



# Elimination of Heavy Metals from Aqueous Solutions using Zeolite LTA Synthesized from Sudanese Clay

Ismail M.A.\*, Eltayeb M.A.Z. and Abdel Maged S.A.

Department of Chemistry, Faculty of Science and Technology, Al Neelain University, Khartoum 11121, SUDAN

Available online at: [www.isca.in](http://www.isca.in)

Received 27<sup>th</sup> April 2013, revised 9<sup>th</sup> May 2013, accepted 14<sup>th</sup> May 2013

## Abstract

The synthesis of zeolite LTA from Sudanese clay has been studied by hydrothermal treatment with various sodium hydroxide concentrations. The process for synthesis have been optimized to produce zeolite LTA at economical manner. Also, the chemical composition of clay and synthesized zeolite were investigated and they were analyzed using the X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and X-ray Fluorescence (XRF). It was found that, the Zeolite LTA was successfully synthesized under controlled conditions (750 °C/1h) for the clay calcination, 100°C/2h for the reaction time, temperature and 5 M NaOH for the alkali concentration. The removal capacity for Pb<sup>2+</sup> was 99.99 % and for Zn<sup>2+</sup> was 95.68.

**Keywords:** Zeolite LTA, clay, hydrothermal, heavy metal.

## Introduction

The elimination of heavy metal ions on mineral substrates is an necessary process in soil chemistry and also in hydrometallurgy, in addition to the treatment of industrial wastewaters<sup>1,2</sup>. The process of the elimination by adsorption is very complex, which is much more difficult than a simple ion-exchange on the surface of the minerals. There are many factors affects on the amount of heavy metal ions being adsorbed by mineral substrates such as pH, adsorbent dose, nature of the adsorbent, ionic strength, initial metal ion concentration and presence of competing ions. This process is widely applied. However, it is not totally understood. It is known that some chemical substances, if present in certain concentrations in aqueous solutions, may cause health risk to Human. Some toxic heavy metals such as zinc and lead are classified as strongly hydrating cations<sup>3,4</sup>. These heavy metals are mostly toxic to some vertebrates, causing kidney and blood disorders in addition to other negative symptoms. These ions are mostly discharged by certain of industries into rivers, lakes, sea and oceans causing serious contamination. The activities of industrial emissions, plating and mining contributes to the presence of these heavy metal ions in water either direct or indirect discharge into water bodies or as atmospheric discharge, which are deposited on water surfaces<sup>5,6</sup>. The lead ions causes poisoning and affect gastrointestinal track, or nervous system<sup>7,8</sup>. 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<sup>9,10,11</sup>. 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<sup>11</sup>.

Recently, many adsorbents have been used to eliminate many heavy metal ions such as: China clay<sup>12</sup>, Fly ash<sup>13</sup>, Montmorillonite<sup>14</sup>, Zeolites<sup>14</sup>, activated carbon from fertilizer waste<sup>15,16,17</sup>, Cypress leaves<sup>18</sup> and Bagasse fly ash<sup>19</sup>. The removal by clay is particularly extractive because it is local product; therefore, cheap and easily available source of aluminosilicate. However, its adsorption capacity can greatly be improved via transfer into zeolite using thermal and chemical treatments<sup>20,21</sup>.

Zeolites are defined as a crystalline microporous aluminosilicates, consists of 3-dimensional framework of silicon tetraoxide [SiO<sub>4</sub>]<sup>4-</sup> and Aluminum tetraoxide [AlO<sub>4</sub>]<sup>5-</sup>, bonded by oxygen atoms<sup>22</sup>. The general formula of zeolites can be represented as M<sub>x/n</sub>[(AlO<sub>2</sub>)<sub>x</sub>(SiO<sub>2</sub>)<sub>y</sub>].zH<sub>2</sub>O,<sup>23</sup> 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<sup>20</sup>. 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<sup>24,25</sup>. NaA type zeolites were synthesized from Spanish and Argentinian and Chilean kaolins<sup>26</sup> 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<sup>20</sup>. 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 LTA.

## Material and Methods

**Apparatus:** 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, and X-Ray diffractometer (XRD) Model D5005, Bruker.

