

REMOVAL OF VANADATE FROM INDUSTRIAL WASTEWATER USING SURFACE MODIFIED OF ANALOUGES OF ZEOLITE

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Abstract-Vanadium release from speed-steel and in electroplating industries generally. These industries produce huge amounts of vanadium in wastewater that are harmful to the environment and require treatment to minimize the damaging effects on environment life. It is therefore imperative that advanced wastewater treatment techniques, such as adsorption, which are economically and environmentally essential in the removal of this hazardous contaminant from industrial wastewater, be studied. As such, batch and column adsorption modes were investigated. In the present work surfactant modified ZEOLITE ALPHA, ZEOLITE LINDE TYPE A AND MORDENITE as a low cost adsorbent was used to remove vanadium from industrial wastewater. The effects of sorbent dosage, adsorption on removal efficiency were investigated. Up to 90%-98% removal efficiency was obtained when the 0.25 gm of LTA was used having 25 ml of vanadate solution. The synthesized zeolite was characterized using FTIR, XRD, SEM/EDS and PSA. The outcome of this study reveals that sorbent mass, concentration, kinetics have significant effect on Linde Type A zeolite performance.

Keywords: Zeolite ,Vanadium removal; Adsorption; LTA

Introduction

Over the last few years the problem of pollution from heavy metals has caused increasing concern ,this apply to both industrilized zones and highly technological populated areas, even though in different ways. Therefore the problem of pollution from heavy metals involves the whole popullation and regards all three receiving compartments namely air, water, soil. The presence of heavy metals ions in water bodies is becoming a serious threat to public health and the environment. Of these heavy metals, vanadium has recently received more attention because of its adverse effect on human health and the

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environment. At high concentration vanadium is an environmentally harmful substance and causes diverse toxic effects on humans such as anaemia, cough, emaciation, and irritation of mucous

membrane, gastrointestinal disturbances, and bronchopneumonia. [1,2]

The principal metal emission sources come from the industries like petrochemical, Extractive, Metallurgical, Mechanical, Chemical and Ceramic. It has been estimated that around 65 000 tonnes of vanadium annually enter the environment from natural sources (crustal weathering and volcanic emissions) and around 200 000 tonnes as a result of man's activities. The major anthropogenic point sources of atmospheric emission are metallurgical works (30 kg per tonne of vanadium produced), followed by the burning of crude or residual oil and coal (0.2-2 kg per 1000 tonnes and 30- 300 kg per 10⁶ litres) [3,4]. Vanadium is an ubiquitous metal. The average concentration of vanadium in the earth's crust is 150 µg/g [5] concentrations in soil vary in the range 3-310 µg/g [6] and may reach high values (up to 400 µg/g) in areas polluted by fly ash [7]. The concentration of vanadium in water is largely dependent on geographical location and ranges from 0.2 to more than 100 µg/litre in freshwater [5], and from 0.2 to 29 µg/liter in seawater [6]. Long-term

exposure causes vanadium to accumulate in the bone, from which it is slowly released into the blood. Vanadium can be detected in urine, whole blood, and serum. Urine levels provide information about recent exposures and whole blood and serum levels represent long-term exposure. [8] Environmental chemistry of vanadium is based on the distribution of its different oxidation states in an environment [9]. Watering is a significant way in which vanadium is redistributed around the environment due to the fact that vanadates are mostly soluble in water and it is abundant in most soils, in different amounts, which can be taken up by plants at levels that show its bioavailability. It can cause breathing disorders and inhibition of certain enzymes in animals [10]. Removal of vanadium from industrial wastewater has been done conventionally with systems comprising physical, chemical, and biological methods. The use of these techniques is restricted owing to their cost or limited performance. For instance, precipitation methods are specifically dependable but large settling tanks are required for the large capacity of alkaline sludge precipitation and a subsequent treatment is needed. On the other hand, ion-exchange methods can allow the recovery of metallic ions sufficiently, but it is expensive and complicated [11]. Among these technologies, adsorption has been found as one of the most effective and efficient methods in water pollution control owing to its simplicity and cost effectiveness [12]. Due to the high treatment costs involved and the limited performance of others, they have not been optimally utilized mostly in developing countries. There is therefore the need to develop alternative adsorption media which are readily available, highly effective and cost-effective. Adsorption materials are defined as low-cost if they are abundant in nature, are by-products or waste materials from other industries. In this regard, naturally existing materials, for example zeolites, are considered as low-cost media and have been widely applied in pollution control. Zeolites have been widely used to remove heavy metals from polluted water because they have a relatively high cation exchange capacity, highly developed porosity and internal surface area [13]. Zeolites are characterized

