International Archive of Applied Sciences and Technology
Int. Arch. App. Sci. Technol; Vol 8 [2] June 2017: 08-17
© 2017 Society of Education, India
[ISO9001: 2008 Certified Organization]
www.soeagra.com/iaast.html

ONLINE ISSN 2277- 1565
PRINT ISSN 0976 - 4828

CODEN: IAASCA **ORIGINAL ARTICLE**

DOI: .10.15515/iaast.0976-4828.8.2.817

Sorption of metal oxoanions from aqueous solution by surfactant modified zeolite Mordenite, Linde Type A and Alpha

Vandana Kushwah, Rashmi Tomar, Priyanka Sahu
Department of Chemistry, ITM University, Gwalior - Madhya Pradesh
Email: psvd2017@gmail.com

ABSTRACT

The hazardous ill effects of heavy metals on the environment and public health is an issue of serious concern. The use of zeolites for environmental applications is gaining new research interests mainly due to their properties and significant worldwide occurrence. The present work describes the synthesis, surface modification of zeolite and their use as sorbent. The removal efficacy of synthesized zeolite materials for the selective removal of metal as oxoanions from waste water was investigated. Chromium, arsenic and vanadium were the target metals, which had a strong oxidation ability and migration capability. The modified zeolite were characterised by X-ray diffraction, scanning electron microscopy, particle size analysis and evaluated for chromate Cr(VI), arsenate As(V) and vanadate V(V) removal. An uptake of chromate, arsenate and vanadate from aqueous solutions on modified zeolite has been studied. The efficiency of removal is different for Cr(VI) and As(V) and for V(V) oxoanions on to different zeolite. Sorption of metals revealed dependence on sorbent dose, time and sorbate concentrations with high sorption efficiencies at optimum operating parameters. The batch method has been employed, using metal concentrations in solution ranging from 5µg/ml to50µg/ml. The studies showed the selectivity of the different modified zeolites for the different metal oxoanions. At the same time modified zeolites hold great potential to remove oxoanions heavy metal species from waste water.

Keywords: *Zeolite LTA, Mordenite, Alpha, sorption, oxoanions*

Received 12.02.2017 Revised 10.04.2017 Accepted 04.04.2017

Citation of this article
V Kushwah, R Tomar, P Sahu. Sorption of metal oxoanions from aqueous solution by surfactant modified zeolite Mordenite, Linde Type A and Alpha. Int. Arch. App. Sci. Technol; Vol 8 [2] June 2017. 08-17.

INTRODUCTION

Growing concern for the presence and contamination of heavy metals in water supplies has steadily increased over the last few years. The pollution of water is one big problem in each country. At the global level, heavy metal may enter the environment mainly through uncontrolled anthropogenic fluxes related to rapid industrialization that has led to increase in heavy metal concentration into the environment [1]. The main industries and sources responsible for huge heavy metals are the mining and extractive industry, metallurgy, metal surface treatment processes, electroplating and metal coating, [2] chemical manufacturing , sludge and water reuse, fossil fuel, tannery, battery manufacturing industries. Further, the modern chemical industry is based largely on catalysts, numerous of which are metals or metal compound. Production of plastics, such as polyvinyl chloride, involves the use of metal compounds particularly as heat stabilizers etc. [3]. The wastewater coming from these industries is contaminated with various metals including Cr, As and V. The presence of heavy metals in water bodies like springs, streams and lakes is of serious concern due to their non biodegradibilty and bio accumulation capability [4, 5]. The metals are of particular concern because of their persistency and are toxic to even at low concentrations. Toxicity level depends on the type of metal, its biological role and the type of organisms that are exposed to it [6].

Arsenic is known to be carcinogenic and its contamination, both natural or anthro-pogenic, is a known cause for concern, especially as there are widespread reports of populations depending on As-contaminated water sources that have cause health effects among people like gastrointestinal irritation and potential necrotic changes in the liver and kidney [7, 8]. Excessive human intake of Arsenic leads to severe mucosal irritation, widespread hepatic and renal damage, capillary damage, and central nervous system irritation followed by depression [9]. Hexavalent chromium (Cr[VI]) is known to be a strong oxidant and to be highly toxic [10]. All vanadium compounds are considered to be toxic, though they are not regarded as serious health hazard. Effects of toxic amounts of vanadium can range from loss of appetite and common digestive problems to damage of liver and nervous system, kidney failure and lack of growth. The optimization of waste water purification processes requires a development of new operations based on low cost raw materials with high pollutant-removal efficiency. The complexity of the effluents makes the process of heavy metals removal more difficult as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients [11, 12].

Attention has been focused on the various sorbents, which have metal-binding capacities and are able to remove redundant heavy metals from contaminated water. Many methods have been developed and used to remove metal ions from wastewater such as granulated activated Carbon[13,14], manganese oxides [15], peat [16], recycled alum sludge [17], peanut hulls [18], fly ash [19], resins [20], kaolinite [21], biomaterials; [22, 23] coal and oxides. The removal efficiencies of metal ions of these sorbents were low and most of these methods have limitations, which include unavailability, generation of large volumes of secondary waste, high cost and poor removal efficiency [24, 25]. Considering from the economy and efficiency point of view, sorption is regarded as the most promising and widely used method among all these [26]. Sorption by zeolite minerals is one of the easiest, safest and most cost effective methods for the removal of these metals from aqueous solutions [27, 28].

Zeolites are microporous crystalline solids with well defined structures, which have unique ion exchange and sorption properties, and are widely used in a large number of water treatment processes [29, 12].The overall negative charge of the anions is balanced by cations that occupy the channels within the structure, and can be replaced with heavy metal ions[30]. The efficiency of sorption depends on many factors, including the surface area, pore size distribution, polarity, and functional groups of the sorbent [31]. LTA, Mordenite and Alpha are the type of zeolite, can be synthesized artificially. In order to induce affinity for anions surface of zeolite is modified [32]. This can be achieved by using surfactants and thus produced surfactant modified zeolite. The formation of a stable bilayer gives the zeolite anionic exchange capabilities. Diverse types of cationic surfactants are available and have been tested on zeolite. Most commonly used surfactant hexadecyltrimethylammonium (HDTMA) [33]. The process of sorption is now widely accepted, very effective and economically viable to be used to remove heavy metal ions in industrial waste as well as in drinking water.

