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Synthesis of Zeolite A from Sudanese Montmorillonite Clay to remove Nickel and Copper ions from Aqueous Solutions

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Abstract

The main objective of this research is to prepare Zeolite A with high efficiency from local Sudanese montmorillonite clay. This is considered as an effective alternative to chemical adsorbents in the removal of heavy metals such as nickel and copper from aqueous solutions. To synthesize Zeolite, montmorillonite clay was heated at 800oC for1hour and thermally treated with 5M sodium hydroxide solution at 100oC for 2h.The chemical composition of montmorillonite clay and synthesized Zeolite were also investigated. Furthermore, it was analyzed using the X-ray Diffraction (XRD), Fourier Transform Infra-Red(FT-IR),Scanning Electron Microscopy (SEM) and X-ray Florence (XRF).The removal capacity and percentage of zeolite A was studied. XRD patterns and FT-IR spectra were ascertained the formation of Zeolite A successfully. The results revealed that, the adsorption process onto synthesis Zeolite A depend on many factors such as initial metal ion concentrations, adsorbent dose, contact time and initial pH of the solution. Moreover, it was found that Zeolite A is very effective in removing copper ions than nickel ions from aqueous solutions.

Key words: Montmorillonite, Zeolite A, Hydrothermal, Heavy metal

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1. Introduction

Rivers, streams and Groundwater wells have always been an important freshwater resource in Sudan .They play an important role in human development and natural potential sources of irrigation water. However pollution with heavy metals that produce from industrial effluents, sewage wastes, chemical pesticides, drainage water , hazardous medical wastes, cosmic rays and Radiation Pollution find their way into rivers and streams leading to a large scale deterioration of water quality[1].Essential metals such as Cu , Ni and Fe have normal physiological regulatory functions are naturally present,but it may bio-accumulate and reach toxic levels[2], for example when copper present in high levels it can cause gastrointestinal distress while long term exposure can damage liver or kidney and exposure to nickel cause dermatitis and allergic sensitization [3]. People are using the rivers and streams waters for drinking, swimming, bathing, car and clothes washing, so their health will be in risk due pollution with heavy metals[4,5].The extraction of these heavy metal ions from aqueous solutions has become an issue of interest for researchers all over the world. Recently, different techniques have been used to eliminate heavy metal ions from aqueous solutions. common methods were used include ion-exchange, reverse osmosis, adsorption electrochemical treatment[6-,9]. These techniques could be used to reduce heavy metal ions, but they are not highly effective because of limitations in the pH range in addition to the high material and operational costs[8].In recent times, many Alternative adsorbents have been used to eliminate many heavy metal ions such as : China clay[10], Fly ash [11] , Black Carbon [12] , Zeolites[13], Cypress leaves [14] activated carbon from fertilizer waste [15,16,17], Clinoptilolite [18] and Bagasse fly ash[19].The removal by montmorillonite clay is particularly extractive because it is local product; therefore, cheap and easily available source of aluminosilicate. However, its removal capacity can greatly be improved via transfer into zeolite using thermal and chemical treatments [20, 21]. Zeolites are defined as a crystalline, hydrated aluminosilicate compounds, that have three-dimensional structures arising from a framework of tetrahedral units SiO_4 and AlO_4, each tetrahedral unit being linked by an oxygen atom [22]. The three dimensional structure is constructed from pores of molecules dimension. The framework is generally open and contains channels and cavities in which water molecules, heavy metals ions and other cations are located]. The general formula of zeolites can be represented as $M_{x/n}[(AlO_2)x(SiO_2)_y].zH_2O$, [23] where *n* represents the charge of the cation M, and the

values of *x*, *y* and *z* depends on the type of the zeolites itself. It can be found naturally, or can be synthesized. Synthetic zeolites were first utilized commercially as molecular sieve adsorbents[20]. Zeolites are first synthesized from solution of sodium silicate and sodium aluminate. They can also be synthesized from variety of raw materials, such as natural and synthetic glasses, aluminosilicate gels, and clay minerals, e.g., kaolin, Kaolinite and montmorillonite [24,25] . Zeolites type Na-A were synthesized from Spanish and Argentinian and Chilean kaolin[26] For the present study zeolite was synthesized from Sudanese clay from Blue river bank in Bahary province by calcination and hydrothermal treatment with various sodium hydroxide concentrations[20].This study aimed to reduce the heavy metals from aqueous solutions and wastewater for treatment purpose. It is also an opportunity to effectively use raw material in Sudan for production of zeolites A.

2. Material and Methods

2.1. Analytical instruments

The following instruments were used in this investigations; Inductively Coupled Plasma mass spectrometry (ICP-AES, Perkin-Elmer 3000 XL), Philips X-ray fluorescence spectrometer (XRF), Scanning electron microscope (SEM) Model JSM6400, JEOL, X-Ray diffractometer (XRD) Model D5005, Bruker and Fourier Transform Infra-Red(FT-IR) Shimadzu IR-470 Spectrophotometer.

2.2. Reagents and Chemicals

Nickel (II) nitrate $Ni(NO_3)_2.6H_2O$, Copper (II) nitrate trihydrate Cu $(NO_3)_2.3H_2O$, Sodium hydroxide pellets (98.6% NaOH), Nitric acid (0.1N) and Sodium hydroxide (0.1N), in addition to clay and zeolites Na-A . All the reagents and chemicals used in the experiments were analytical grade.

