

Synthesis and Characterization of Surface Modified Zeolite and its Application as Adsorbent for Pesticide

Shikha Singh*, Adya Jain, Kautily Rao Tiwari,
Neeraj Kumar and Radha Tomar

School of Studies in Chemistry, Jiwaji University Gwalior (M.P.) 474011, India.

Abstract

This paper illustrates studies of surface modification of zeolite with cetyl trimethylammonium bromide (CTAB), to explore the adsorption effectiveness for the removal of pesticide in aqueous solution. Surfactant modified zeolite has been appraised and found to be potential adsorption media for this study. The effect of change in pH on the adsorption process was also studied. It was found that the best adsorption is at pH=7. The effects of different temperatures within the range (303.15, 313.15 and 323.15K) were studied. Zeolite and surfactant modified zeolite were characterized through Fourier Transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Electron dispersion spectroscopy (EDS) and X-ray Diffraction techniques (XRD) whose results are in good agreements and confirmed this synthesis process.

Keywords: Zeolite Alpha, Cationic Surfactant CTAB, Pesticide (Methoxychlor).

1. INTRODUCTION

Zeolites are microporous crystalline aluminosilicate minerals that have enormously high adsorption aptitude and good catalytic properties with outstanding chemicals [1]. They are thermally stable. These mineral-based functional materials demonstrate a great assortment of applications in catalysis, adsorption, environmental remediation, polymers, etc. Zeolites disclose good properties of adsorption and have been used for the minimization of toxicological effects of toxic metal ions and other pollutants such as pesticides [2]. Zeolite surfaces have a well-built affinity for cation exchange, which enables them to be used as sorbents, catalysts, molecular sieves, etc [3]. Zeolites are exploited to remove organic matter, drug residues, trace metal ions and lots of pollutant from the wastewaters due to their adsorption. Zeolites are of vast attention in pesticide remediation due to their high adsorption capacities, catalytic chemical reactivity and the intrinsic capacity to be regenerated while maintaining their initial

properties [4, 5]. Several solid sorbents were modified with surfactants such as aluminum hydroxide [6], silica [7], alumina [8,9], magnetic nanoparticles [10], graphene [11], soils [12], and zeolite [13,14-18]. Surfactant-modified clays are 10 to 30 times more valuable than natural soil organic matter for sorbing nonpolar or weakly polar organic contaminants [19,20]. The modified zeolites are cheaper than grainy activated carbon and synthetic ion exchange resins [21].

Pesticides are chemical substances applied in agriculture, released into the environment and come into human contact directly or indirectly. The exercise of pesticides facilitated to considerably diminish crop losses and to perk up the yield of crops [22]. Plant fortification chemicals widely used for raising the concern of environmental contamination, especially surface and groundwater resources. Organochlorine pesticides (methoxychlor) have been widely used to control pests in agriculture, forestry, and some household activities in India [23]. More than a few methods, either independent or in conjugation with others, have been used for the removal of pesticides, and these include chemical oxidation with ozone [24], Photo degradation [25], combined ozone and UV irradiation [26], and adsorption [27-34].

The present study spotlights on the appraisal of adsorption potential of surfactant modified zeolite for methoxychlor in aqueous solution. Adsorption of methoxychlor with distinction of surfactant loading, adsorbent doses, pH of solution, equilibration time and temperature was studied.

2. EXPERIMENTAL

2.1 Materials

Anhydrous sodium aluminate from Merck, tetramethylammonium hydroxide (TMAOH), from Aldrich, precipitated silica from Merck, and deionized water. The surfactant selected for this study i.e. cetyl trimethylammonium bromide (CTAB) from HI-Media, while methoxychlor was received from E Merck, India Limited. All these materials and chemicals were used without any further decontamination. Teflon lined autoclave for zeolite-Alpha synthesis. X-Ray diffraction spectra have been obtained from Miniflex 600 Diffractometer instrument. Spectrumto- Perkin Elmer was used to record Infrared spectra of the synthesized zeolite by using KBr pallets. ESEM quanta 200 FEI, SEM-EDAX for scanning electron microscopy (SEM) was used to see morphology and to see presence of elements of zeolite. UV-Vis spectrophotometer (Systronics 114) was used to calculate the concentration of methoxychlor.

2.2 Materials preparation

2.2.1 Synthesis of zeolite-Alpha. The hydrothermal synthesis of aluminosilicate zeolite alpha was performed under stable situation using tetra methyl ammonium hydroxide (TMAOH) as an organic template for maintaining its pore. 3.9g of anhydrous sodium aluminate was dissolved in 11.6 g of distilled water. The solution was systematically stirred until complete dissolved, and then 27.92 g of tetra methyl

ammonium hydroxide was added and stirring until mixed. To this, 11.12 g of precipitated silica was added in small portions and the resulting slurry continued to be stirred strongly. After 30 min of stirring, at room temperature, a gel formed was kept for 48 h in polypropylene bottle and then placed in a Teflon lined autoclave at 90°C for 24–30 h for crystallization. After quenching the autoclaves in cold water, the resultant material was washed and dried at 110°C.

2.2.2 Surface modification of zeolite

Required concentration of Cetyl Trimethyl Ammonium Bromide-CTAB) is dissolved in 10 ml each of distilled water and ethanol. The concentrations of surfactants solutions used for preparation for surface modification were 0.729g, 2.18g and 3.64g. The CTAB-water–alcohol solution i.e. solution ‘A’ has been used for rising the solubility of surfactants in water and then heated to 80°C temperature for one hour stirring. Solution ‘B’ has been prepared by mixing 1.66 g of zeolite and 33.33 ml of water, heated at 100°C for 2 h with continuous stirring. Thereafter both the solutions i.e. solution ‘A’ and solution ‘B’ were mixed with 50 mL distilled water under continuous stirring and heated to 100°C temperature for 1 h, filtered with a vacuum filter. To eliminate bromide ions from the reaction mixture 0.5 g AgNO₃ in 25 ml of distilled water was mixed. Finally, the mixture was filtered and dried at 100°C for 24 hour.