**Reagents and Chemicals:** Lead nitrate ( $Pb(NO_3)_2 \cdot 4H_2O$ ), Zinc nitrate  $Zn(NO_3)_2 \cdot 6H_2O$ , Sodium hydroxide pellets (98.6% NaOH), Nitric acid (0.1N) and Sodium hydroxide (0.1N), in addition to clay and zeolites LTA. All the reagents and chemicals used in the experiments were analytical grade.

**Preparation of Zeolite LTA from Clay:** 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 clay. This clay 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<sup>27</sup>. The mineralogical and the chemical composition of the purified clay was shown in table-1. Philips X-ray fluorescence spectrometer was used for major element analysis. Then the kaolin was calcined in muffle furnace for 1 hours at 750°C, 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°C. The concentrations of NaOH were 1-4 mol L<sup>-1</sup>, and the reaction time was varied at 1-5 hours. The mixture was laid in an electric oven at 100°C 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°C.

**Table-1**  
**Chemical composition of the clay and zeolites LTA**

Composition wt%	clay	Zeolite LTA
SiO <sub>2</sub>	67.77	54.32
Al <sub>2</sub> O <sub>3</sub>	11.10	15.04
Na <sub>2</sub> O	3.15	4.99
K <sub>2</sub> O	2.3	0.2
Fe <sub>2</sub> O <sub>3</sub>	5.13	4.75
CaO	4.85	8.45
MgO	2.60	10.4
TiO <sub>2</sub>	1.50	0.81
BaO	1.55	0.60
LOI*	0.05	0.62

LOI\* = loss on ignition

**Preparation of standard solutions:** Stock solutions of mixed lead and zinc ions were prepared by dissolving Lead nitrate and Zinc 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.

**Batch adsorption experiments: XRD, SEM and XRF measurements:** X-ray diffraction (XRD) for zeolites LTA was analyzed following the standard method<sup>20</sup>. Experiment was

performed using a Philips PW1732/10 diffractometer and CuK $\alpha$  radiation and Ni filter. The working conditions of this experiment were 40 kV and 20 mA. The composition weight percentage of clay was determined using X-ray reflective fluorescence spectrometer. The morphology and particle size of the clay and zeolite LTA were studied by SEM, the studied heavy metal ion concentrations were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometry.

**The influence of concentrations:** 0.5 gm of prepared zeolites LTA with particle size <75 microns was treated with 50 ml mixture of lead and zinc standards (80, 40, 20, 10 mg/l) in a conical flask and stirred at 250 repetition per minute (rpm) for different time (30 – 180 min). After attainment of equilibrium, the content of the flask was filtered through Whitman 0.45 $\mu$ m. The final concentrations of Pb<sup>2+</sup> and Zn<sup>2+</sup> were measured using Inductively Coupled Plasma instrument. Then, the elimination capacity was calculated.

**The influence of pH:** 0.5 gm of prepared zeolites LTA samples were placed in separate conical flasks, then 50 ml of 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 1 to 6. Sodium hydroxide solution (0.1N) and Nitric acid solution (0.1 N) were used for pH adjustment. Final concentrations of Pb<sup>2+</sup> and Zn<sup>2+</sup> were measured and the elimination capacity besides the elimination percentages were calculated using the equations (1) and (2).

**The influence of the amount of zeolites LTA :** 0.5 , 1 , 1.5 and 2 g of prepared zeolites LTA 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 Pb<sup>2+</sup> and Zn<sup>2+</sup> were determined by (ICP). Furthermore and the quantity of Pb and Zn ions eliminated by zeolite LTA were identified as well as in equation (1).

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

Where " C<sub>i</sub> " is the initial metal ions concentrations (mg/l), " C<sub>f</sub> " 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 Pb and Zn ions were calculated using the equation (2):

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

## Results and Discussion

**Zeolite LTA characterization:** XRD diffraction pattern for synthesized sample were shown in figure-6. The results show that the synthesized zeolite LTA spectra is similar to the reference zeolites LTA spectra<sup>25</sup>. Also XRD peaks of zeolites LTA at 2 $\theta$  = 7.18, 10.17, 30.15, 34.81, 43.96, 61.33 and 63.82 degrees, indicated that zeolite LTA 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 SEM image of the particles is shown in figure-7, which shows uniform particle morphology and small particle size in range of 25-72  $\mu\text{m}$  for raw clay and 29- 74.3 for zeolite LTA. In addition to chemical composition of the raw clay and synthesized zeolite were reported in table-1.