2.3. Preparation of Zeolite LTA from Clay

Montmorillonite clay was collected from Blue River bank, Khartoum State, Sudan. Which has been selected for economic considerations, for zeolite preparation. After that, the impurities were removed from the montmorillonite clay. It was crushed to fine particles and sieved through a 230-mesh size sieve. Iron content of the clay was removed by digestion with 6 M HCl. Then, it was washed with distilled water and dried overnight[27]. The mineralogical and the chemical composition of the purified clay was shown in Table1. Philips X-ray fluorescence spectrometer was used for major element analysis. Then the montmorillonite clay was calcined in muffle furnace for 1 hours at 750 ^oC, in order to convert clay to amorphous solid. Then it was reacted with NaOH solution in Teflon beaker and stirred at 250 rpm at temperature of 100^oC.The concentrations of NaOH were 1-4 mol L^{-1}, and the reaction time was varied at 1-5 hours. The mixture was laid in an electric oven at 100^oC for 10h for crystallization. The reaction product was washed to remove excess alkalinity and then centrifuged several times with double distilled water for solid- liquid separation. The solid powder was dried overnight at 120^oC.

2.4. Preparation of standard solutions

Stock solutions of mixed Nickel and Copper ions were prepared by dissolving Nickel nitrate and Copper nitrate salts in distilled water. Different concentrations from these salts were prepared (80 , 40 , 20 , 10 mg/l). Also, sodium hydroxide solution (0.1N) and nitric acid solution (0.1N) was prepared for pH adjustment.

2.5. Batch adsorption experiments

2.5.1. XRD , SEM and XRF measurements

X-ray diffraction (XRD) for zeolites A was analyzed following the standard method [20]. Experiment was performed using a Philips PW1732/10 diffractometer and CuKα radiation and Ni filter. The working conditions of this experiment were 40 kV and 20 mA. Also zeolites A was analyzed by Fourier Transform Infra-Red(FT-IR), in which a mixture of 0.005g of zeolite A and 0.2g of KBr were pressed into disk for IR measurement [27]. The composition weight percentage of montmorillonite clay was determined using X-ray reflective fluorescence spectrometer. The morphology and particle size of the clay and zeolite A were studied by SEM, the studied heavy metal ion concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry.

2.5.2. The influence of concentrations

0.5 gm of prepared zeolites A with particle size <75 microns was treated with 50 ml of standard solutions from mixture of lead and zinc (80, 40, 20, 10 mg/l) in a conical flask and stirred at 250 repletion per minute (rpm) for different time (30 – 180 min). After attainment of equilibrium, the content of the flask was filtered through Whitman 0.45µm. The final concentrations of Ni^{2+} and Cu^{2+} were measured using Inductively Coupled Plasma instrument. Then, the elimination capacity was calculated.

2.5.3. The influence of pH

0.5gm of prepared zeolite A samples were placed in separate conical flasks, then 50mlof standard solutions of mixture ions (10 mg/l) were added and stirred at 250 rpm for 180 min . This step was repeated several times with different pH standards ranged from 1to 6. Sodium hydroxide solution (0.1N) and Nitric acid solution (0.1 N) were used for pH adjustment. Final concentrations of Ni^{2+} and Cu^{2+} were measured and the elimination capacity besides the elimination percentages were calculated using the equations (1) and (2).

2.5.4. The influence of the amount of zeolites LTA

0.5 , 1 , 1.5 and 2 g of prepared zeolites A samples were placed in four conical flasks , then 50 ml of standard solutions of mixture ions (10 mg/l) were added in each conical flask, respectively. The content of conical flasks were stirred for 180 min by Over-head stirrer at 250 rpm . Final concentrations of Ni^{2+} and Cu^{2+} were determined by (ICP). Furthermore and the quantity of Ni and Cu ions eliminated by zeolite A were identified as well as in equation (1).

$$Q = \frac{(C_i - C_f) \times V}{m} \longrightarrow (1)$$

Where " C_i " is the initial metal ions concentrations (mg/l), " C_f " is the equilibrium metal ions concentrations (mg/l), "V" is the volume of the aqueous phase (l), and "m" is the amount of zeolites in grams. Also the elimination efficiency of Ni and Cu ions were calculated using the equation (2):

$$\text{Removal (\%)} = \frac{(C_i - C_f) \times 100}{C_i} \longrightarrow (2)$$

3. Result and Discussion

3.1. Zeolite Na-A characterization

XRD diffraction pattern for synthesized sample were shown in Figure 1. The results show that the synthesized zeolite A spectra is similar to the reference zeolites A spectra[28]. Also XRD peaks of zeolite A at 2θ = 4.68, 6.84, 8.25, 16.18, 17.5, 22.73, 30.01, 34.78 , 40.11, 42.49 and 63.82 degrees, indicated that zeolite A successfully synthesized. However some peaks were not sharp enough, may be according to the mixture of metal oxide that present in the starting material clay. The FT-IR spectra of commercial synthetic zeolite A in Figure 2 , which considered as reference and synthetic zeolite A from montmorillonite clay in Figure 3, showed better matching with finger prints of wave number values . the first class of spectra vibration found in both zeolites at 900 – 1000cm^{-1} which were assigned to the internal tetrahedron vibrations. Stretching modes involving mainly the tetrahedral atom were assigned in region of 678 cm-1 for both zeolites[29].The SEM image of the particles is shown in Figure 4 , which shows uniform particle morphology and small particle size in range of 1.13-2.14 µm for montmorillonite clay and 3.72-8.61 µm for zeolite A. In addition to chemical composition of the montmorillonite clay and synthesized zeolite were reported in Table 1.