2.2.3 Adsorption Experiment.

The adsorption of the methoxychlor onto modified zeolite was investigated by batch adsorption experiment. In a 150 ml conical flask at temperature 303.15 K, 200 mg of various Si/Al adsorbents were added to each flask containing 50 ml pesticide solution of known concentration. All flasks were kept at 5000 rpm in a reciprocating thermostatic water bath shaker for 24 h. Solid and solution phases were separated by filtration using Whatman filter paper 42 followed by high speed centrifugation of the filtrate solution to restrict the interference of any suspended nanoparticles present in the solution. Methoxychlor concentration in the filtrate was determined by using UV-visible spectrophotometer. The amount of methoxychlor adsorbed by the adsorbent was calculated from the difference between the initial and equilibrium solution concentrations. Hence, the amount of methoxychlor adsorbed was calculated from the following equation:

$$\text{Sorptions \%} = \frac{C_i - C_e}{C_i} \times 100$$

C_i and C_e represent the initial and equilibrium concentration of methoxychlor solution (mg L⁻¹). V is the volume of the solution in ml and W is the weight of the adsorbent in g.

3. RESULTS AND DISCUSSION (1)

3.1. Characterization of zeolite-Alpha:

3.1.1. X-ray diffraction:

To calculate the structural properties of synthesized materials and to monitor the effect of surfactant modification on structure stability. The X-Ray Diffraction pattern shows the crystalline phase of zeolite without any amorphous phase. Figure 1 and 2 present XRD graph of Zeolite Alpha and its CTAB modified form. X-ray diffraction patterns of the synthesized zeolite Alpha, as shown in Fig. 1, it is observed that the level of crystallinity is very high and all the materials are crystalline in nature without having any amorphous phase. On comparing the unmodified and modified zeolites, from figure 2 it was observed that they closely resembled with each other with slight differences between in 2θ and d spacing values. Which indicate that the structure integrity of the sample is retained a surfactant treatment.