**Effect of time:** as shown in figure-1, 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 shown in figure-3, the elimination percentage of metal ions at the first 30 min. recorded higher degree of removal. There were (99.93%) for Pb ions and 65.4 for Zn ions. These concentration became almost decreasing gradually and became constant after 90 min. The fast initial uptake of heavy metal ions refer to their accumulation on zeolite LTA. Also, the results indicate that high elimination for heavy metal ions occurs in first thirty minute.

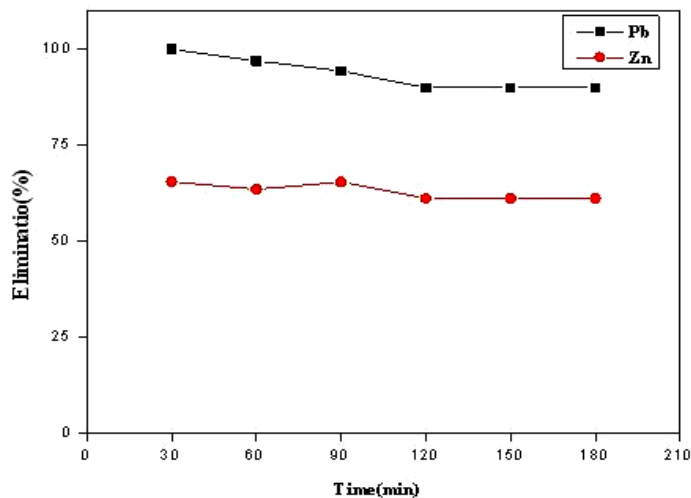


Figure -1

**The elimination percentage of metal ions on to zeolite LTA against contact time**

**Effect of pH:** The results of pH are shown in table-2 and figure-2. By the increase of pH the efficiency of Zeolite increases in elimination of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ . The percentage of the elimination efficiency of Zeolite was 99.93% for  $\text{Pb}^{2+}$  and 98.93% for  $\text{Zn}^{2+}$ . The removal percentage of  $\text{Pb}^{2+}$  at pH 4 was found more effective than at pH 5. Similar studies were in agreement with this findings<sup>29</sup>. 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.

**Effect of amount of sorbent:** As presented in figure-3 and table-3, by increase of the amounts of the zeolites LTA the elimination capacity decreases for  $\text{Pb}^{2+}$  from 7.994 to 0.25 mg/g and for  $\text{Zn}^{2+}$  from 5.17 to 0.164 mg/g.

Table-2

**The results of different pH on the elimination of lead and zinc onto zeolite LTA**

pH	Pb Q (mg/g)	Zn Q(mg/g)	% Re Pb	% Re Zn
1	0.722	0.353	72.2	35.28
2	0.833	0.473	83.32	47.29
3	0.87	0.488	86.92	48.8
4	0.999	0.654	99.93	95.4
5	0.994	0.989	99.42	98.93
6	0.778	0.555	77.8	55.5

