{\text{Total adsorption capacity in the first run}} \times 100$$

It was tested by loading the resin with both metal ions at maximum capacity of 410 and 380 mg/g for U^{6+} and 365 and 335 for Cu^{2+} of both MCHA1 and MCHA2 respectively. From Table 3, there is no appreciable loss in activity was observed over at least five cycles. Moreover, U^{6+} and Cu^{2+} were eluted by 1M HNO_3.

**Table 3:** Effect of recycling on regeneration efficiency.

Number of cycle	Regeneration efficiency (%)	
	Cu (II)	U (VI)
1	95.2	96.0
2	93.5	95.6
3	92.4	95.1
4	92.1	94.5
5	92.1	93.2

From the above data, the most parameters for selective separation of copper and uranium is the adsorption at pH 1.8 for uranium uptake then loading at pH 6 for copper ions followed by desorption using of 0.1 M EDTA for elution of copper ions (in the loaded pH 6 resin) and eluted by HNO_3 for elution of uranium ions (for resin of pH 6 adsorption). This method is used to separate more than 90 % of dissolved copper and uranium form each other in their solution.

3.4 Application of MCHA1 for separation of Cu^{2+} and U^{6+} ions from acid leachate of dolostone ore material

In the present work, a proper sample of the dolostone ore materials from the Um Bogma area formation of Abu Zeneima in southwestern Sinai; is located to the east of Abu Zeneima town on the eastern coast of the Gulf of Suez (Figure 7).
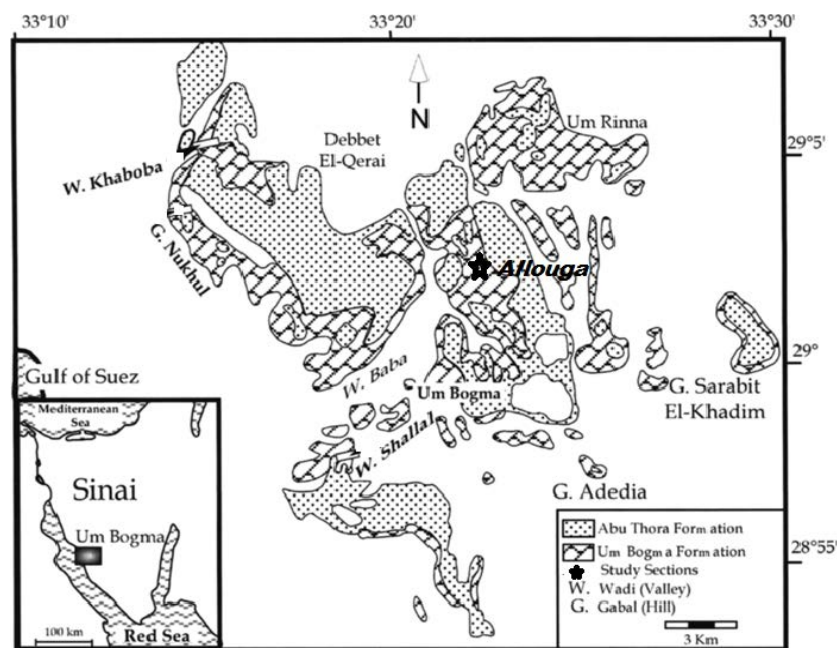
Figure 7: Location map showing the distribution of the Lower Carboniferous in the Um Bogma area, Western Sinai, Egypt. According to Kora and Jux [31].

It is covered by Paleozoic rocks unconformably overlain the Precambrian basement rocks. The Paleozoic rocks (Early Cambrian to Permian) Sinai are well developed in Um Bogma area; attain a thickness which varies from 120 to 500 m [32]. The Early Paleozoic sediments of Sarabit El Khadim, Abu Hamata and Adedia Formations comprise continental to shallow marine clastic rocks [33, 34]. Most of mineralization (ferromanganese, copper, uranium and gibbsite) occurs within the Um Bogma Formation. This rock unit is composed mainly of dark grey and pink dolostone, especially in the lower and upper parts, with alternating ocherous yellow marl, ocherous soft earthy dolostone and soft yellowish siltstone making up the middle section. [35].