3.2. Effect of time

As shown in Figure 3, the elimination capacity of metal ions on the modified clay can be described as a function of the contact time. The majority of metal ions in adsorption equilibrium were achieved 30 min for all studied ions. As the elimination percentage of metal ions at the first 30 min. recorded higher degree of removal. There were 99.53% for Cu ions and 73.14 for Ni ions. These concentrations became almost decreasing gradually, and became constant after 90 min. The fast initial uptake of heavy metal ions refer to their accumulation on zeolite Na-A. Also, the results indicate that high elimination for heavy metal ions occurs in first thirty minute

3.3. Effect of pH

The results of pH are shown in Table 2 and Figure 6.By the increase of pH the efficiency of Zeolite increases in elimination of Cu^{2+} and Ni^{2+}. The percentage of the elimination efficiency of Zeolite was 99.53% for Cu^{2+} and 73.14% for Ni^{2+}The removal percentage of Ni^{2+}at pH 4 was found more effective than at pH 5. Similar studies were in agreement with these findings [30]. Generally, it was found that by increase the amount of zeolites the efficiency of elimination of heavy metals increases. This observation may be related to the increase in surface negative charges with the decrease in the electrostatic potential close to the solid surface that favors sorbent-solute interactions.

3.4. Effect of amount of adsorbent

As presented in Figure 7 and Table 3,by increase of the amounts of the zeolites A the elimination capacity decreases for Cu^{2+} from 0.975 to 0.249 mg/g and for Ni^{2+} from 0.384 to 0.228_mg/g. On the other side, as shown in Figure 8 and Table 3 , the percentage elimination of these metal ions increased from 97.54 to 99.72% for Cu^{2+} and 38.35 to 91.15% for Ni^{2+}. These findings are in agreement with other published studies[31].It was found that, when the adsorbent dose increases the total surface area decreases, this increase in diffusion path length, could be explained as a result of aggregation of zeolite A clay particles[32].

3.5. Effect of initial metal ion concentrations

The effect of nickel and zinc ions concentrations on the sorption by the zeolite A was investigated by varying the metal concentration from 10 to 80 mg/l at a pH of 5.0 for 30 min equilibrium time Figure 9. It was observed that the percent metal ions removal of the modified clay increased with increasing metal ion concentrations. It is obvious that increasing the initial metal ion concentration in aqueous solutions increased the amount of both metal ion adsorbed , Similar studies were in agreement with this findings [33]. This could be due to increasing driving force of metal ions towards active sites on the adsorbent. In addition, the percentage of metal ion adsorbed decreased with increasing initial metal ion concentrations. This indicates that, decrease in active sites on zeolite A are more metal ions as adsorbed.

4. Conclusion

Adsorption by Zeolite A synthesized from Sudanese montmorillonite clay is a very effective technique for the elimination of heavy metals from aqueous solutions. Zeolite A is very good adsorbents for removal of copper and nickel ions from aqueous solutions. Removal of these ions by Zeolite A was enhanced after the calcinations of clay and treated with Sodium Hydroxide (5 M). This modified montmorillonite clay thus can be useful in removal of heavy metals from aqueous solutions. It is recommended to use Zeolite A in industrial areas as well as some rural areas in Sudan which suffering from water pollution by heavy metals.

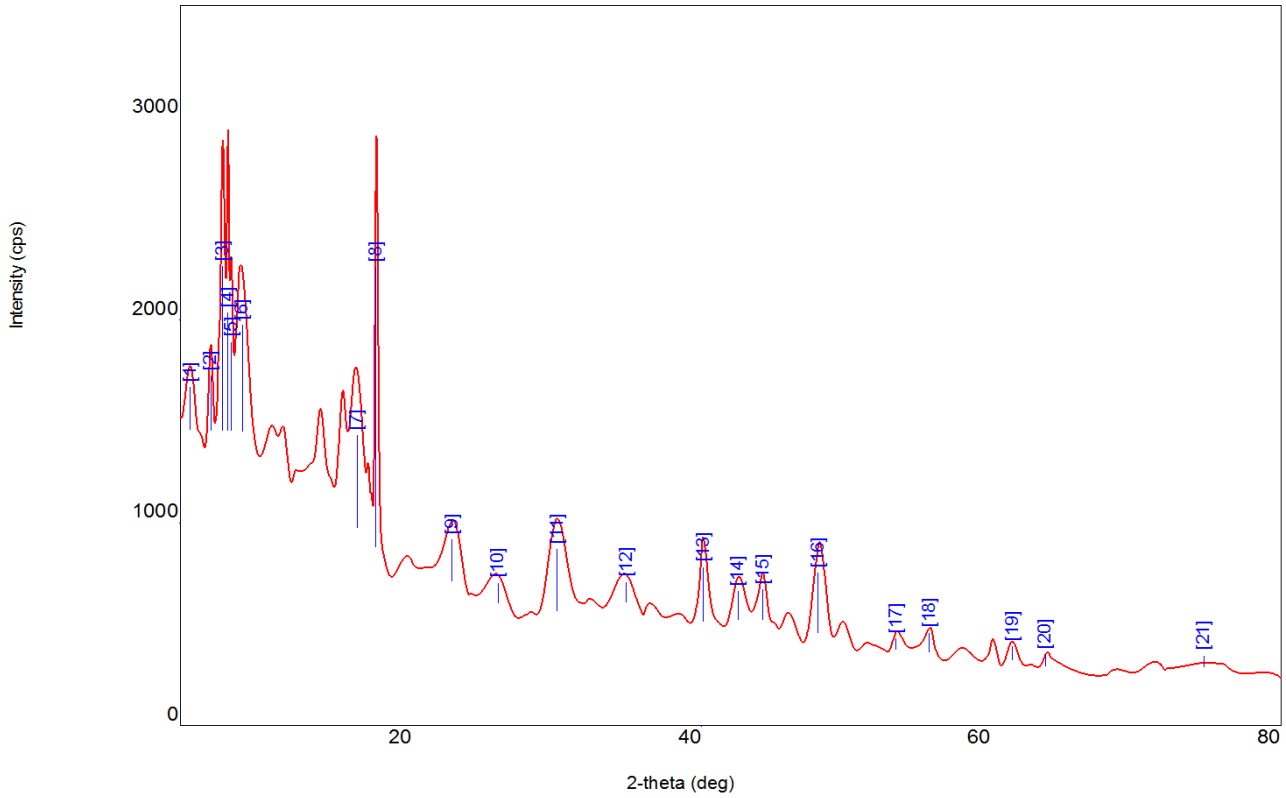

Fig.1. X-ray diffraction pattern of zeolite A synthesized zeolite A from montmorillonite clay