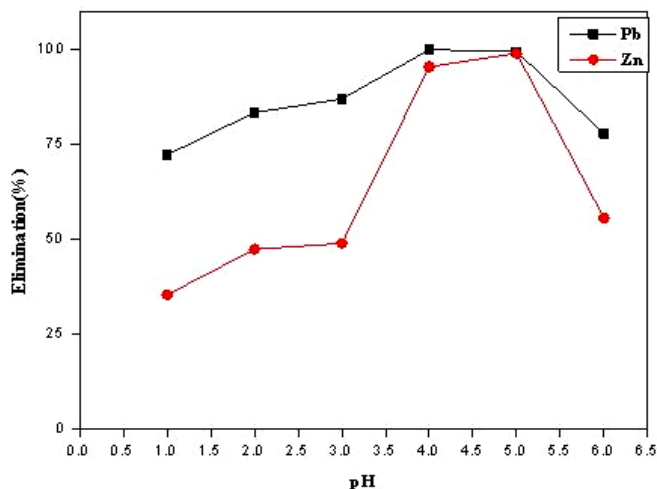


Figure -2

**Effect of pH on the elimination percentage of metal ions on to zeolite LTA**

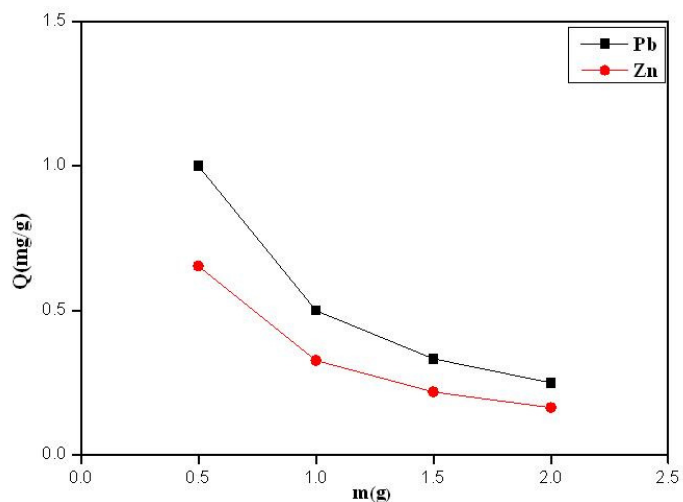


Figure -3

**Variation in the elimination capacity against the different amount to zeolite LT**

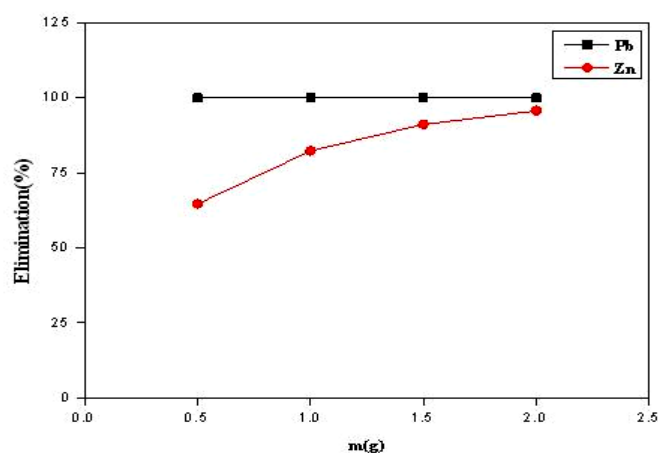
On the other side, as shown in figure-4 and table-3, the percentage elimination of these metal ions increased from 99.93 to 99.99% for  $\text{Pb}^{2+}$  and 64.63 to 95.68% for  $\text{Zn}^{2+}$ . These

findings are in agreement with other published studies<sup>30</sup>. 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 LTA clay particles<sup>31</sup>.

**Table-3**

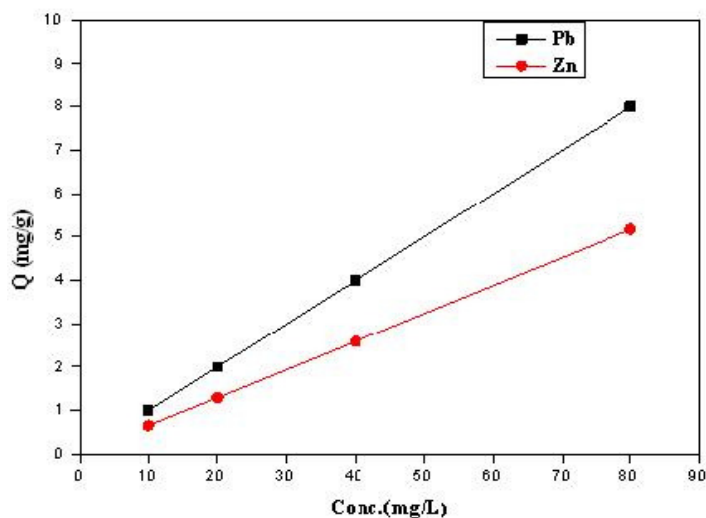
**The influence of different zeolite LTA amount on the elimination capacity percentage removal of lead and zinc ions**

Amount (g)	Pb Q (mg/g)	ZnQ(mg/g)	%Re Pb	%Re Zn
0.5	7.994	5.17	99.93	64.63
1	1.999	3.292	99.96	82.3
1.5	0.666	0.431	99.98	91.15
2	0.25	0.164	99.99	95.68



**Figure- 4**

**Variation in the elimination percentage against the different amount to zeolite LTA**



**Figure-5**

**Variation in the elimination capacity of zeolite LTA against the different concentrations of metal ions**

**Effect of initial metal ion concentrations:** The effect of lead and zinc ions concentrations on the sorption by the zeolite LTA 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-5. 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. 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 LTA are more metal ions as adsorbed.