In this study, Modified zeolite was investigated for their ability to sorb various metal oxoanions and describe the effects of sorbent dosage, contact time, metal ion concentration on sorption. Capacity of modified Zeolite have also been investigated.

MATERIALS AND METHODS

Chemicals and sorbent Materials

All chemicals used were of analytical grade. The synthetic solution were prepared from Aluminate, Silica gel, Sodium hydroxide, Tetra methyl Ammonium Hydroxide (TeOH). hexadecyltrimethyl ammonium bromide HDTMA-Br, Ammonium meta vanadate, naphthalene -1,5 diamine, nitric acid, buffer solutions.

Sorbent synthesis experiments

The synthesis course of action for different analogue is described below:

Preparation of Zeolite Mordenite

Analogue of mordenite was hydrothermally synthesized according to IZA synthesis. Sodium Aluminates was amended with an aqueous solution of Sodium Hydroxide then Silica was added to the mixture and the mixture was homogenized. The gel obtained was transferred to a Teflon lined autoclave and crystallization was passed out at 443K under autogeneous pressure without agitation for 24 hours. The product was then recovered by filtration, washed thoroughly with deionized water and dried at 373 K overnight.

Preparation of Zeolite Linde type A

In a Beaker calculated amount of sodium hydroxide was added to water until sodium Hydroxide dissolved completely. This solution divided in two parts, one half of this solution calculated amount of sodium Aluminate mixed gently in a caped bottle. In second half of Sodium hydroxide solution calculated amount of sodium metasilicate was added and mixed gently. Silicate solution was then Poured in to Sodium Aluminate solution. A thick gel solution obtained which was stirred until homogenized. Finally the blend was transferred to polypropylene bottle and crystallization was carried out at 372K for 30 minutes. The product was filtered and washed thoroughly with deionized water until filtrate's pH become less then 9. Product was dried overnight at 353K-383K.

Preparation of Zeolite Alpha:

In a beaker sodium aluminate solutions was prepared by adding calculated amount of sodium aluminate to water and stirred till dissolved completely. In this solution calculated amount of Tetra methyl ammonium Hydroxide was added and mixed gently for 30 minutes. After 30 minutes calculated amount of precipitated silica was added to Aluminate solution gradually with stirring and solution was blended for 30 minutes. Finally the blend was transferred to autoclave vessel and crystallization was carried out at 363K without agitation for 24 hours. After incubation at room temperature for 48 hours, the product was recovered by filtration. The product was washed thoroughly with deionized water and dried at 383K.

The product was kept in powdered form for further use after completion of the synthesis by the above methods.

Surface Modification of sorbent

Synthesized zeolite was treated with HDTMA– Br (Hexadecyltrimethylammonium) surfactant. 5 gms of zeolite was mixed with 2.5 gms of HDTMA and 180 ml water was added to it. The mixture was equilibrated on a water bath shaker at 150 RPM and 25^0C for 24 hours with intermittent shaking. Surfactant HDTMA formed double layer by exchange of its cation with the cation of zeolite there after, attraction of its hydrophobic end. After 24 hours zeolite was filtered, washed with deionized water and allowed to dry naturally.

Preparation of standard solutions:

Chemicals supplied by Merck as analytical-grade were used for preparation of standard solutions.The metal oxoanions studied were chromate Cr(VI), arsenate As(V) and vanadate V(V). Stock solutions of these oxoanions were prepared by dissolving calculated amount of Potassium dichromate ($K_2Cr_2O_7$), Sodium arsenate (Na_2HAsO_4), Ammonium Metavanadate (NH_4VO_3) in deionized water respectively and used as sorbate. Solutions of various concentrations were obtained by diluting the stock solution. Experiments were carried out in 100 ml volumetric flask at the ambient temperature.

Characterization of synthesized material

The composition of zeolite was characterized by powder X-ray diffraction (RigakuMiniflex) using Cu- K α radiation source of wavelength 1.54056 A^o and diffrectrograms were recorded in the range $2\theta = 0^o - 70^o$ at the scanning speed of 1 step/ sec. Powdered XRD were obtained from SICART Gujarat. Powder X Ray diffraction pattern of synthesized zeolite are shown in Figure 1. The main components were SiO_2, Al_2O_3, and Fe_2O_3 with others found in low concentrations. The structures of zeolites consist of three-dimensional frameworks of SiO_4^+ and AlO_4^+ tetrahedra. Samples were also scanned using Particle size analysis to determine zeolite particle sizes are shown in Figure 2. Surface Morphology of zeolite characterized by Scanning Electron Microscopy (SEM) is shown in Figure 3. for the main functional that might be involved in metal sorption, a Fourier Transformed Infrared Analysis (FTIR) was done on the zeolite to determine the surface functional group, and the structural features of zeolite. Fourier Transform Infra Red Spectroscopy (FTIR) was performed at room temperature, the sample were prepared with KBr and pressed into wafer/ pellet. Spectra were collected in the mid IR range of 400-4000 cm^{-1} with resolution of 1 cm^{-1}. The IR peaks observed for pure zeolite and modified zeolite (Figure 4.) were compared and found almost similar with each other indicating structure stability of the sample. In contrast modified zeolite has additional intense bands around 2850cm^{-1} -3200cm^{-1} which assigns to symmetric stretching vibration of C-CHO of the alkyl chain.

Batch Ion Exchange sorption experiments

The sorption of heavy metals on Surfactant Modified (LTA, Mordenite, Alpha) zeolite was carried out using the batch method. Batch sorption experiments were conducted using 0.25 g of sorbent zeolite with 25ml of solutions containing heavy metal ions of different concentrations at constant temperatures (25 ◦C) in 100 ml conical flask. The flask was sealed and placed on water bath shaker at constant speed 150 RPM and room temperatures. After desirable equilibrium time, solutions containing heavy metals were filtered through filter paper. The exact concentrations of metal ions in filtrate were determined by UVspectrometer (Perkin Elmer spectrophotometer) with regard to its concentration range. The sorption wavelengths used are 540 nm, 840 nm and 578 nm for chromate, arsenate and vanadate respectively. The efficiency of sorption were calculated using the formula; Sorption %= [(Ci - Ce)/ Ci] × 100, where Ci and Ce are the initial and equilibrium concentration of metal ions in solution, respectively.