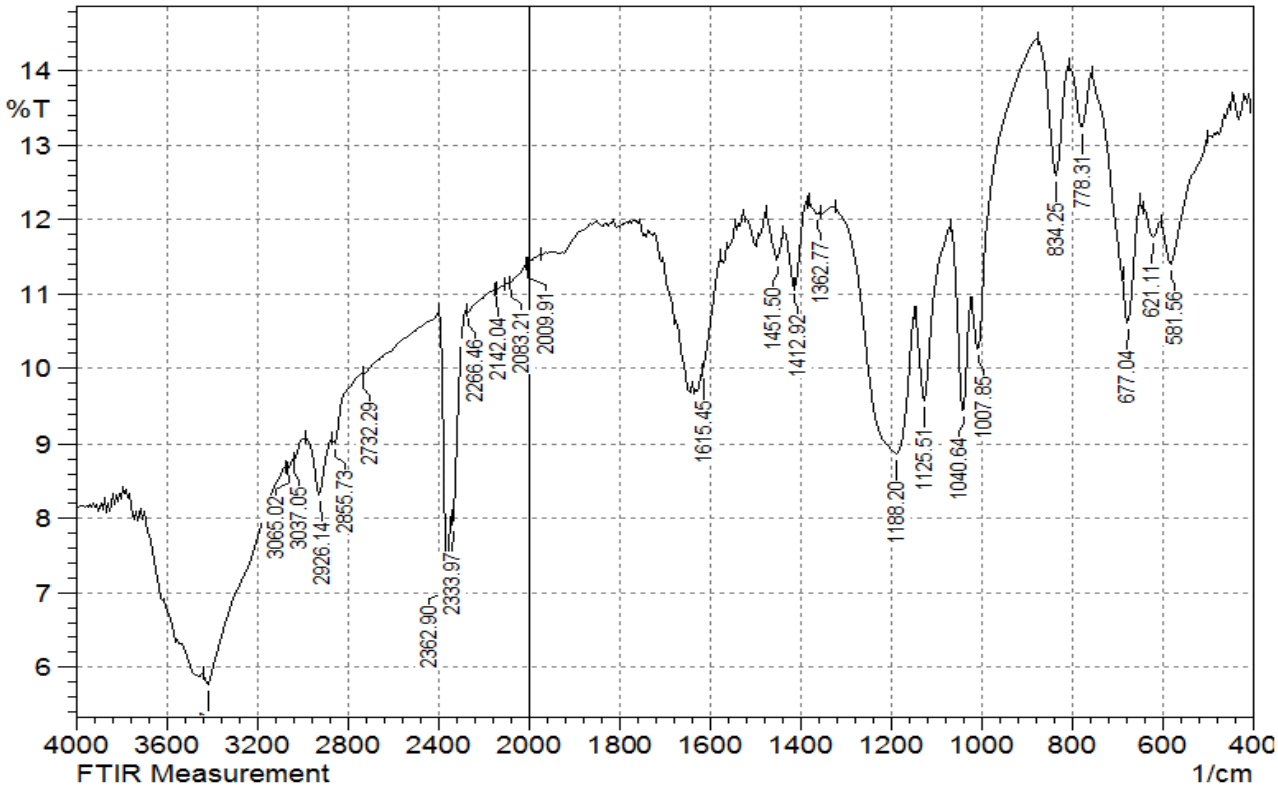

Fig.2. FT-IR spectra of commercial synthetic zeolite A**(**Reference zeolite A)