### Conclusion

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

### Acknowledgement

We are thankful to the staff members of the Department of Chemistry, Faculty of Science and Technology, Al Neelain University for support and co-operation. Thanks also to Dr. Emad M. Abdallah for interest and help.

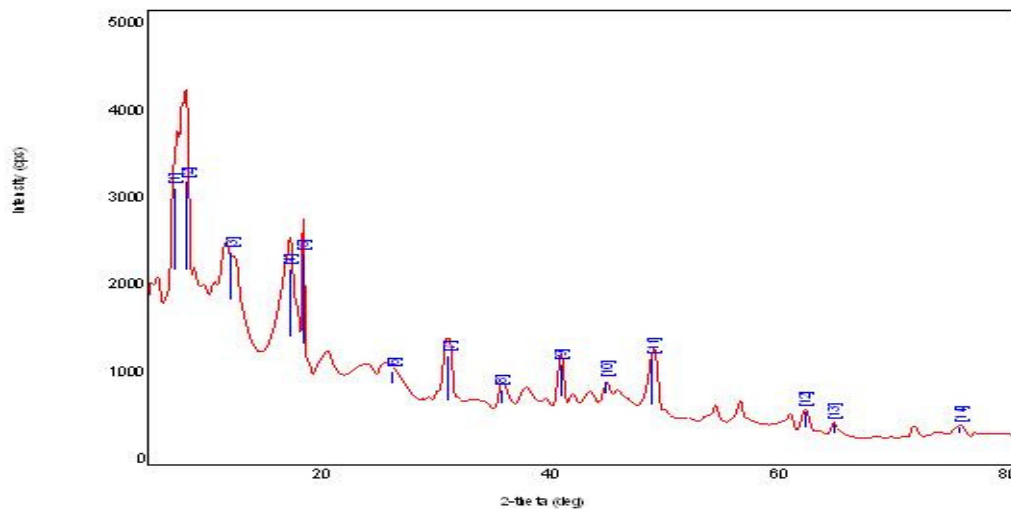


Figure-6  
X-ray diffraction pattern of zeolite LTA

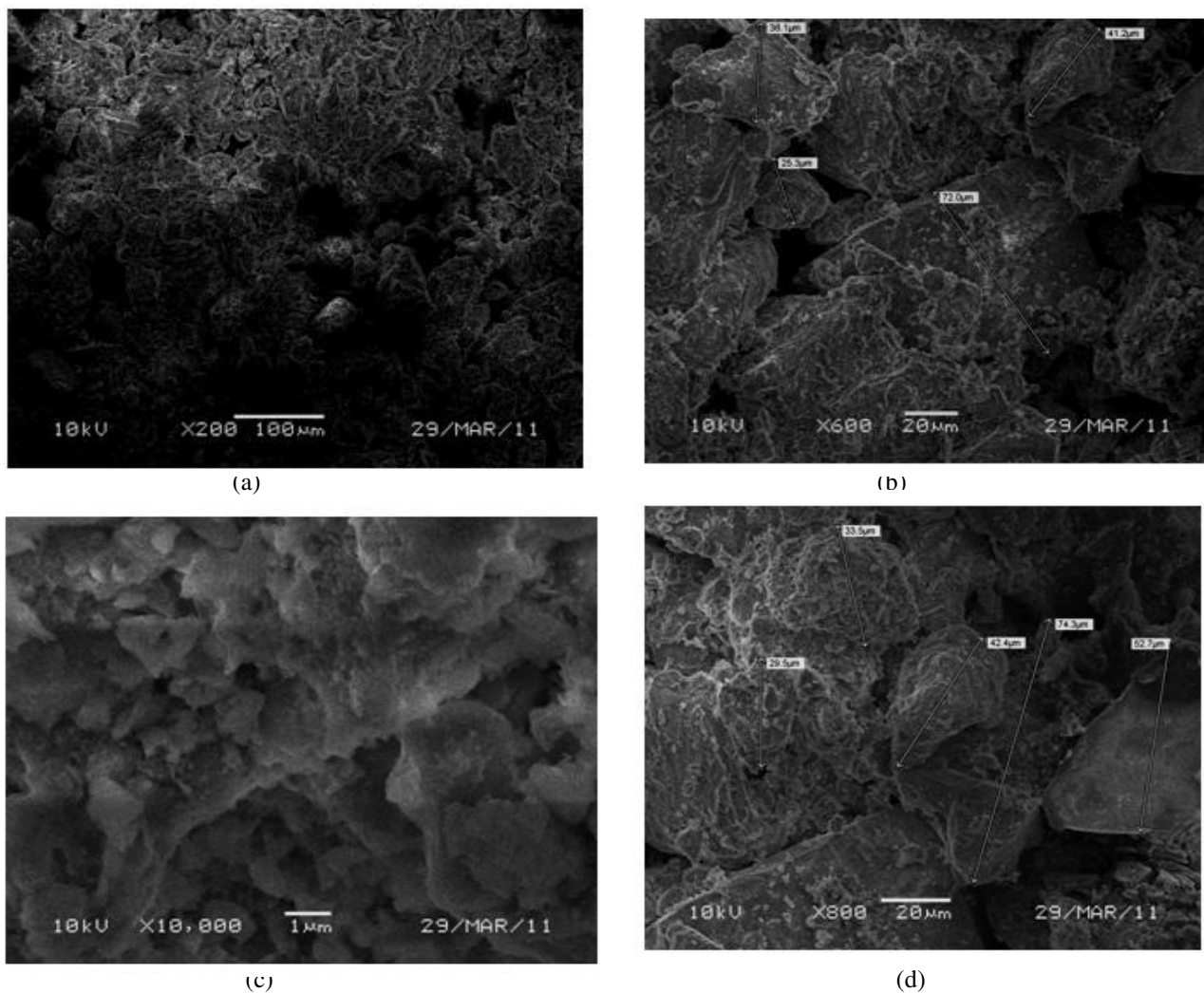


Figure-7  
SEM images of clay surface (a-b) and SEM images of zeolites LTA surfaces (c-d)