RESULTS AND DISCUSSION

The efficiencies of the synthesized and modified zeolites for the selective removal of the metal oxoanions have been clearly demonstrated. The sorption of Cr, As and V as chromate, Arsenate, vanadate on to modified zeolite studied as a function of one parameter, keeping other parameters constant and percentage sorption were calculated for each case. This is evident that the appearances of metal oxoanions were minimized from the solution treated with modified zeolite. The results are explained one by one.

The Influence of contact time on sorption

Basically, the efficiency of sorption strongly depends upon the time of sorption. For a fixed concentration of heavy metals and a fixed sorbent mass, the retention of heavy metals increases with increasing contact time. In order to accomplish the kinetics study, sorption by surfactant modified Mordenite, LTA, Alpha was carried out keeping 50μg/ml concentration using 0.25 g of zeolite at room temperature (25±0.1°C) for time ranging from 5 min to 24 hours. The results of the study are shown in Table 1. The sorption rate was observed rapid in the first 4 hr, followed by a gradual increase with time until equilibrium. The fast sorption at the initial stage was probably due to the initial concentration gradient between the sorbate in solution and the number of vacant sites available on the sorbent surface. The attainment of equilibrium sorption might have been due to reduction in the available active sorption sites on the sorbent with time resulting to limited mass transfer of the sorbate molecules from the bulk liquid [34].

This trend emphasizes that the time of sorption have an important effect on the sorption efficiency which increases significantly with increasing contact time with metal as oxoanions solution. This is the consequence the ability of surfactant modified Mordenite, LTA, Alpha to sorb Chromate, Arsenate, vanadate is due to the anion exchange at the positive sites brought about by the reversed charge resulting from the HDTMA double layer on to zeolite sutface. The equilibrium (maximum) value was attained at around 6-7 hr. In some cases, the removal efficiencies decreased by about 4–10% with increasing contact time after equilibrium had been reached. This probably resulted from saturation of sorbent surfaces with heavy metals followed by sorption and desorption processes that occur after saturation. From the economic point of view, the role of the equilibrium time assessment is very important especially in many waste water treatment applications.

Table 1. The Influence of contact time on sorption

S.N.	Time	Cr(VI)% sorption			As(V) % sorption			V(V) % sorption		
		MOR	LTA	ALPHA	MOR	LTA	ALPHA	MOR	LTA	ALPHA
1	5 min.	39.12	10.10	7.33	21.29	27.45	46.84	11.98	85.99	11.18
2	10 min.	48.54	10.14	8.2	29.92	43.85	51.71	13.65	90.39	11.71
3	15 min.	65.97	10.86	9.15	35.99	51.56	51.95	14.36	94.00	20.08
4	30 min.	68.57	11.00	10.25	38.06	51.56	53.47	22.46	94.97	29.6
5	60 min.	71.34	11.58	10.45	42.13	53.89	57.46	23.34	96.47	33.92
6	2hrs	74.13	12.89	12.95	42.53	59.94	58.65	31.27	97.44	43.8
7	3hrs	77.24	12.89	19.92	44.29	61.05	58.85	36.12	98.06	70.74
8	4hrs	78.41	13.50	23.25	50.11	61.85	64.4	39.47	98.23	83.08
9	6hrs	79.51	15.07	26.81	52.19	63.69	65.28	39.64	98.41	85.01
10	7hrs	79.57	17.25	29.48	53.55	65.52	72.62	40.52	98.59	86.14
11	24hrs	79.44	18.71	30.04	54.43	66.56	72.7	41.05	99.11	86.16

Table 2.The Influence of amount of zeolite on sorption

S.N.	Amount gm	Cr(VI) % sorption			As(V) % sorption			V(V) % sorption		
		MOR	LTA	ALPHA	MOR	LTA	ALPHA	MOR	LTA	ALPHA
1	0.1	41.32	11.24	6.72	24.2	53.71	21.86	34.14	42.31	45.55
2	0.2	53.78	14.19	6.79	46.99	59.93	29.36	37.56	93.74	56.82
3	0.25	68.45	30.04	7.87	49.07	75.41	38.7	43.5	93.92	80.17
4	0.4	75.55	30.92	7.91	50.45	77.15	45.41	54.12	94.88	95.33
5	0.5	77.26	31.44	9.78	50.54	81.01	59.01	59.39	95.41	96.29

The Influence of amount of zeolite on sorption

The sorbate in the solution affects the sorption process, since it determines the availability of active sites. Most studies report that higher zeolite concentrations resulted in increased metal removal and reduced amount of metal sorbed per unit mass of sorbent [35-36]. Two reasons can explain this decrease in the sorption capacity: the first is associated with the unsaturated sorption sites and the second one with particle aggregation resulting in a decrease of the total surface area and an increase of the diffusion path length. These interactions between zeolite particles become important when the sorbent mass in the solution is high and may physically block some sorption sites from the incoming metal ions [37]. The results of the investigations are displayed in Table 2. At the initial stage generally, there is gradual increase in removal efficiency of Chromate, Arsenate and Vanadate with corresponding increase in sorbate concentration which may be attributed to the increasing presence of adsorption sites. However, as the binding sites of the modified zeolites get saturated the curves level off due to the independence of the sorption on concentration of the sorbate. To achieve this aim, a series of batch experiments were conducted with the sorbent dose of 0.1, 0.2, 0.25, 0.4 and 0.5 g per 25 ml of test solution. As expected the percentage of Chromate, Arsenate, Vanadate sorption increased with increasing surfactant modified zeolite. It can be seen from the data that sorbent dose of 0.25 g is sufficient for optimal removal of metal ions in aqueous solutions. A further increase in the quantity of sorbent dose will not have any significant effect on the removal of metal ions from the solution.