3.4.1 Methods of Analysis

3.4.1.1 Major and Trace Elements Analyses

All the elements were analyzed by icp technique including economic and trace metals.The economic metal values namely Cu were measured using a Unicam atomic absorption spectrophotometer model-969 (AAS) flame type at λ 324.8 nm. The results of elements were listed in Table 4 that assayed about 2883 ppm of Cu, 142 ppm Co, 97 ppm Ni, and 758 ppm U. In addition the ore assays 0.46 % MnO as in Table 4.

Table 4: Chemical analysis of dolostone ore materials from the Um Bogma area formation at Abu Zeneima in Southwestern Sinai.

| Component	Content, Wt. %	Component	Content, ppm
SiO_2	25.5	Cu	2883
Al_2O_3	0.38	U	758
TiO_2	0.01	Co	142
Fe_2O_3	2.22	Ni	97
CaO	22.29	V	53
MgO	16.58	Cr	26
Na_2O	0.06	Zn	33
K_2O	0.08		
P_2O_5	0.02		
MnO_2	0.46		
H_2O (110°C)	0.87		
LOI (550°C)	3.9		
LOI 1000°C	29.23		
Total	**101.60**		

3.4.1.2 Leaching procedures

Different leaching conditions are studied to attain the maximum possible leaching efficiency of the metal values. These conditions include the type of leaching (agitation leaching or percolating leaching process); reagents use (as carbonate, nitrate, chloride or sulfate), time of agitation, temperature, the ore grain size, Solid /Liquid ratio (S/L) and oxidant.

Studying of these factors would appear in Figure 8 that the most leaching reagent used for uranium and copper was being sulfuric acid especially when it was relatively low cost and wide availability. Other applicable acids, such as hydrochloric and nitric, are more costly and cause more serious environmental pollution than sulfuric acid. Carbonate / bicarbonate mixture is selected to uranium only. Ammonium carbonate / ammonia solution   is selected to both uranium and copper with high yield.
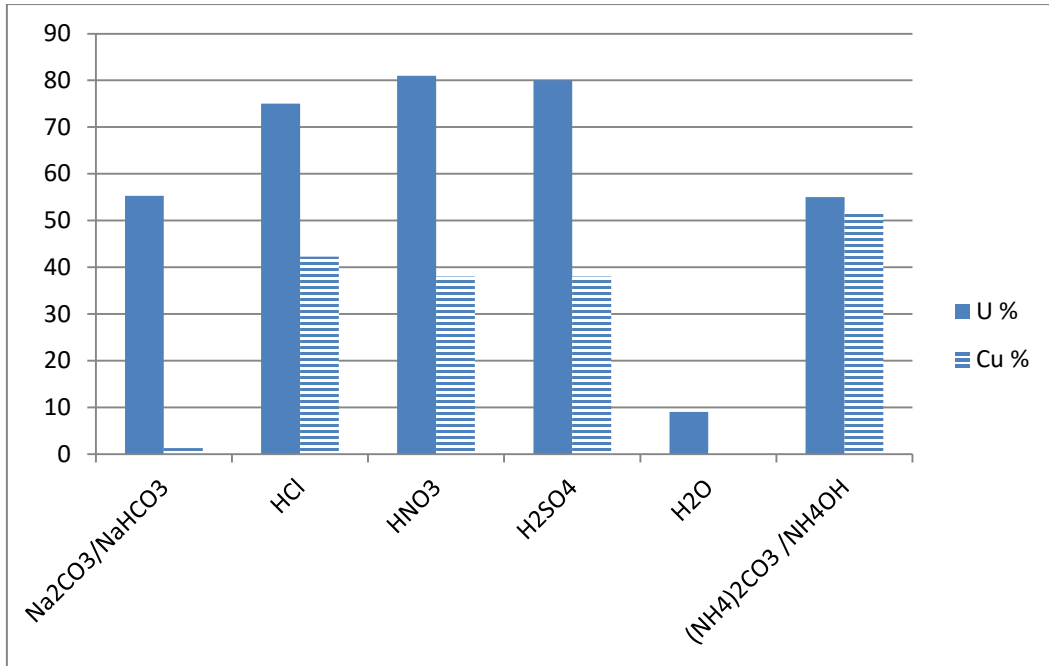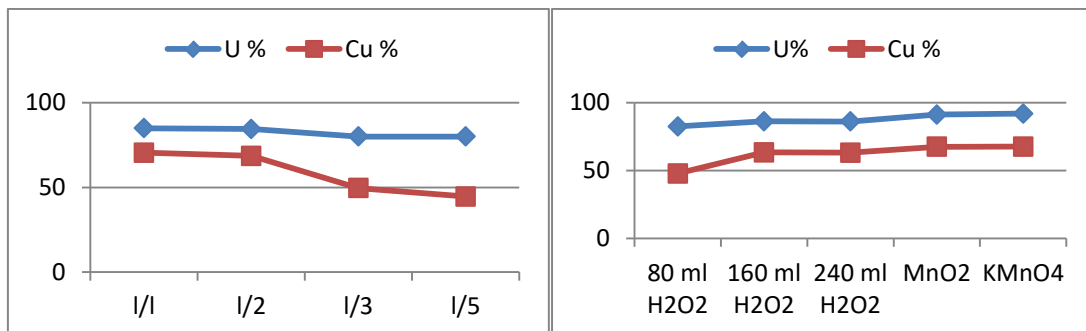
Figure 8: Effect of different lixving on uranium and copper leaching.