## References

1. Abii T.A., Levels of Heavy Metals (Cr, Pb, Cd) Available for Plants within Abandoned Mechanic Workshops in Umuahia Metropolis, *Res. J. Chem. Sci.*, **2(2)**, 79-82 (2012)
2. Shaikh Parveen R. and Bhosle Arjun B., Heavy Metal Contamination in Soils near Siddheshwar Dam Maharashtra, *Res. J. Chem. Sci.*, **3(1)**, 6-9 (2013)
3. Bride M.B., Environmental Chemistry of Soils, Oxford University Press, New York, **14**, 310 (1994)
4. Kumar Sukender, Singh Jaspreet, Das Sneha and Garg Munish, AAS Estimation of Heavy Metals and Trace elements in Indian Herbal Cosmetic Preparations, *Res. J. Chem. Sci.*, **2(3)**, 46-51 (2012)
5. Eruola A.O., Ufoegbune G.C., Eruola A.O., Awomeso J.A. and Abhulimen S.A., Assessment of Cadmium, Lead and Iron in Hand Dug Wells of Ilaro and Aiyetoro, Ogun State, South-Western Nigeria, *Res. J. of Chem. Sci.*, **1(9)**, 1-5 (2011)
6. Eruola A.O., Ufoegbune G.C., Eruola A.O., Awomeso J.A. and Abhulimen S.A., Assessment of Cadmium, Lead and Iron in Hand Dug Wells of Ilaro and Aiyetoro, Ogun State, *Res. J. Chem. Sci.*, **1(9)**, 1-5 (2011)
7. Clayton G.D., Clayton F.E., Patty's Industrial Hygiene Toxicology, 4th ed., A Wiley-Interscience Publication, New York., 2157-2173 (1994)
8. Bhattacharya Tanushree, Chakraborty S., Fadadu Bhumika and Bhattacharya Piyal, *Res. J. Chem. Sci.*, **1(5)**, 61-66 (2011)
9. Farooq U., Kozinski J.A., Khan M.A. and Athar M., Biosorption of heavy metal ions using wheat based biosorbent : a review of the recent literature, *Bioresource Tech.*, **101**, 5043-5053 (2010)
10. Faust S.D., and Aly O.M., Adsorption Processes for Water Treatment, Butterworth Publishers, Boston, **7**, 27 (1987)
11. Kalavathy M.H., Karthikeyan T., Rajgopal S., Miranda L.R., Mobile Crystalline of materials, *J. Coll. Interf. Sci.*, **292**, 354-362 (2005)
12. Sharma Y.C., Prasad G., Rupainwar D.C., Removal of some heavy metals from sewage wastewater, *Int. J. Environ. Studies.*, **37**, 183-191 (1991)
13. Panday K.K., Prasad G., Singh V.N., Copper (II) removal from aqueous solutions by fly ash, *Water Res.*, **19**, 869-873 (1985)
14. Kwon J.S., Yun S.T., Lee J.H., Kim S.O., Jo H.Y., Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic (III) from aqueous solutions using scoria: kinetics and equilibrium of sorption., *J. of Hazard Mater.*, **174**, 307-313 (2010)