The Influence of metal concentration on sorption

The initial metal concentration in the liquid phase significantly affects the sorption process. Experimental studies were carried out for a wide range of metal concentrations between 5µg/ml to 50µg/ml. It is clear from data that the percentage of Chromate, Arsenate and Vanadate removal decreases by increasing initial metal concentration. The result of the study is shown in Table. 3 pointed out that with increasing metal concentration less favorable spaces become involved in the aqueous solution. In this study the metal ion uptake could be referred to ion-exchange kinetics in the micro porous of zeolite. Metal ions had to move through the pores of the zeolite as well as through channels of the lattice during the ion-exchange process and they had to substitute their oxoanions [38, 39].

Moreover, sorbent provides driving force to overcome all mass transfer resistance of the metal ion from the aqueous to the solid phase resulting in higher probability of collision between all metal oxoanions and the active sites. Consequently in lower concentration there are sufficient active sites which the sorbate could easily occupy, hence at higher concentration all metal oxoanions are left unsorbed in solution due to saturation of binding sites.

Table 3.The Influence of metal concentration on sorption

S.N.	Concentration µg/ml	Cr(VI) % sorption			As(V) %sorption			V(V)) % sorption		
		MOR	LTA	ALPHA	MOR	LTA	ALPHA	MOR	LTA	ALPHA
1	50	52.15	11.82	1.98	40.42	41.66	15.00	12.11	35.38	72.17
2	40	59.28	13.04	2.51	33.52	61.37	19.38	13.65	81.81	74.12
3	30	55.27	14.68	2.84	42.16	66.00	33.33	25.00	89.33	85.84
4	20	59.46	18.29	3.00	47.32	66.79	39.96	25.37	93.75	90.05
5	10	70.22	31.28	4.63	81.10	69.63	62.5	34.57	98.29	94.25
6	5	74.12	62.33	7.21	88.61	74.78	64.64	44.82	99.38	96.36

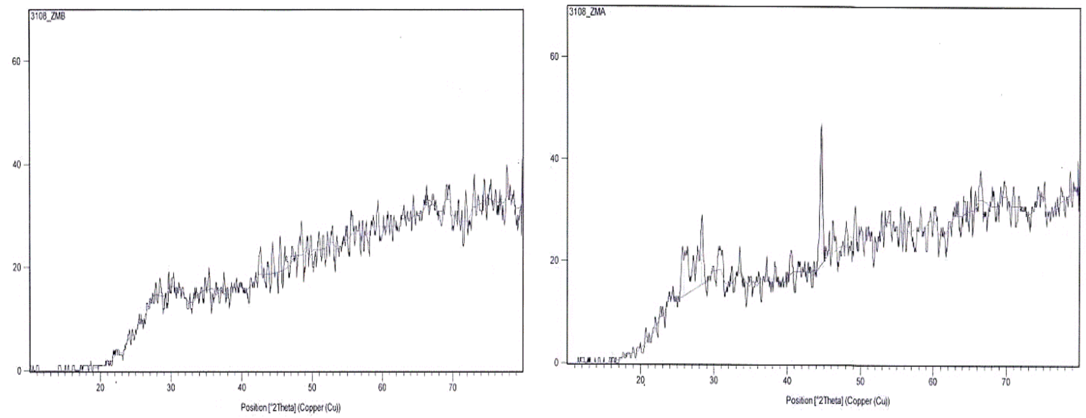

Fig. 1(i) X-ray analysis of (A) Mordenite (B) Modified Mordenite.

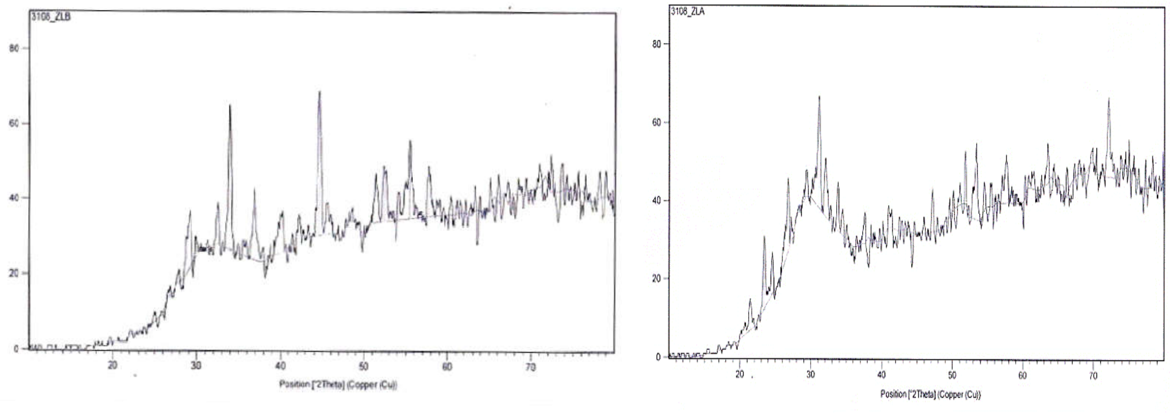

Figure 1(ii). X-ray analysis of (A) Linde Type A (B) Modified Linde Type A.

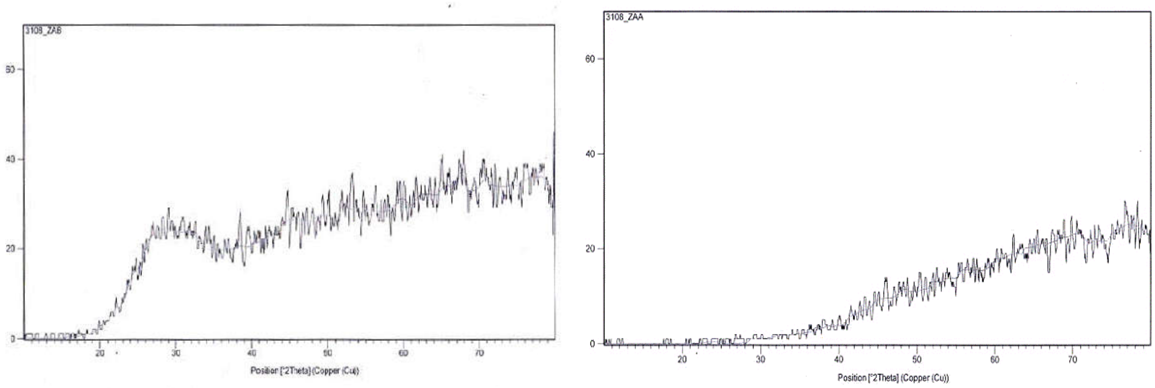

Figure. 1(iii). X-ray analysis of (A) Alpha (B) Modified Alpha.