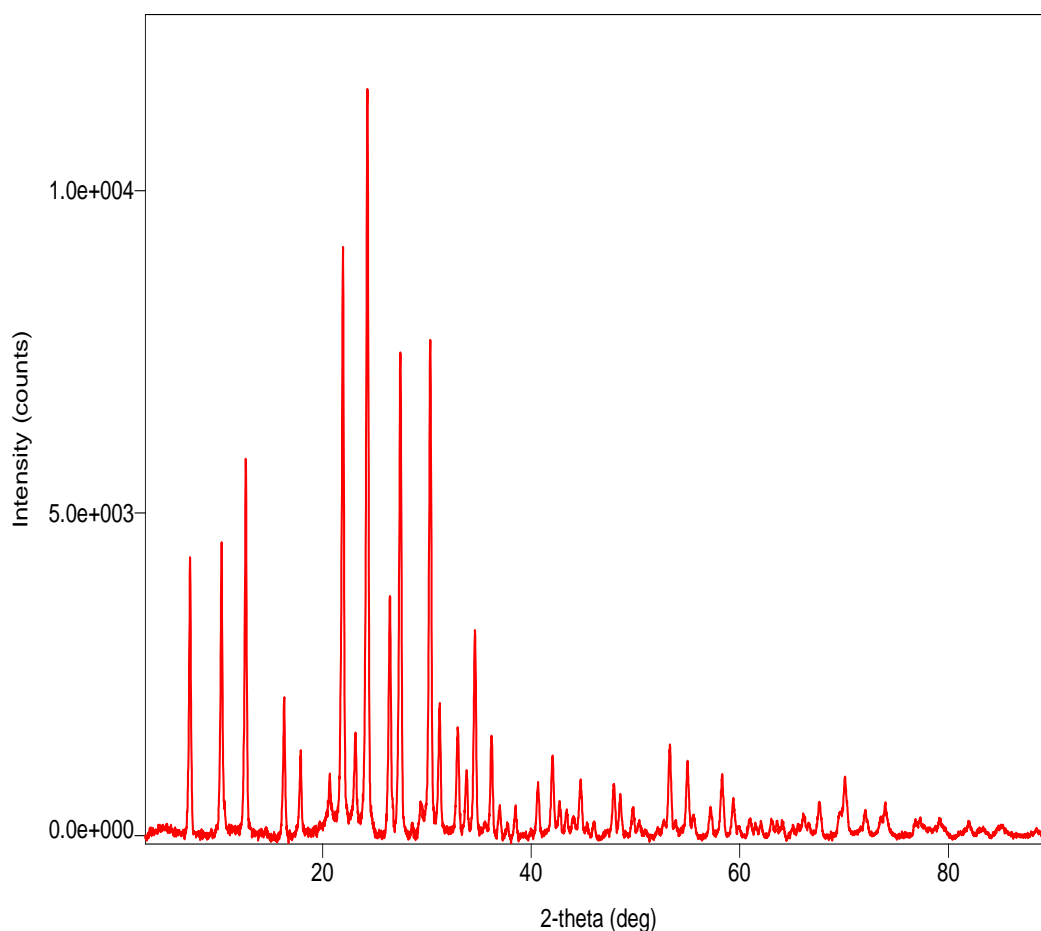


Fig 1: XRD of Zeolite Alpha

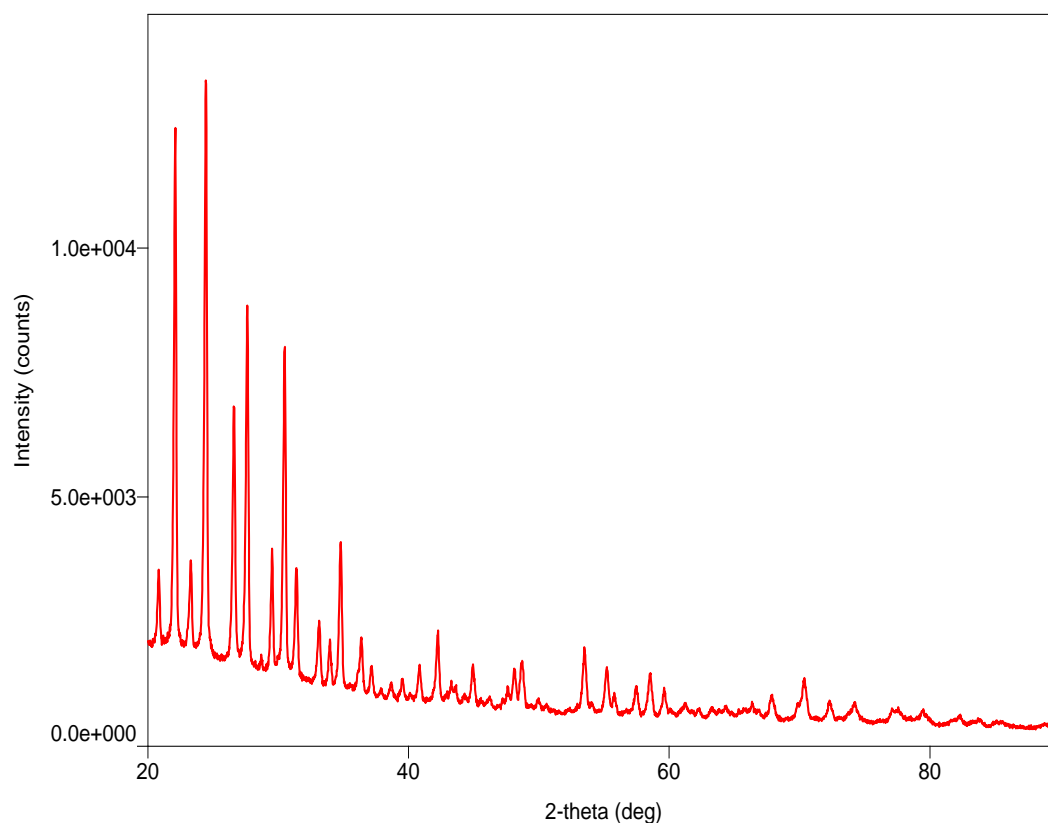


Fig 2: XRD of CTAB modified Zeolite Alpha

3.1.2. Fourier transform-infrared spectroscopy:

Using Perkin-Elmer (Spectrum) an extensive FTIR is used to identify and Characterized the organic species and to analyze the chemical bonding. The obtained FTIR spectra using KBr pellets of Zeolite Alpha and their modified CTAB surfactant in the frequency range 450 – 4000 cm^{-1} (mid-infrared range) are shown in figure 3 and 4. FT-IR spectra of zeolite-Alpha shows the characteristics peaks at wave numbers 3434, 3019, 1652, 1488, 1022.84, 474 cm^{-1} . The adsorption peak at around 474 cm^{-1} is attributed to Si, Al–O bond, and those at 1022 and 757 cm^{-1} are, respectively attributed to asymmetric and symmetric stretches of the zeolite framework. The adsorption band around 1488 assigned to vibrational mode of NH_4^+ functional group. The peak at 3434 confirms the presence of OH group. For the modified zeolites peaks at 3422.35, 2924.65, 1645.10, 1486.82, 1038.61, 577.39 and 473.57 cm^{-1} confirm the structural stability after surfactant modification. The band at 2924.65 cm^{-1} is attributed to the C–H stretching vibrations of the CTAB. The absorption band of -OH bending vibration of interlayer water unmodified zeolite (1652 cm^{-1}) moved to 1645.10 cm^{-1} for modified zeolite. Simultaneously, the intensity of this absorption band decreases, which indicated the water content reduced with the replacement of the hydrated cations by CTA^+ . This observation showed that the

surface properties of unmodified zeolite had been changed from hydrophilic to hydrophobic by modifying it with CTAB.