A series of tests were performed to select the optimum condition that appeared in Figure 6 as sulfuric acid concentration (a), leaching time (b), solid: liquid ratio (c), oxidant type (d) and temperature (e)
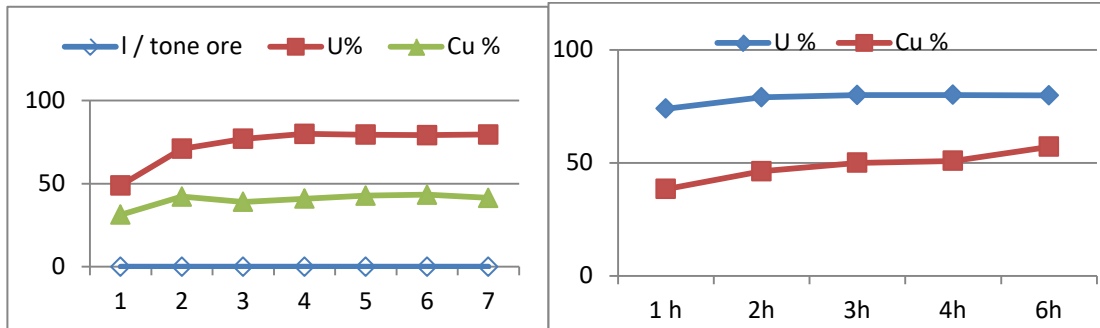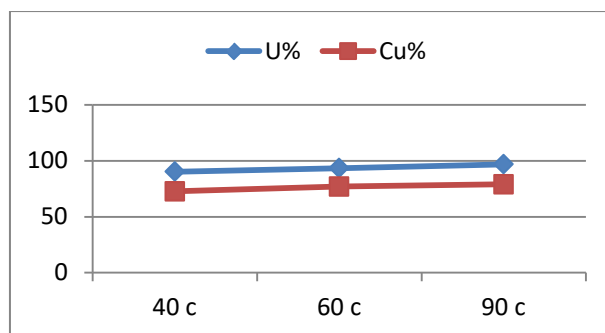

(a)

(b)

(c)

(d)

(e)

Figure 9: Effect of leaching conditions sulfuric acid concentration (a), leaching time (b), solid: liquid ratio (c), oxidant type (d) and temperature (e)

In spite of high carbonate content of the working mineralized dolostone sample which is not indeed the general case of Cu and U mineralization in Um Bogma Formation, it was found convenient to prepare a sulfate leach liquor of these two metal values using sulfuric acid. This is due the fact that the ore material is not adequately rich in Cu or U and their leach liquor would be diluted; a matter which would render their separation from the latter by IX technique greatly beneficial and economic. The proper selection of the optimum conditions is as follow: for each 1 kg ground ore sample leaching with well-agitation by mechanical stirring with 956 gm. H_2SO_4 with a S/L ratio of 1/3 and 1 g $KMnO_4$ at 90^oC for 3hr then the slurry was filtered and the residue was washed. The maximum leachability was reached to 91 % and the composition of leach liquor was appeared in Table 5 for 2.5 L leaching solution.