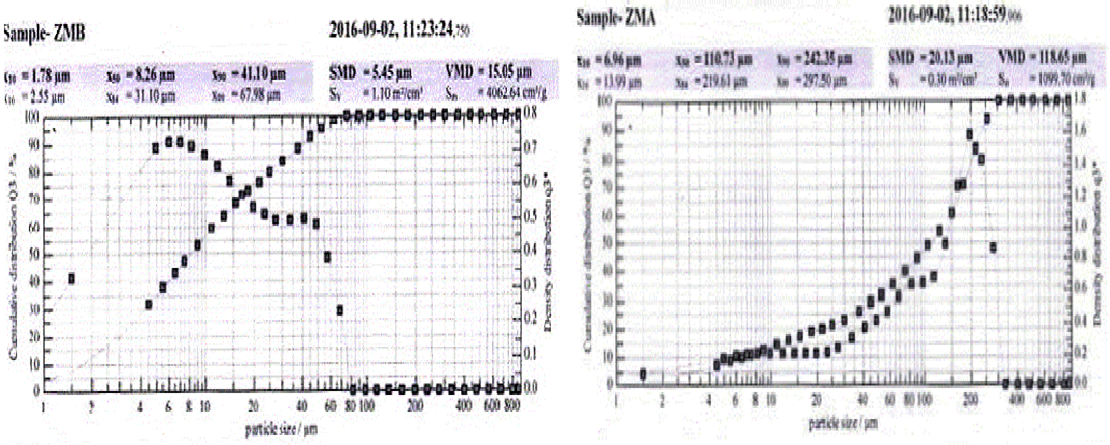

Figure 2(i). PSA of (A) Mordenite (B) Modified Mordenite.

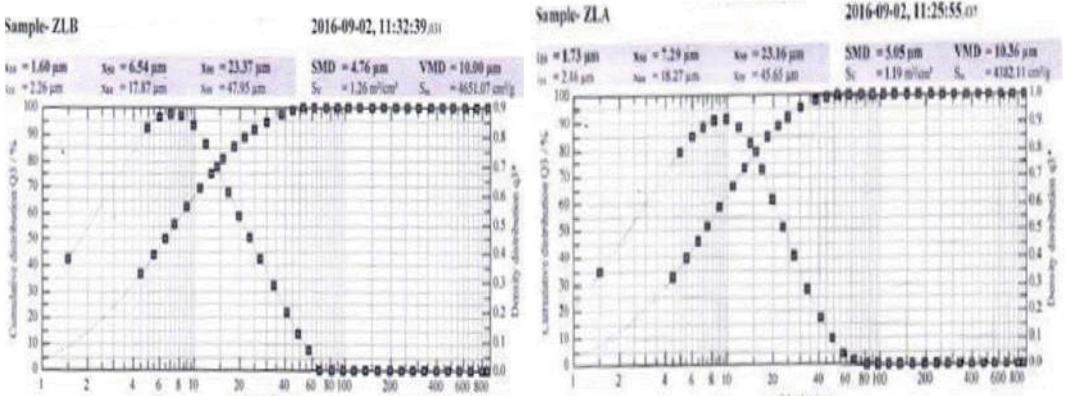

Figure 2(ii). PSA of (A) Linde Type A (B) Modified Linde Ty

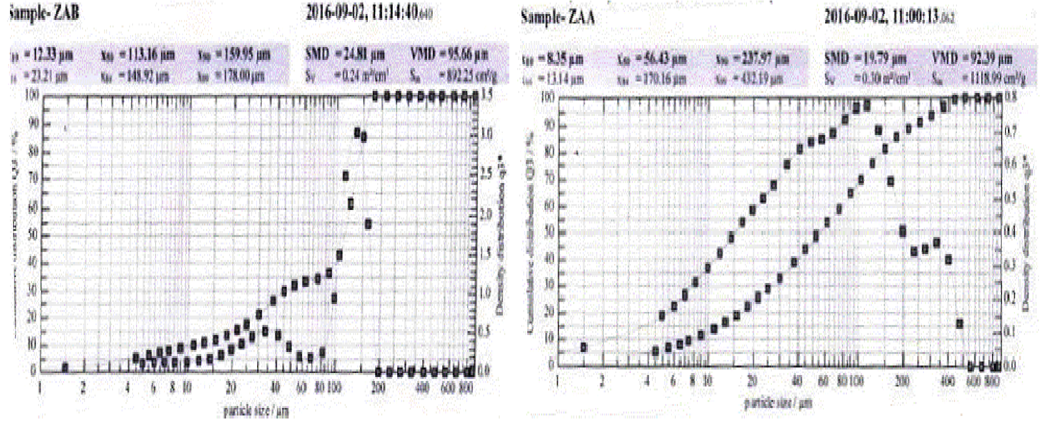

Figure 2(iii). PSA of ((A) Alpha (B) Modified Alpha.