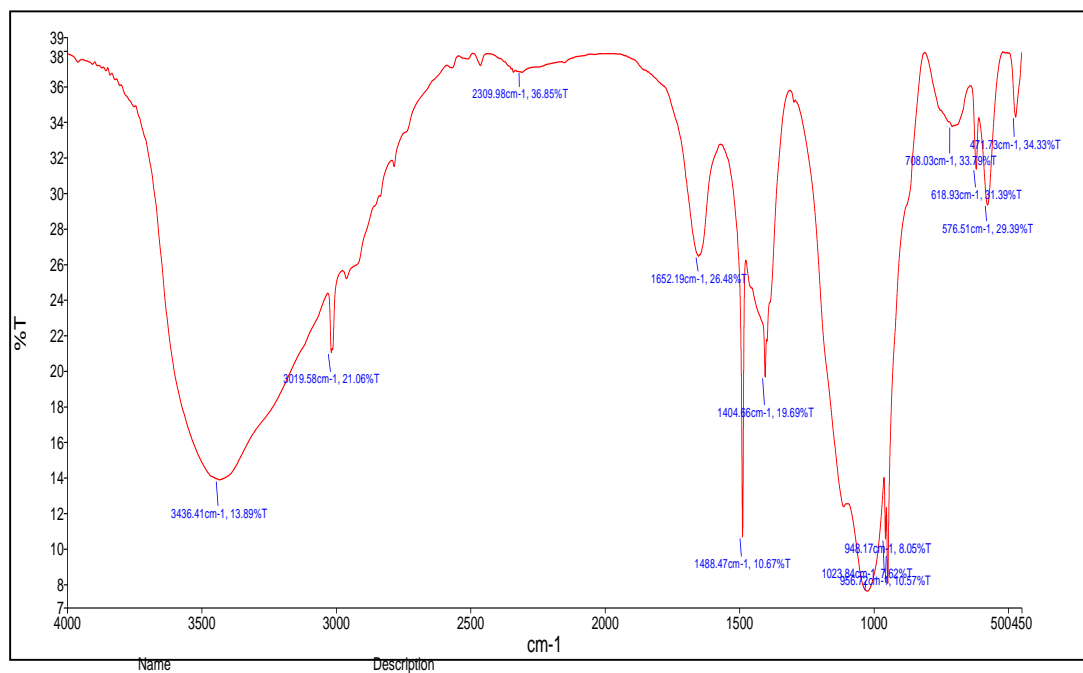


Fig 3: FTIR of Zeolite-Alpha

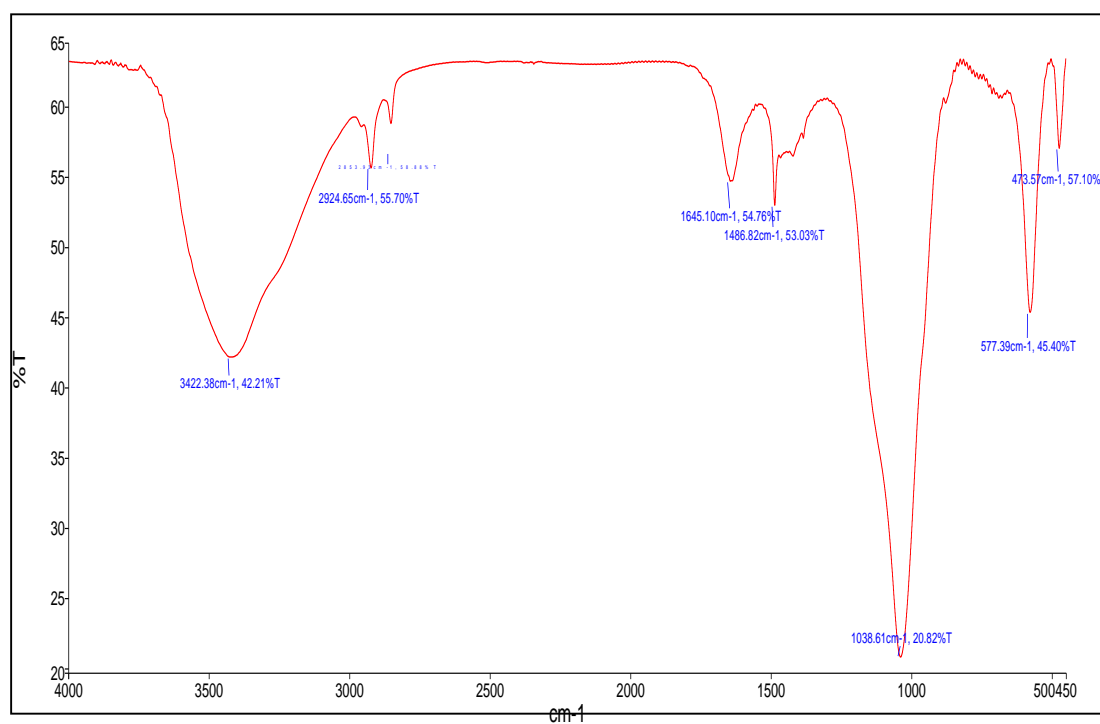


Fig 4: FTIR of CTAB modified Zeolite-Alpha

3.1.3. Scanning electron microscopy:

The SEM photographs of natural zeolite-Alpha are presented in figure 5. Zeolite-Alpha was obtained by ESEM Quanta 200, FEI (Scanning Electron Microscopy–Energy Dispersive X-ray Spectroscopy) instrument. Scanning electron micrograms of zeolite-Alpha were taken at various magnifications (10,000×, 20,000×) for understanding its surface morphology. The SEM-micrograph of Zeolite-Alpha appears in polyhedrons crystal shape with sizes around 5–10 μm.