Table 5: Chemical composition of leach liquor

Element	Conc. ppm	Element	Conc. ppm
U^{6+}	273	Zn^{2+}	13
Al^{3+}	766	Cu^{2+}	840
Fe^{3+}	5216	$Ni2^{+}$	37
Mn^{2+}	1031	Ti^{4+}	22
Ca^{2+}	89	K^{+}	195
Mg^{2+}	29584	Co^{2+}	nil
Na^{+}	154		

The data in Table 5 indicates that with this acid concentration, temperature and the leaching time being greatly beneficial to Cu and U dissolution that over 72 and 91 % respectively we obtained.

3.4.1.3 Loading properties

161

Two types of polymer used in uranium recovery, D263B resin (quaternary amine polymer) use for uranium recovery and synthetic one with crosslinking degree 5% (MCHA).

a. Uranium recovery by commercial resin

Fifteen grams of D263B resin was shacked with 500 ml leaching solution with above specification at pH 1.8 and the maximum recovery being 7.5 mg/g decreasing than the normal uptake by nearly 8 times. It is very low loading capacity, this is due to highly concentration of ions as sulfur, Mg^{2+}, Ni^{2+}, Fe^{3+}, Ti^{4+}, Al^{3+} that make competition with uranyl sulfate complex and poisoning of resin [36]

From the above data the authors directed to detect synthetic polymer of MCHA resin (5% crossliker polymer which is more loading capacity) for uranyl and copper recovery. The most parameters affecting on the separation were the pH in the adsorption process and type of eluent used.

b. Cu (II) and U (VI) Recovery by using synthetic polymer

1. For U (VI) recovery

The prepared polymer with crosslinking ratio of 5 % was used for uranium recovery at pH 1.8 (pH was adjusted by H_2SO_4 and NaOH), 15 g of polymer is shacked with 2500 ml for 3 h. the loading capacity of the synthesized polymer reached after 2.5 h and was 43 mg/g of U (VI) and 3 mg/g of Cu (II). Increasing on uranium adsorption by about 29 times than commercial one. After loading the resin washed with water and subject to elute by 105 ml 1 M HNO_3, in which the elution efficiency reached over 95 % of uranium and copper. The resultant eluate has 6170 ppm and 407 ppm of U (VI) and Cu (II) respectively. The final concentration of leach liquor having about 15 ppm uranium and 822 ppm of copper.

2. For Cu (II) recovery

The effluent from the previous experiment was directed to another loading. A 15 g of 5% polymer was subjected for loading from 2.5L effluent solution from previous loading at pH 5.5 for 3 h, the saturation ratio was reached within 1.5 h and the maximum loading capacity of resin being 135 mg/g and 1 mg/g for Cu (II) and U (VI) respectively. Low loading capacity of uranium due to the decreasing in the initial concentration of liquor used. In which the uranium concentration was 9 ppm and copper concentration was 12 ppm, also there are a decreasing in concentration for other heavy elements as iron, nickel, cobalt this is due to high tendency of amine groups toward these ions. Elution of loaded resin performed by 200 ml 1 M HNO3, to elute ions as much as possible, the conc. of uranium is too low to be negligible in which the Cu (II) concentration is being 9618 ppm with efficiency 95%

4. Conclusion

Studying of selective separation of copper (II) and uranium (VI) by using synthesized magnetic resins bearing of hydrazenyl amine groups is the main target of this research. It based on chloromethyl styrene with both 5 % and

10% divinylbenzene as a crosslinking agent and this was reflect in the dense of active sites that was 13.1 and 12.7 mmol/g respectively, the synthesized resins were performed in the presence of Fe_3O_4 as a magnetite. This group work as week anion group at low pH and good chelating one in higher or slightly acidic solution.

The most dependent factor on the metal ion complexation of polymeric ligands is the equilibrium pH of the medium. The Cu (II)-imprinted micro beads exhibited a low affinity in acidic conditions (pH $\leq$ 2.0), higher affinity at pH 6.0, but it was relatively high for U^{6+} in both pH and this is the main parameter for selective separation of these ions from the natural leach liquor of dolostone ore materials from the Um Bogma formation of Abu Zeneima in southwestern Sinai whereas commercial resins for uranium as D263B resin shows decreasing than the normal uptake by nearly 31 times. the loading capacity of the synthesized polymer reached after 2.5 h and was 43 mg/g of U (VI) Increasing on uranium adsorption by about 29 times than commercial one with loading capacity 135 mg/g for Cu.

Acknowledgment

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