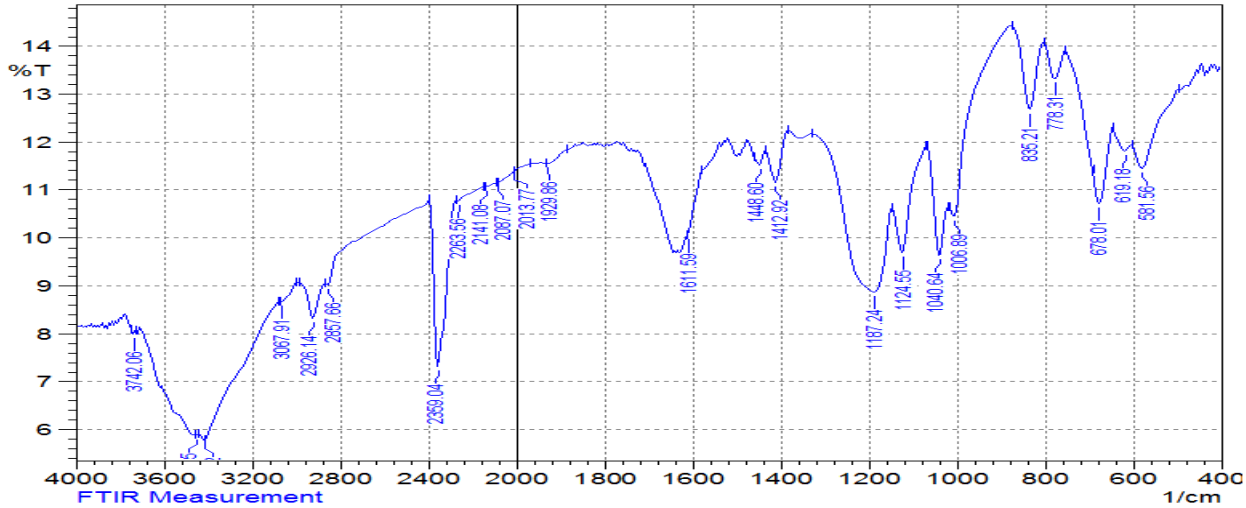

Fig.3. FT-IR spectra of synthesized zeolite A from montmorillonite clay

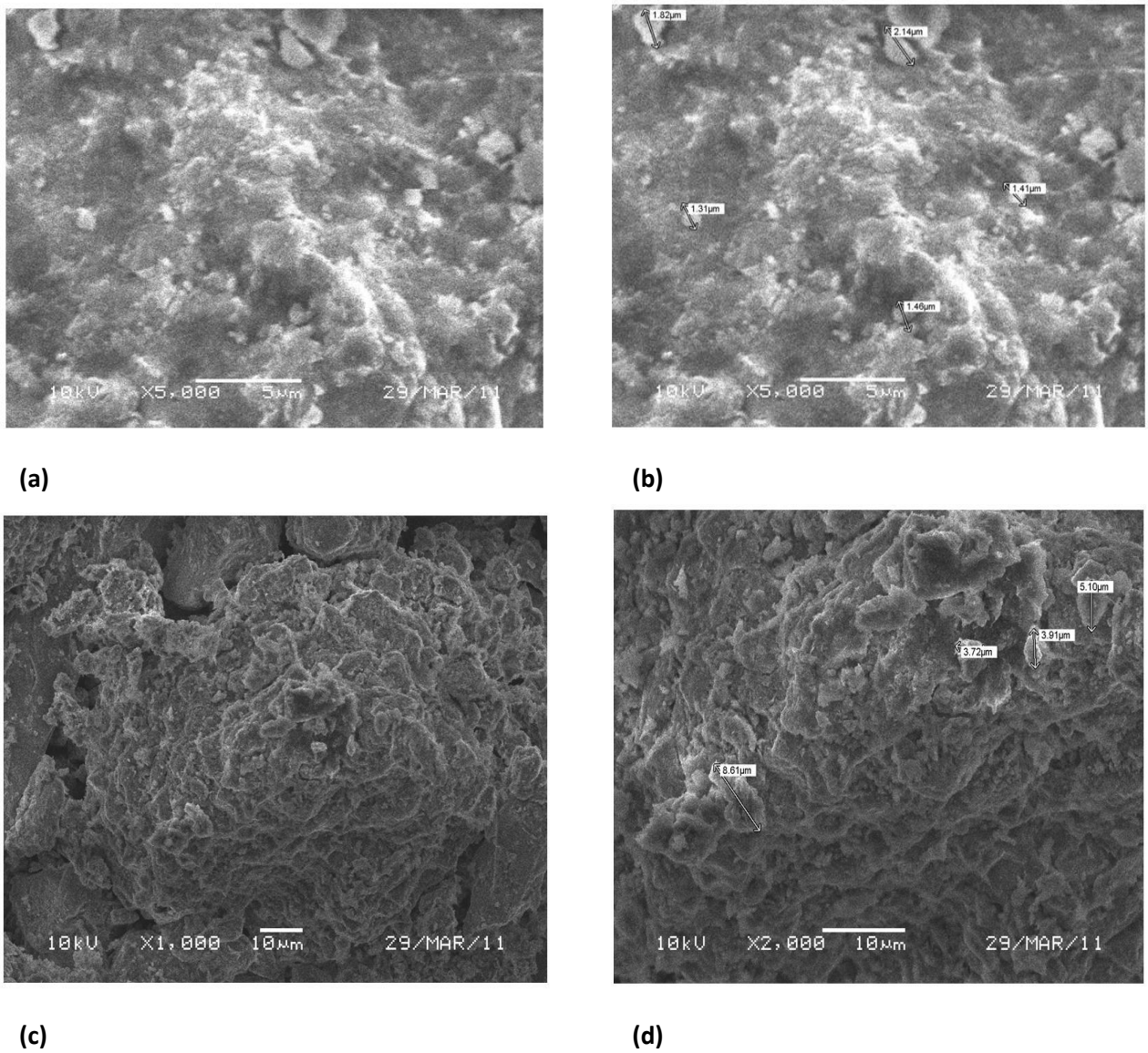

Fig.4. SEM images of montmorillonite clay surface (a-b) and SEM images of zeolites A surfaces (c-d)