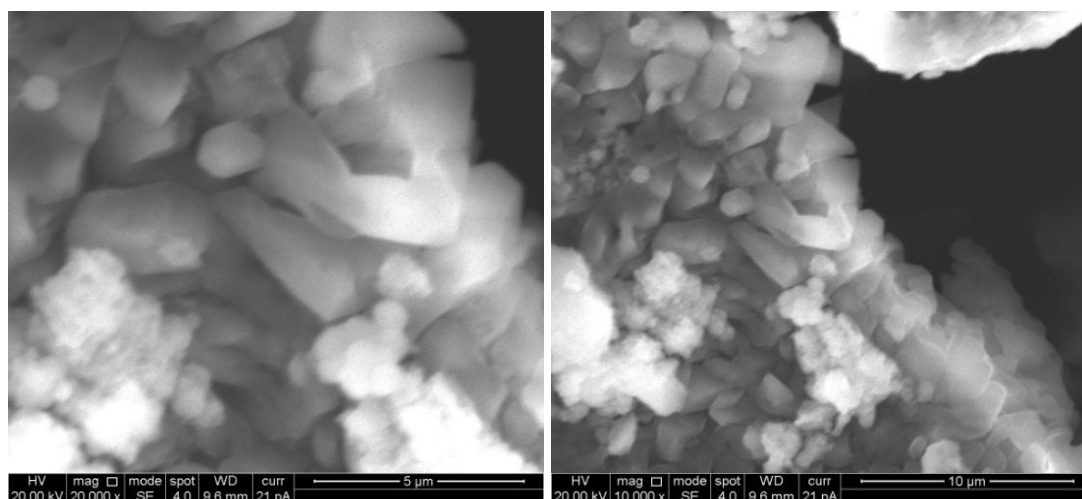


Fig 5: SEM images of zeolite-Alpha at various magnifications

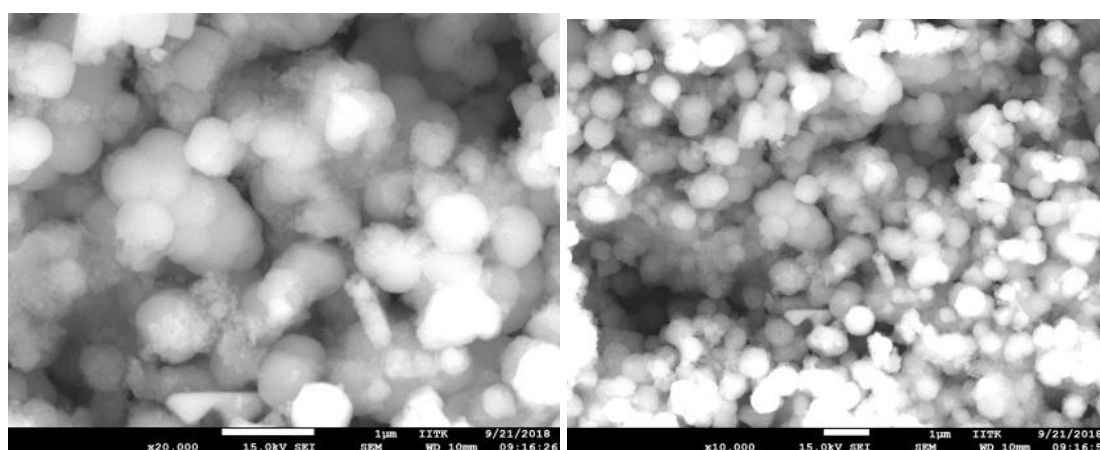


Fig 6: SEM images of CTAB modified zeolite-Alpha at various magnifications

3.1.4. Electron dispersion spectroscopy. Sample for EDS analysis was layered with thin gold foil in order to avoid charge influence. The chemical composition of the material was obtained quantitatively from energy dispersive analysis (EDS) (Fig. 6). Results obtained for elements like Al, Na, O and Si show that Al is present in

abundance and is almost more than half of the overall weight of material. Among Si and Al, Si is found to be in abundance confirming Si/Al ratio greater than 1 and also the elemental ratios are in accordance to the molar composition taken during the synthesis of zeolite-Alpha.

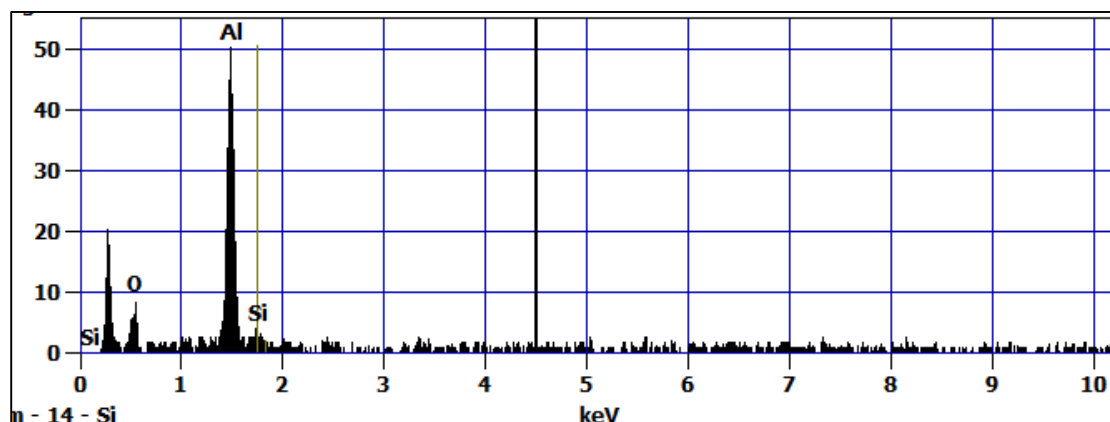


Fig 7: EDS graph of Zeolite-Alpha

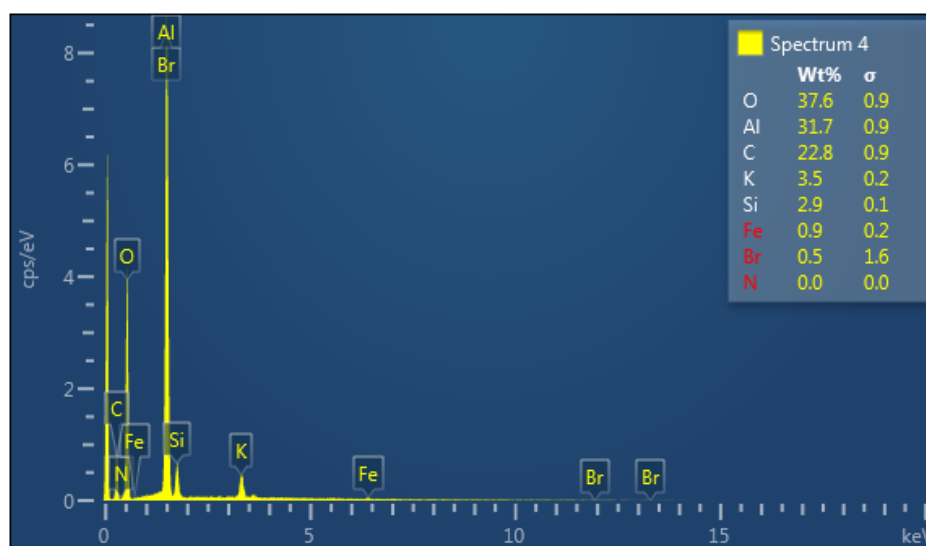


Fig 8: EDX graph of CTAB modified Zeolite-Alpha

3.2. results and discussion (2)

3.2.1 Adsorption studies of Methoxychlor

3.2.1.1 Effect of the Adsorbent dose. The amount of adsorbed methoxychlor with a changeable amount of adsorbent presented in Fig. 9 make known that increase in the adsorbent dosage outcome in increased percentage adsorption of methoxychlor for all adsorbents. A greater concentration of the adsorbent means more number of active sites for adsorption. As a result, the increased amount of adsorbent make easy higher

adsorption sites for diverse adsorption, ion-exchange, binding processes etc. to take place on the adsorbent surface. Maximum adsorption is distinguished with 200 mg adsorbent dosage.