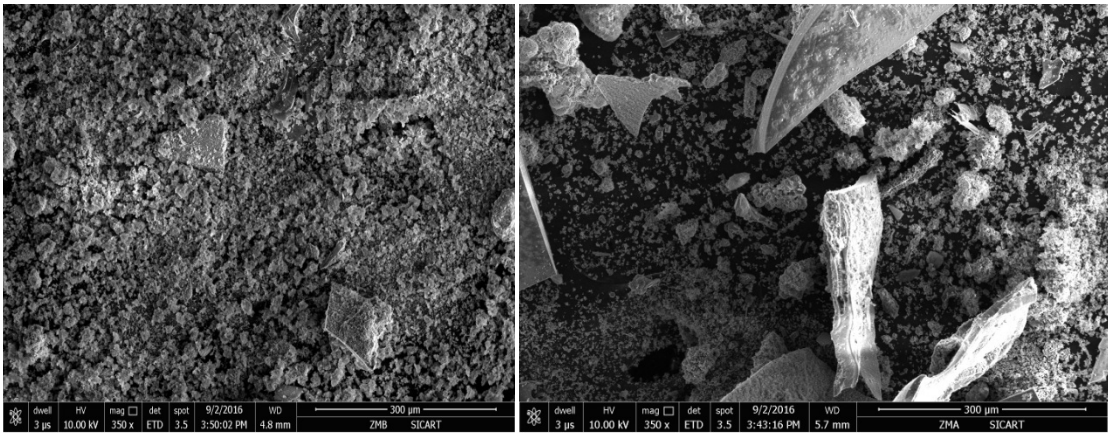

Figure 3 (i). SEM analysis of (A) Mordenite (B) Modified Mordenite.