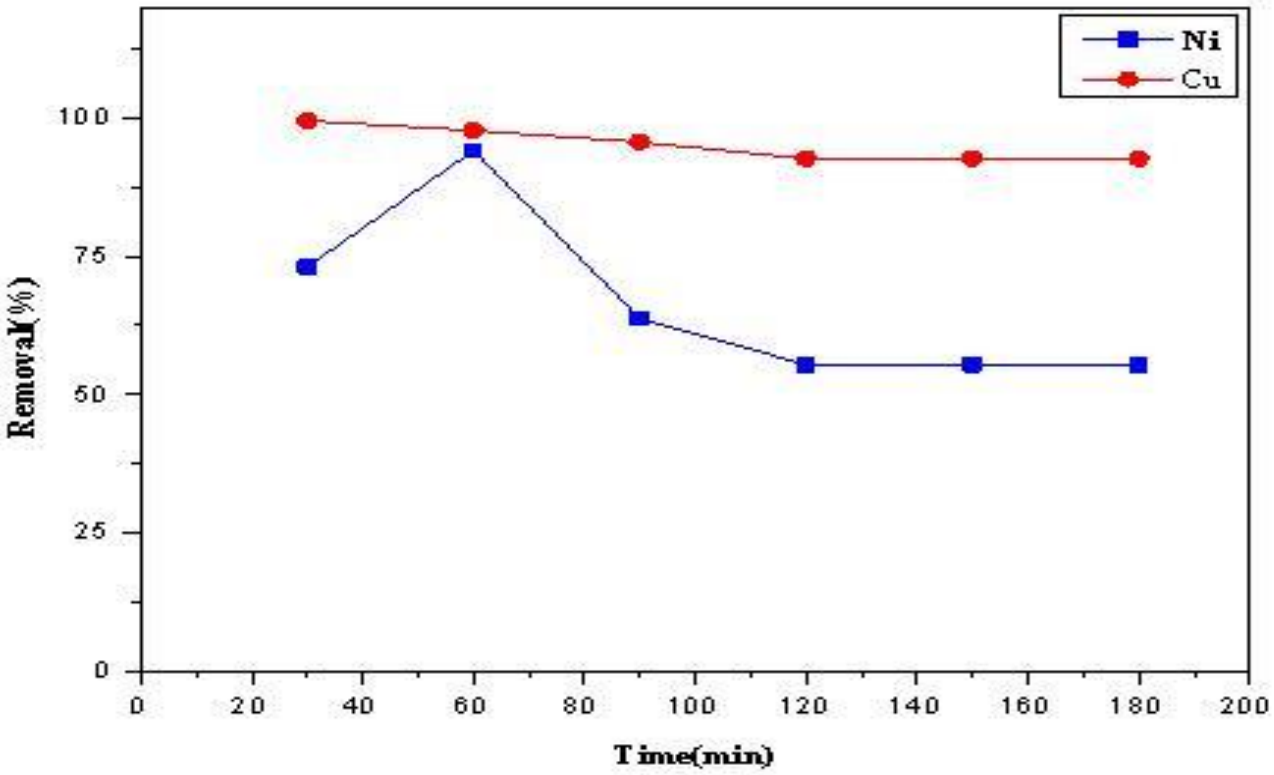

Fig.5. The percentage elimination of metal ions on to zeolite A against contact time