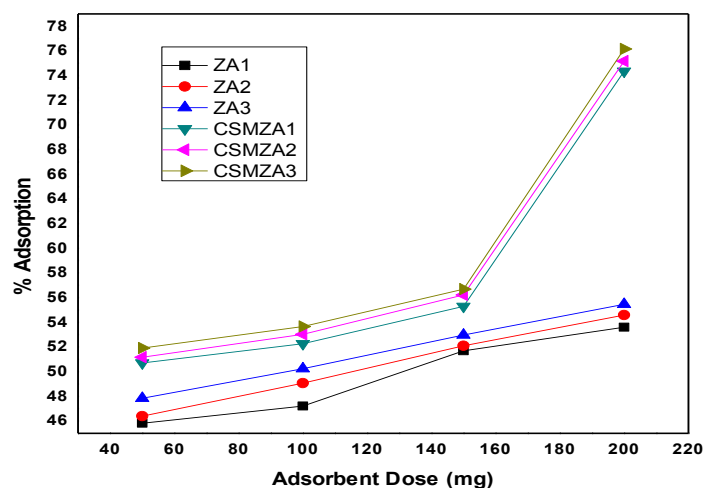


Fig. 9: Effect of adsorbent dose on sorption of methoxychlor onto unmodified and modified zeolite

3.2.1.2 Effect on surfactant loading

The adsorption of methoxychlor on zeolite Alpha modified with different concentrations of CTAB is presented in Fig. 10. It is clear from Fig. 10 that surface modification to a great extent enhances the adsorption potential of the material for methoxychlor adsorption. Furthermore, it is observed that the amount of adsorbed methoxychlor increases with increase in surfactant loading and maximum adsorption is observed for alphaCTAB3.

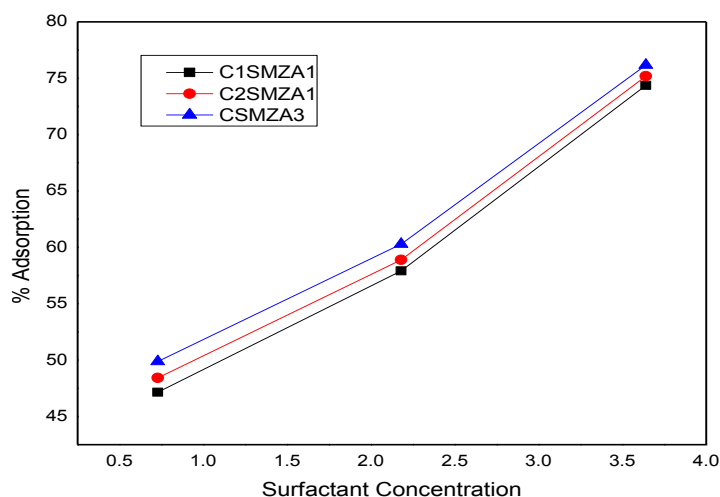


Fig. 10: Effect of surfactant loading on sorption of methoxychlor

3.2.1.3. Effect of pH solution on methoxychlor adsorption

The adsorption performance of methoxychlor on unmodified and surfactant modified adsorbents at different pH (viz. 3, 5, 7, 9 and 11) of the solution was studied. The adsorption data to be had in Fig. 11 make known that the maximum adsorption of methoxychlor is obtained at neutral pH for all materials. The results show that the amount of methoxychlor adsorbed per gram of adsorbent increases with increase in pH up to pH 7. while further increase in pH results in a decrease of methoxychlor adsorption. The experimental study in the pH range 3 to 11 surface functional groups of zeolite become deprotonated and the amount of deprotonation increases with an increase in pH. This deprotonation results in a less positively or more negatively charged zeolite surface at higher pH than at the lower one. It has been observed that with further increase in pH up to 11.0, the extent of adsorption becomes poor. As a result of full experimentation, 7 pH was selected as the optimum and used all over the study.

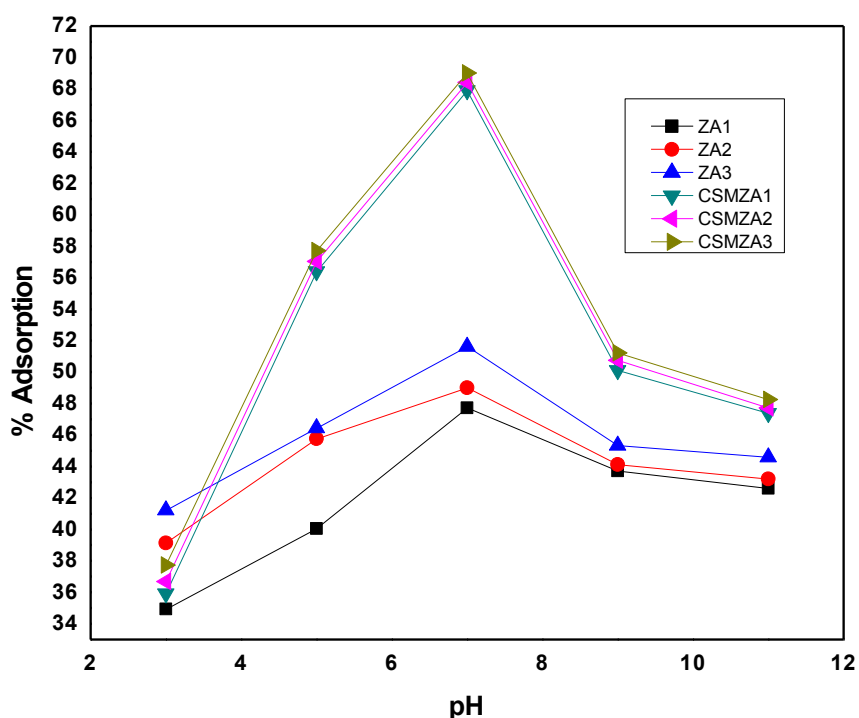


Fig. 11: Effect of pH on sorption of methoxychlor onto unmodified and modified zeolite.