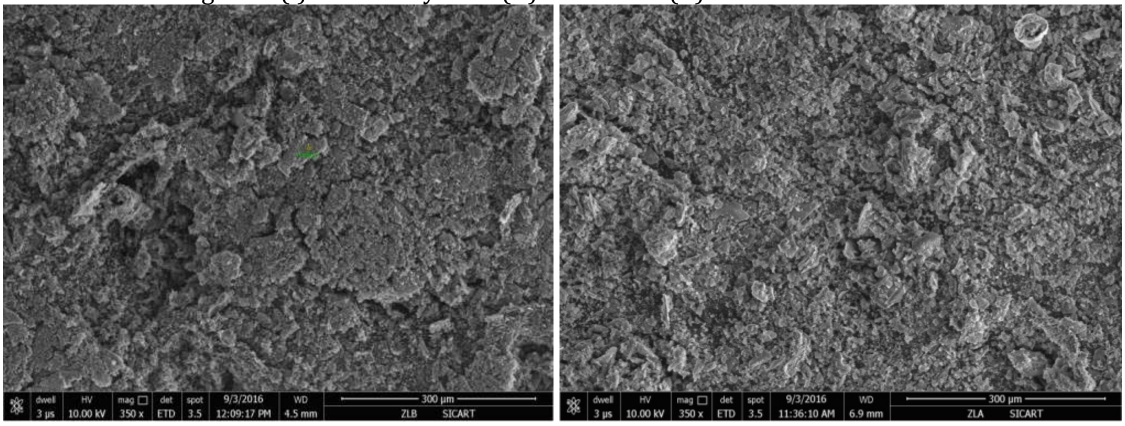

Figure 3(ii). SEM analysis of (A) Linde Type A (B) Modified Linde Type A

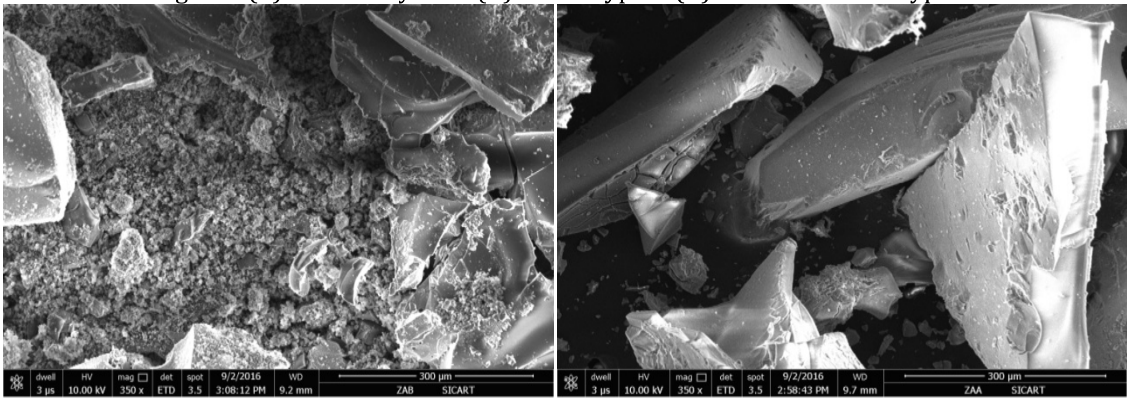

Figure 3 (iii). SEM analysis of (A) Alpha (B) Modified Alpha

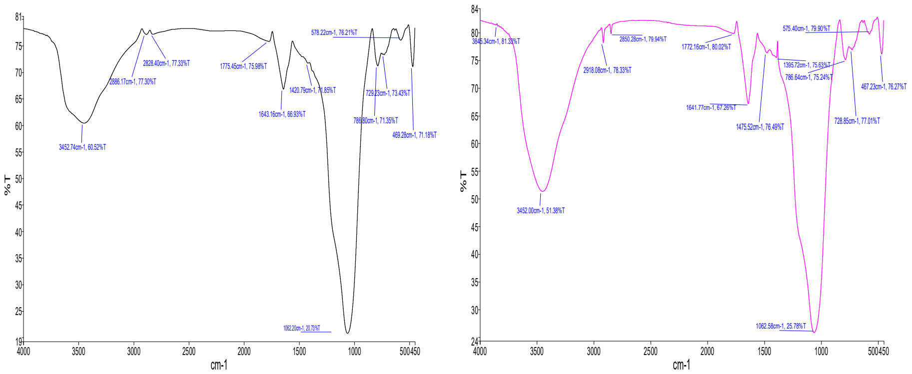

Figure 4(i). FTIR analysis of (A) Mordenite (B) Modified Mordenite

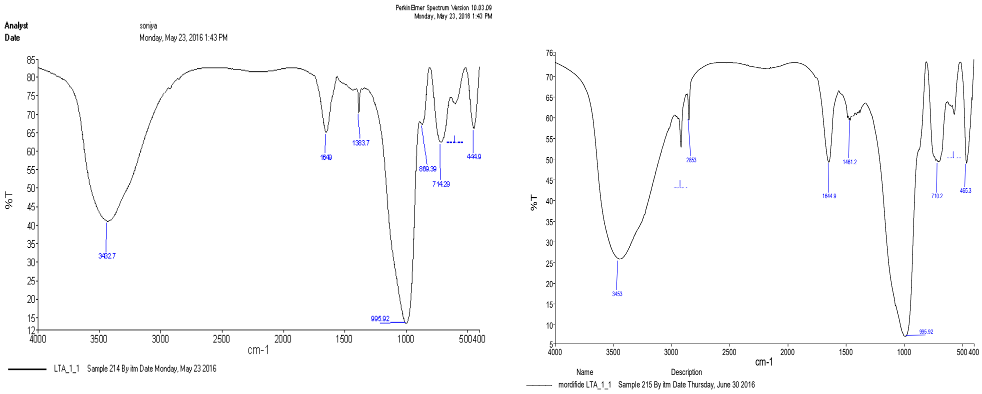

Figure 4(ii). FTIR analysis of (A) Linde Type A (B) Modified Linde Type A

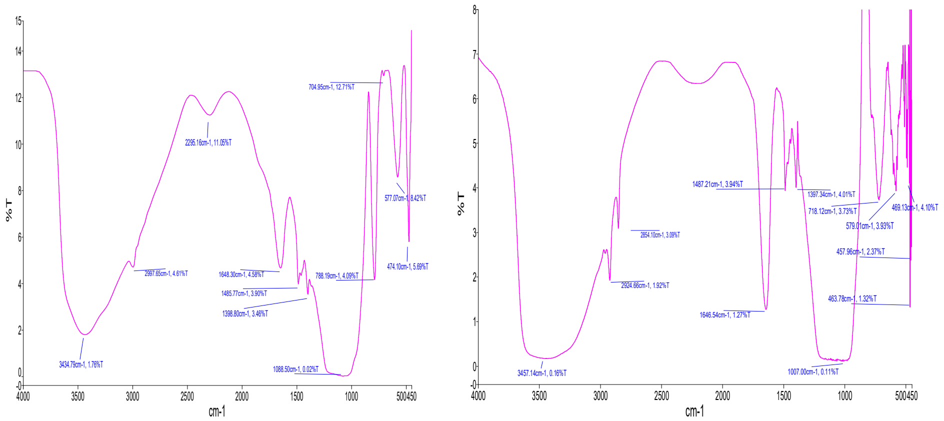

Figure 4(iii). FTIR analysis of (A) Alpha (B) Modified Alpha.

CONCLUSIONS

As it is presented in this paper, the versatility of zeolites is simple that it offers interesting options to overcome their own natural limitation for anions, by conducting chemical modification. The synthetic zeolites investigated have proven to contribute positively in the removal of the metal oxoanions. In spite of the scarcity of consistent cost information, the widespread uses of low-cost sorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness. The comparison between chromium, vanadium and arsenic oxoanions also brings to light some interesting subtle physicochemical differences concerning their interaction with the environment and for the development treatment/remediation procedures. Their differences are also highlighted through the interaction of Cr (VI), As (V) and V (V) with zeolites. Heavy metal elimination capacity increases with high concentration and dose of sorbent while elevated concentration of metals and occurrence of competitive ions decreases removal capacity. However, as the concentration becomes exceedingly high, in most cases beyond the optimum concentration, the removal efficiency declines. Concentration 50μg/ml was selected as optimum and used in the study to investigate the effect of contact time, sorbent dosage. However the removal efficiency of Chromate by Mordenite, Arsenate by alpha and Vanadate by Linde type A was found maximum.

The results are promising for the use of synthetic zeolites to treat contaminated water and industrial waste effluents. Sorbents zeolite are found highly efficient for heavy metal removal. Not only the industries, but the living organisms and the surrounding environment will also be benefited from the potential toxicity due to heavy metal. Thus, the use of low-cost sorbents may contribute to the sustainability of the surrounding environment.

ACKNOWLEDGEMENTS

This project is funded by MP Council of Science and Technology (MPCST), Bhopal, Government of India, (Project no. and date of sanction: A/RD/RP-2/2014-15/219). Authors acknowledge the financial support of MPCST. Support of SICART, Gujarat and SAIF Punjab University Chandigarh for the characterization of the synthesized material and analysis of product is also acknowledged.