15. Pollard S.J.T., Fowler G.D., Sollars C.J. and Perry R., Low cost adsorbents for waste and wastewater treatment: a review, *Sci. of Total Environment*, **116**, 31-52 (1992)
16. Satapathy D., Natarajan G.S., Potassium bromate modification of the granular activated carbon and its effect on nickel adsorption, *J. of Analytical Chem.*, **12**, 147-154 (2006)
17. Kinhikar V.R., Removal of Nickel (II) from Aqueous Solutions by Adsorption with Granular Activated Carbon, *Res. J. Chem. Sci.*, **2(6)**, 6-11 (2012)
18. Wan Ngah W.S., Hanafiah MAKM Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review, *Bioresource Tech.*, **99**, 3935-3948 (2008)
19. Gupta V.K., Sharma S., Removal of Zinc from aqueous solutions using bagasse fly ash-a low cost adsorbent, *Ind. Eng. Chem. Res.*, **42 (25)**, 6619-6624 (2003)
20. Breck D.W., Zeolite Molecular Sieves, John Wiley and Sons, Inc., New York, **10**, 122 (1974)
21. Dyer A., An Introduction to Zeolite Molecular Sieves, John Wiley and Sons, Brisbane, **22**, 149 (1988)
22. Querol X., Moreno N., Umaña J. C., Alastuey A., Hernández E., López-Soler A. and Plana F., Synthesis of zeolites from coal fly ash, *Int. J. Coal Geol.*, **50(1-4)**, 413-423 (2002)
23. Anuwattana R. and Khummongkol P., Conventional hydrothermal zeolite from cupola slag and aluminum sludge, *J. Hazard. Mater.*, **166**, 227-232 (2009)
24. Antonio de Lucas, M. Angeles Uguina, Ignacio Covian, and Lourdes Rodriguez, Industrial Engineer Chemical Resources, **31**, 2134-2140 (1992)
25. Motoharu K., and Katsutoshi T., Synthesis of zeolites materials starting from Sedimentary, *Clays and Clay Minerals.*, **45**, 365-377 (1997)
26. Sanhueza V., Kelm U., and Cid R., Synthesis of Molecular sieves from Chilean kaolinites, *J. of Chem. Tech. and Biotech.*, **74**, 358-363 (1999)
27. Moore D.M., Reynolds Jr R.C., X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, **8**, 389-404 (1989)
28. Treacy M.M., Higgins J.B., Collection of Simulated XRD Powder Patterns for Zeolites, Elsevier, Amsterdam, **20**, 9 (2001)
29. Coles C.A., Yong R.N., The sorption of the rare earth element, Nd, onto kaolinite, *J. Appl. Clay Sc.*, **22**, 39-45 (2002)
30. Ho Y.S., Ofomaja A.E., Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber, *J. Hazard. Mater.*, **B129**, 137-142 (2006)
31. Shukla A., Zhang Y.H., Dubey P., Margrave J.L., and Shukla S.S., The role of sawdust in the removal of unwanted materials from water, *J. Hazard Mater.*, **95(1-2)**, 137-152 (2002)