3.2.1.4 Effect of Temperature:

In the usual cases adsorption decreases with rise in temperature, and molecules adsorbed earlier on a surface tend to desorb from the adsorbent surface at elevated temperatures which is in accordance to the adsorption theory. Thus, system temperature is considered to be a crucial parameter in the adsorption reaction.

Therefore, the purpose of this study is to ascertain the effect of temperature on the adsorption of Methoxychlor on unmodified and modified zeolite forms.

The obtained results of temperature effect have been presented in Fig. 12 and indicate that an increase in temperature from 303.15 to 323.15 K results in a decrease in methoxychlor adsorption. This decrease in adsorption may be attributed to change in the energy of adsorption or weakening of the van der Waals forces of attraction between methoxychlor molecule and the adsorbent surface, causing decrease in physical adsorption. The other reason for the decrease in methoxychlor adsorption with increase of system temperature is change in the solubility of pesticides with change in temperature. Results of the thermal study confirm that all reported adsorbents show a negative response to an increase in temperature for methoxychlor adsorption, and 303.15K has been considered as optimum temperature for the adsorption studies.

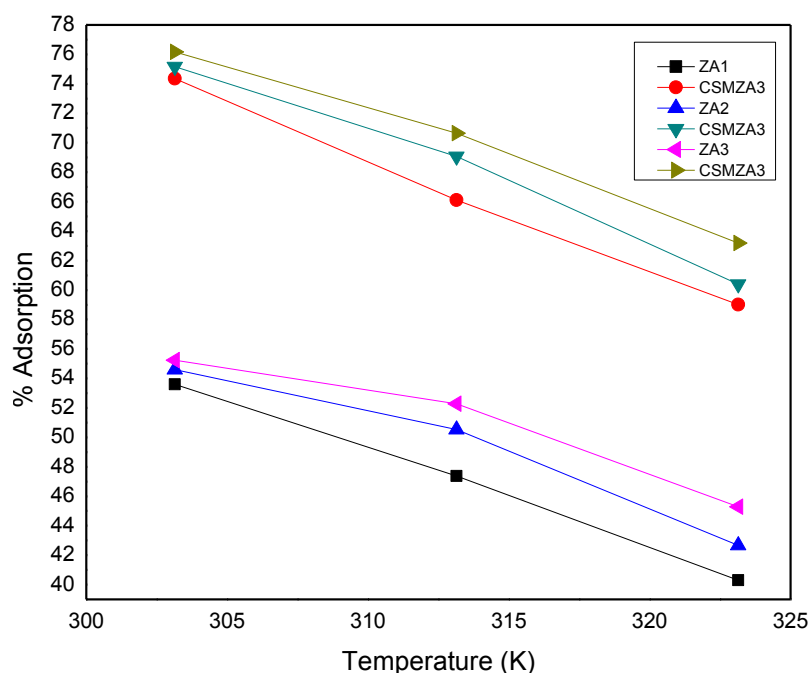


Fig. 12: Effect of temperature on sorption of methoxychlor onto unmodified and modified zeolite.

3.2.1.5 Effect of equilibration time:

Kinetic studies for Methoxychlor adsorption on all original and surfactant modified zeolites have been made to find out the most favorable equilibration time for maximum adsorption. Adsorption data presented in Fig. 13 shows that the amount of Methoxychlor adsorbed per mg of adsorbent increases with increase in equilibration time. The plot of the amount of Methoxychlor adsorbed per gram of adsorbent versus the contact time between adsorbate–adsorbent indicates that the adsorption becomes

asymptotic to the time axis after 12 h of equilibration and stand for nearly an equilibrium pattern. Since the maximum adsorption for all adsorbents is observed at 24 h of equilibration, therefore, 24 h is measured as the most favorable equilibration time for other adsorption studies.

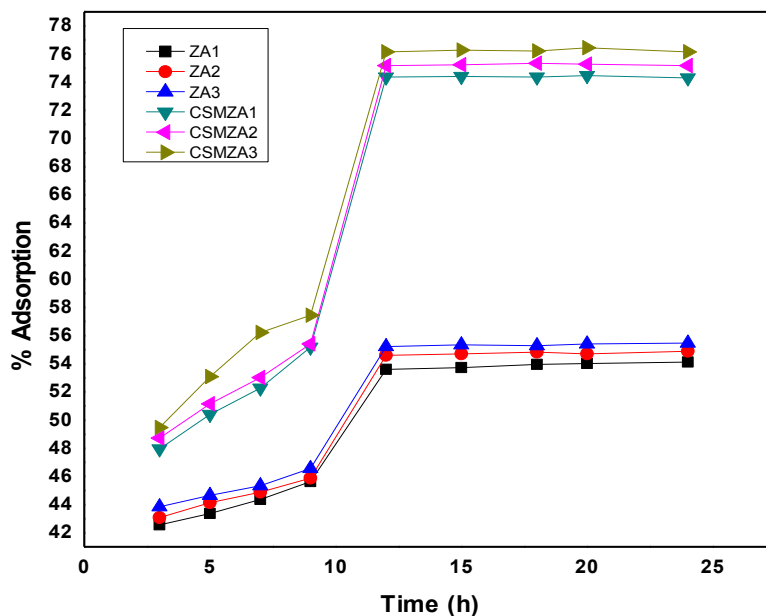


Fig. 13: Effect of time on sorption of methoxychlor onto unmodified and modified zeolite

CONCLUSIONS

The results of the batch experiment showed that surface modified zeolite can be served as a unique means for the removal of methoxychlor from aqueous solution. The high adsorption value indicates that these materials possess good adsorption potential for the removal of methoxychlor from aqueous solution. The silicates after surfactant treatment with CTAB can be utilized as an efficient adsorbent for these agrochemicals, and the extent of adsorption increases with increasing surfactant loadings. The aluminosilicate materials show highest adsorption capacity after modification with the surfactant.