REFERENCES

1. Järup, L. (2003). Hazards of heavy metal contamination. Br Med Bull., 68:167–182.
2. Nordberg, G. F., Flower, B., Nordberg, M. & Friberg. L. (2007). Handbook on the Toxicology of Metals, 3rd, Academic Press.
3. Shyam, R., Puri, J.K., Kaur, H., Amutha, R.& Kapila, A. (2013). Single and multi-binary adsorption of heavy metals on fly ash samples from aqueous solution. Journal of Molecular Liquids., 178: 31-36.
4. Horsfall, M.J. & Spiff, A.I. (2005). Effects of temperature on the sorption of Pb2+ and Cd2+ from aqueous solution by caladium bicolor (wild cocoyam) biomass. *Electronic Journal of Biotechnology*., 8:162–169.
5. Igwe, J.C. & Abia, A.A. (2006). A bioseparation process for removing heavy metals from waste water using biosorbents. *African Journal of Biotechnology*., 5(12):1167–1179.
6. Sing, S., Lal, S., Harjit, J., Amlathe, S. & Kataria, H.C. (2011). Potential of Metal Extractants in Determination of Trace Metals in Water Sample. Advanced Studies in Biology., 3 (5): 239-246, 33-40.
7. Mandal, B.K. & Suzuki, K.T. (2002) Arsenic round the world: a review. Talanta., 58: 201–235.
8. Mondal, P., Bhowmick, S., Chatterjee, D., Figoli, A. & Van der Bruggen, B. (2013). Reme-diation of inorganic arsenic in groundwater for safe water supply: a critical assessment of technological solutions. Chemosphere ., 92 (2):157–170.
9. Ajmal, M., Khan, A.H., Ahmad, S. & Ahmad, A. (1998). Role of sawdust in the removal of copper(II) from industrial wastes. *Water Research*., 32: 3085–3091.
10. Ouki, S.K. & Neufeld, R.D. (1997). Use of activated carbon for the recovery of chromium from industrial wastewater. *Journal of Chemical Technology* & *Biotechnology*., 70:3–8.
11. Shanableh , A. & Kharabsheh, A. (1996). Stabilization of Cd, Ni and Pb in soil using natural zeolite. *Journal* of *Hazardous Materials*., 45:207–17.
12. Misaelides, P., Godelitsas, A., Charistos, V., Ioannou, D. & Charistos, D. (1994). Heavymetal uptake by zeoliferous rocks from Metaxades, Thrace, Greece: an exploratory study. *Journal* of Radioanalytical and *Nuclear Chemistry journal*., 183(1):159–66.
13. Sekar, M. V., Sakthi & Rengaraj, S. (2004). Kinetics equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell. *Journal* of *Colloid* and *Interface Science.,* 279: 307–313.
14. Ayala, J., Blanco, F., Garcia, P., Rodriguez, P. & Sancho, J. (1998). Asturian fly ash as a heavy metals removal material. Fuel., 77: 1147–115
15. Biskup, B. & Subotic, B. (2004). Removal of heavy metal ions from solutions using zeolites. III. Influence of sodium ion concentration in the liquid phase on the kinetics of exchange processes between cadmium ions from solution and sodium ions from zeolite A. Sepration Science and Technolgy., 39: 925–940.
16. Chu, W. (1999). Lead metal removal by recycled alum sludge. *Water Research.,* 33: 3019–3025.
17. Brown, P., Jefcoat, I.A., Parrish, D., Gill, S. & Graham, S. (2000). Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution. Advance Environmental Research., 4:19–29.
18. Diniz, C.V., Doyle, F.M. & Ciminelli, V.S.T. (2002). Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin dowex M-4195. Sepration Science and Technolgy., 37 :3169–3185.
19. Ho, Y.S. & McKay, G. (1999), The sorption of lead (II) ions on peat, *Water Research.,* 33: 578–58.
20. Arias, M., Barral, M.T. & Mejuto, J.C. (2002). Enhancement of coper and cadmium adsorption on kaolin by the presence of humic acids. *Chemosphere.,* 48 :1081–1088.
21. Sublet, R., Simonnot, M.O., Boireau, A. & Sardin, M. (2003). Selection of an adsorbent for lead removal from drinking water by a point-of-use treatment device. *Water Research.,* 37: 4904–4912
22. Ekmekyapar, F., Aslan, A., Bayhan, Y.K. & Cakici, A. (2006). Biosorption of copper(II) by nonliving lichen biomass of cladonia rangiformis hoffm. *Journal* of *Hazardous Materials.*, 137: 293–298.
23. Rao, G. P., Lu, C. & Su, F. (2007). Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. Sepration Science and Technolgy., 34: 224-231.
24. Esalah, O.J., Weber, M.E., & Vera, J.H. (2000). Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate. The Canadian Journal of Chemical Engineering., 78: 948–954.
25. Kang, K.C., Kim, S.S., Choi, J.W & Kwon, S.H. (2008). Sorption of Cu2+ and Cd2+ onto acid and base pretreated granular activated carbon and activated carbon fiber samples. *Journal* of *Industrial* and *Engineering Chemistry.*, 14:131–135.
26. Manohar, D.M., Noeline, B.F., Anirudhan ,T.S (2006). Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase., *Applied Clay Science* 31:194–206.
27. Ok, Y.S., Yang, J.E., Zhang, Y.-S., Kim, S.-J.& Chung, D.-Y. (2007). Heavy metal adsorption by a formulated zeolite-Portland cement mixture. *Journal* of *Hazardous Materials.*, 147: 91–96.
28. Bolong, N., Ismail, A.F., Salim, M.R., Matsuura, T., (2009). A review of the effects of emerging contaminants in wastewater and options for their removal. Desalination., 239: 229–246.
29. Chunfeng, W., Jiansheng, L.I., Xia, S., Lianjun, W. & Xiuyun , S.(2009). Evaluation of zeolites synthesized from fly ash as potential adsorbents for wastewater containing heavy metals. *Journal* of *Environmental Sciences*., 21:127–136.
30. Bailey, S.E., Olin, T.J., Bricka, R.M. & Adrian, D.D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research.,* 33: 2469–2479.

31. Abusafa, A., Yucel, H., (2002). Removal of 137Cs from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite. Separation and Purification Technology. 28: 103–116.
32. Breck, D.W. (1974) Zeolite Molecular Sieves, John Wiley and Sons, Inc., New York. 10: 122.
33. Tschernich, R.W., (1992). Zeolites of the World. Geoscience Press, Phoenix.
34. Peri, J., Trgo, M. & Medvidovi N.V. (2004). Removal of zinc, copper and lead by natural zeolite – a comparison of adsorption isotherms. Water Res., 38: 1893–1899.
35. Wu, D., Sui, Y., He, S., Wang, X., Li, C. & Kong, H. (2008). Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash, *Journal* of *Hazardous Materials.*, 155: 415–423.
36. Cabrera, C., Gabaldón, C. & Marzal, P. (2005). Sorption characteristics of heavy metal ions by a natural zeolite. *Journal of Chemical Technology* and *Biotechnology.,* 80: 477–481.
37. Mishra, P.C., Patel, R.K., (2009). Removal of lead and zinc ions from water by low cost adsorbents, *Journal* of *Hazardous Materials.*, 168: 319–325.
38. Oren, A.H., & Kaya, A. (2006). Factors affecting adsorption characteristics of Zn2+ on two natural zeolites. *Journal* of *Hazardous Materials.*, 131: 59–65.
39. Arief, V.O., Trilestari, K., Sunarso, J., Indraswati, N. Ismadji, S. (2008). Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. Clean Soil, Air, Water., 36: 937–962.