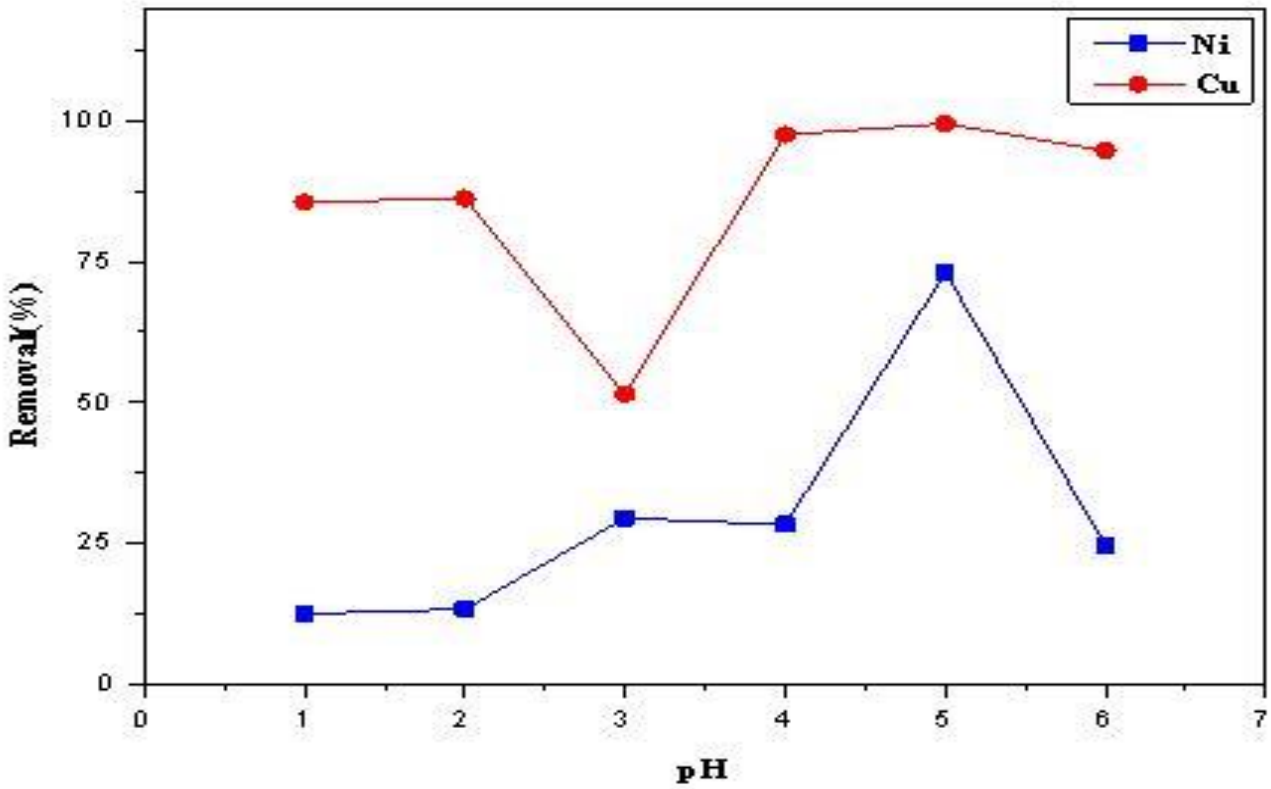

Fig.6. Effect of pH on the removal percentage of metal ions on zeolite A

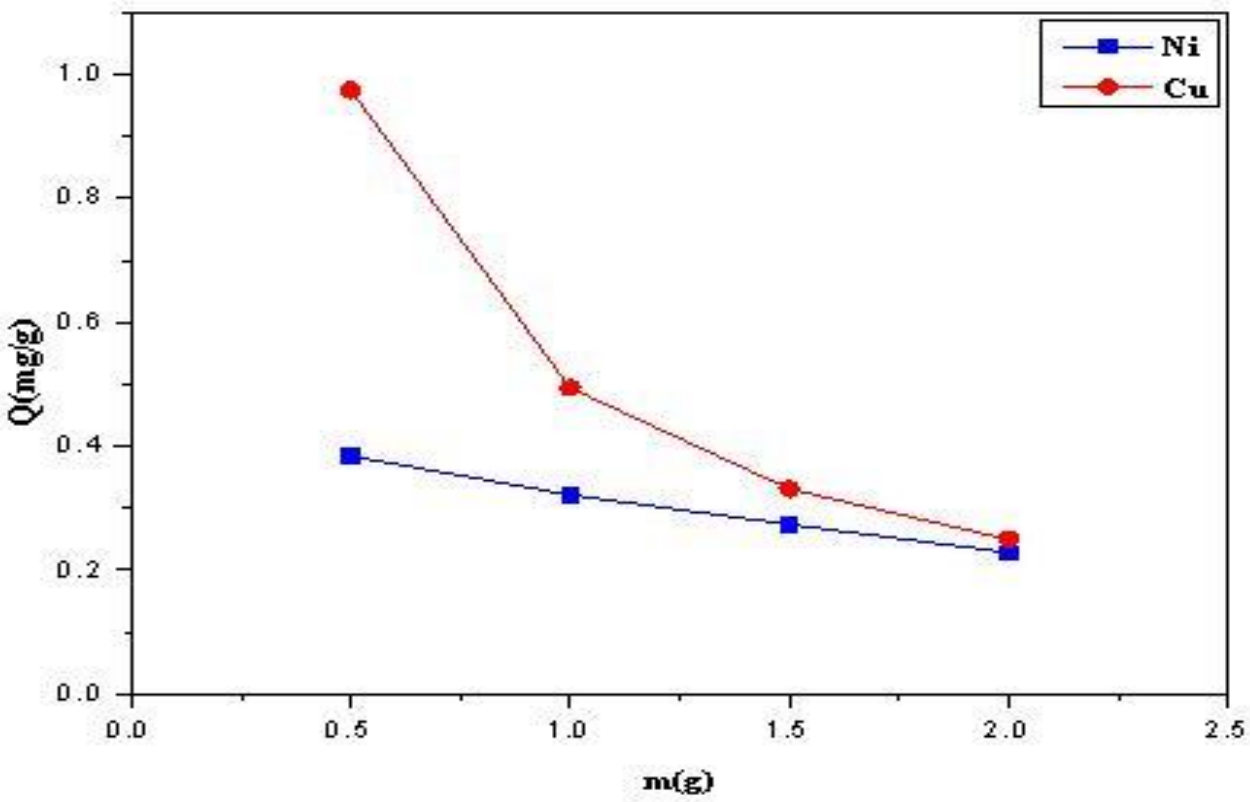

Fig.7. Variation in the removal capacity against the different amount to zeolite A

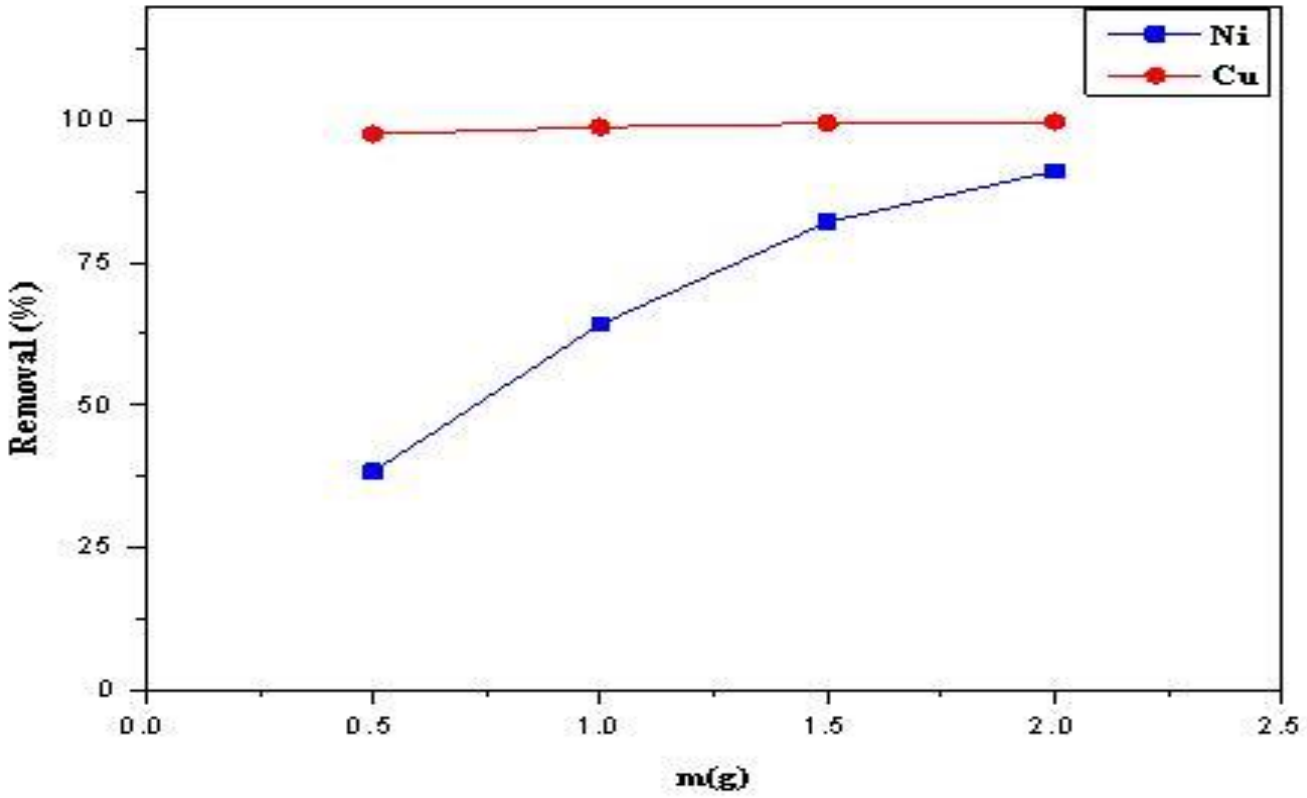

Fig.8. Variation in the elimination percentage against the different amount to zeolite A