ACKNOWLEDGEMENTS

I am obliged to my guide for sustaining and guiding me to put together this work potential and Central Instrumentation Laboratory (CIF), Jiwaji University, Gwalior, M.P. for giving required instrument support (FT-IR, XRD and UV-Vis spectrophotometer). I am also grateful to IISC, Bangalore for providing SEM- EDS studies.

REFERENCES

- [1] S. Akbar, S. Khatoun, R. Shehnaz, T. Hussain, *Science International (Lahore)*, 1999, 11 (1), 73–78.
- [2] W.A. Khanday, S.K. Singh, J. Bhaudoriya, S.A. Majid, S.S. Tomar, R. Tomar, *Colloid J.*, 2012, 74 (5), 573–58.
- [3] D. S. Papaioannou, S. C. Kyriakis, A. Papasteriadis, N. Roumbies, A. Yannakopoulos, and C. Alexopoulos, *Res. Vet. Sci.*, 2002, 72, 51-59.
- [4] B. Koubaissy, G. Joly, P. Magnoux, *Ind. Eng. Chem.*, 2008, 47, 9558–9565.
- [5] L. Damjanovic, R. Vesna, R. Vladislav, S. Dusan, A. Aline, *J. Hazard. Mater.*, 2010, 184, 477–484.
- [6] T. Saitoh, M. Yamaguchi, M. Hiraide, *Water Res.*, 2011, 45, 1879–1889.
- [7] E.Y. Bryleva, N.A. Vodolazkaya, N.O. Mchedlov-Petrossyan, L.V. Samokhina, N.A. Matveevskaya, *Funct Mater.*, 2006, 13, 662–668.
- [8] A. Moral, M.D. Sicilia, S. Rubio, D. Pérez-Bendito, *Anal Chim Acta.*, 2008, 608, 61–72.
- [9] N. Luque, S. Rubio, *J Chromatogr A.*, 2012, 1248, 74–83.
- [10] X. Zhao, Y. Cai, F. Wu, Y. Pan, H. Liao, B. Xu, *Microchem J.*, 2011, 98, 207–214.
- [11] Q. Liu, J. Shi, T. Wang, F. Guo, L. Liu, G. Jiang, *J Chromatogr A.*, 2012, 1257, 1–8.
- [12] S. Stipic evic, L. Sekovanic, V. Drevenkar, *Appl Clay Sci.*, 2014, 88, 56–62.
- [13] J. Xie, W. Meng, D. Wu, Z. Zhang, H. Kong, *J Hazard Mater.*, 2012, 231–232, 57–63.
- [14] A. Shahbazi, R.G. Olmos, F.D. Kopinke, P. Zarabadi-Poor, A. Georgi, *Sep Purif Technol.*, 2014, 127, 1–9.
- [15] H.K. Karapamagioto, D.A. Sabatini, R.S. Bowman, *Water Res.*, 2005, 39, 699–709.
- [16] Z. Li, T. Burt, R.S. Bowman, *Sci Technol.*, 2000, 34, 3756–3760.
- [17] C. Li, Y. Dong, D. Wu, L. Peng, H. Kong, *Appl Clay Sci.*, 2011, 25, 353–357.
- [18] N. Patdhanagul, T. Srithanratana, K. Rangsiwatananon, S. Hengrasamee, *Microporous Mesoporous Mater.*, 2010, 131, 97–102.
- [19] S. A. Boyd, W. F. Jaynes and B. S. Ross, Immobilization of organic contaminants by organo-clays: application to soil restoration and hazardous waste containment, in *Organic substances and sediments in water*, ed. R. S. Baker, Lewis Publication, Chelsea, MI, USA, 1991, pp. 181–200.
- [20] S. Sheng, G. Xu and S. A. Boyd, *Adv. Agron.*, 1997, 59, 25–62.

- [21] Li, Z. and Bowman, R. S. Counterion *Environ. Sci. Technol.*, 1997, 31, 2407-2412.
- [22] N. P. Agnkihotri, Pesticide: Safety Evaluation and Monitoring, All India Co-ordinated Project (AICRP) on Pesticide Residues; Indian Agricultural Research Institute: New Delhi, India, 1999.
- [23] F. J. Beltra'n, J. F. Garcia-Araya, B. Acedo, *Water Res.*, 1994, 28, 2153–2164.
- [24] A. Topalov, B. Abramovic, D. Molnar-Gabor, J. Csanadi, O. Arcson, *J. Photochem. Photobiol. A: Chem.*, 2001, 140, 249–253.
- [25] C. Zwiener, L. Weil, R. Niessner, *Int. J. Anal. Chem.*, 1995, 58, 247–264.
- [26] J. B. Weber, H. D. Coble, *J. Agric. Food Chem.*, 1968, 16, 475–478.
- [27] M. A. El-bid, O. A. Aly, *Water Res.*, 1977, 11, 611–616.
- [28] V. K. Gupta, I. Ali, *Adsorbents for water treatment: Low cost alternatives to carbon*, *Encyclopedia of Surface and Colloid Science*; Hubbard, A., Ed.; Marcel Dekker: New York, 2002, 1, 136–166.
- [29] H. Jian-Ying, A. Takako, O. Yutaka, M. Takeshi, M. Yasumoto, *Water Res.*, 1998, 32, 2593–2600.
- [30] V. K. Gupta, I. Ali, *Water Res.*, 2001, 35, 33–40.
- [31] V. K. Gupta, I. Ali, S. suhas, V. K. Saini, *J. Colloid. Interface Sci.*, 2006, 299, 556–563.
- [32] V. F. Domingues, G. Priolo, A. C. Alves, M. F. Cabral, C. Delerue- Matos, *J. Environ. Sci. Health, Part B* 2007, 42, 649–654.
- [33] J. Boucher, L. Steiner, I. W. Marison, *Water Res.*, 2007, 41, 3209–3216.
- [34] M. Akhtar, S. M. Hasany, M. I. Bhanger, S. Iqbal, *Chemosphere*, 2007, 66, 1829–1838.