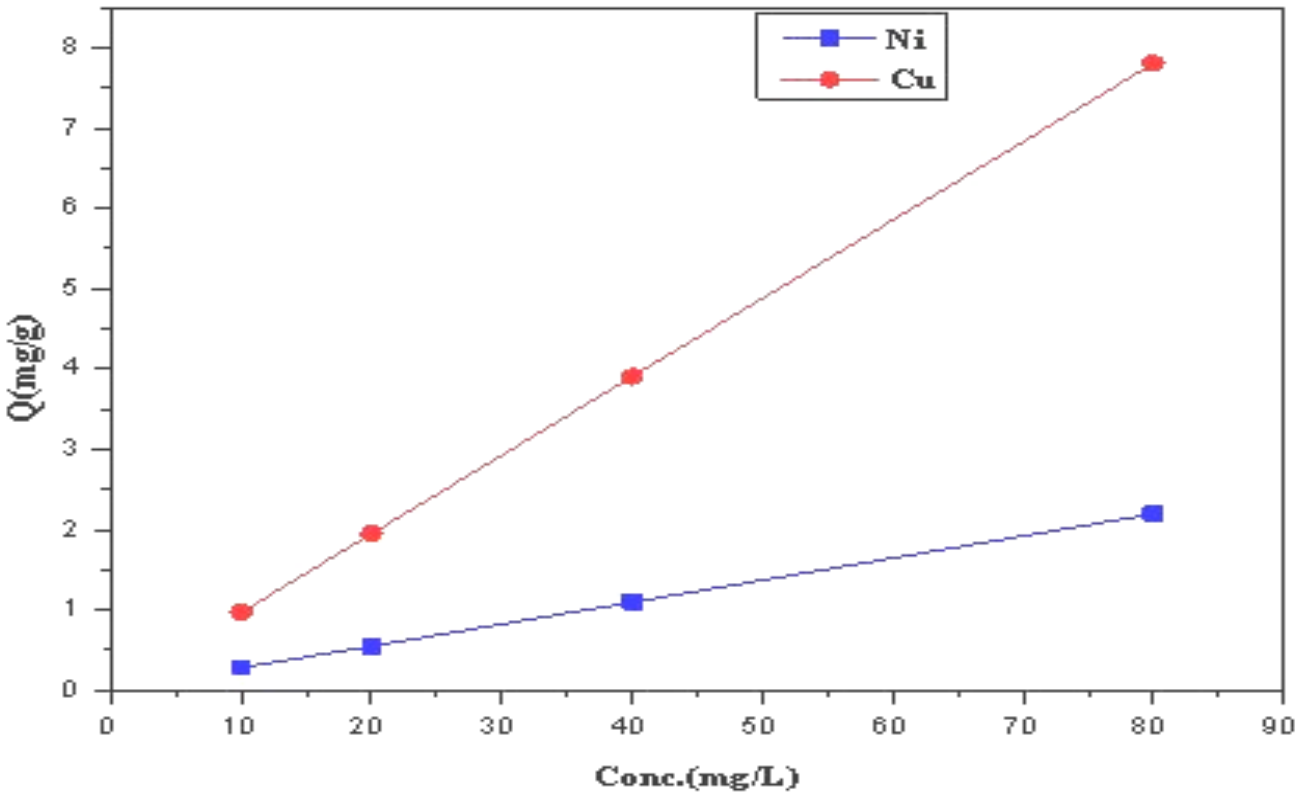

Fig. 9. Variation in the removal capacity of zeolite A against the different concentrations of metal ions

Table 1. Chemical composition of the montmorillonite clay and zeolite A

Composition wt%	*clay*	*Zeolite A*
SiO_2	55.38	54.32
Al_2O_3	16.01	15.04
Na_2O	2.35	4.99
K_2O	2.42	0.2
Fe_2O_3	9.6	4.75
CaO	4.81	8.45
MgO	3.81	10.4
MnO	0.15	……
TiO_2	2.82	0.81
BaO	2.65	0.60
LOI*	…….	0.62

LOI* = loss on ignition

Table 2. The results of different pH on the elimination of copper and nickel onto zeolite A

pH	*Cu Q (mg/g)*	*Ni Q(mg/g)*	*% Re Cu*	*% Re Ni*
1	0.856	0.125	85.6	12.45
2	0.86	0.134	86.3	13.35
3	0.515	0.295	51.45	29.45
4	0.975	0.284	97.54	28.35
5	0.995	0.732	99.53	73.14
6	0.947	0.245	94.67	24.49

Q (mg/g) = Removal capacity; % Re = Removal percentage

Table 3. The influence of different amount of zeolite A on the elimination capacity percentage removal of copper and nickel ions

Amount (g)	*Cu Q (mg/g)*	*Ni Q(mg/g)*	*%Re Cu*	*%Re Ni*
0.5	0.975	0.384	97.54	38.35
1	0.494	0.321	98.85	64.23
1.5	0.331	0.274	99.43	82.12
2	0.249	0.228	99.72	91.15

Amount (g) = amount of zeolite A in gram; Q (mg/g) = Removal capacity; % Re = Removal percentage

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