by high specific surface area and high cation exchange capacity through Zeolites shows superior sorption and hydraulic properties and have found use as molecular sieve and sorbents for waste water treatment. zeolite molecular structure is a framework containing chain of five membered rings of linked silicate and aluminate tetrahedral. Its high ratio of silicon to aluminium atoms makes it more resistant to attack by acids than most other zeolite. The most naturally occurring materials have negative charges on their external surfaces, which will prevent sorption and retention of anions; efforts were made to convert the surface charges from negative to positive by surface modification to increase their anion retention [14]. In these work analogues of zeolite mordenite, zeolite alpha, lindeTypeA was successfully synthesized from sodium aluminates, sodium hydroxide, and silicate solution. All zeolites were modified by using hexadecyltrimethyl ammonium (HDTMA). Modified mordenite, alpha and linde type A zeolite was investigated for their ability to adsorb vanadate.

Experimental Section

Chemicals used in various synthesis

Sodium Aluminate, Silica gel, Sodium hydroxide, Tetra methyl Ammonium Hydroxide (TeOH) Sigma. hexadecyltrimethyl ammonium bromide HDTMA-Br, Ammonium meta vanadate, naphthalene -1,5 diamine, nitric acid, buffer of pH 4-5.5

Materials and method:

The Analogous of Mordenite and Zeolite Alfa were prepared by hydrothermal method according to IZA synthesis commission of zeolite. The method comprises two stages-in first stage a gel containing, Alumina and the templating species is prepared in a 150 ml borosil beaker by dissolving finely divided silica in water or alkaline hydroxide solution. To obtain the fine particle and complete mixing of gel, the gel solution is magnetically stirred for few hours on magnetic stirrer.

In the second stage, the resultant mixture is immediately placed in a 100 ml Teflon lined stainless steel pressure vessel (PARR make) kept in preheated oven at autogeneous pressure and static

condition. After completion of synthesis period the product was filtered, washed repeatedly with distilled water, dried at room temperature in some case at 373K and kept in powder form for further use. Moreover, the template containing synthesized material is calcinated by heating then at 823 K for few hours to make these materials free from template.

1.Synthesis of Zeolite:

The synthesis procedure for different zeolites is described below:

Synthesis of Analogue of Mordenite zeolite:

(6Na₂O: Al₂O₃:30SiO₂: 780H₂O)

Source material; Distilled water, Sodium Hydroxide, Sodium Aluminates, Silica

Preparation method:

Mordenite with a Si/Al ratio of 9 was hydrothermally synthesized according to IZA synthesis. Sodium Aluminates as the aluminum source was mixed with an aqueous solution of Sodium Hydroxide, then Silica (Otto chemika) was added to the mixture and the mixture was homogenized by stirring. Finally, the gel was transferred to a Teflon line, autoclaved and crystallization was carried 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.

2.Synthesis of Analogue of Zeolite Linde type A

Na₁₂ [(AlO₂)(SiO₂)₁₂]:27H₂O

Source Material: Distilled water, Sodium Hydroxide, Sodium Aluminate, Sodium Metasilicate

Preparation method: In a Beaker calculated amount of sodium hydroxide was added to water until sodium Hydroxide dissolved completely. This solution divided in two parts ,to one half of this solution calculated amount of sodium Aluminate mixed gently in a capped 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 was formed. This solution was stirred until homogenized. Finally the blend was transferred to polypropylene bottle and

crystallization was carried out on 372K for half hours. The product was recovered by filtration and washed thoroughly with deionized water until filtrate's pH become less then 9. Product was dried overnight on filter paper at 353K-383K.

3. Synthesis of Analogue of Zeolite Alpha

1.07 Na₂O: 2.37 (TMA)₂ O:
Al₂O₃:10SiO₂:120H₂O

Source material: Distilled water, Sodium Aluminates, Tetra methyl ammonium Hydroxide solution, silica

Preparation method:

In a beaker calculated amount of sodium aluminate was added to water and stirred until sodium aluminate 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 polypropylene bottle and crystallization was carried out a 363K without agitation for 24 hours after incubation at room temperature for 48 hours. The product was then recovered by filtration washed thoroughly with deionized water and dried at 383K.

Surface Modification of Zeolite

Synthesized raw zeolite was treated with HDTMA–Br (Hexadecyltrimethylammonium), surfactant to make it capable to exchange anion. 5 gms of zeolite was mixed with 2.5 gms of HBTMA and 180 ml water was added to it. Each mixture was equilibrated on a water bath shaker at 150 RPM and 250°C for 24 hours with intermittent shaking. Surfactant HDTMA formed double layer by exchange of its cation with the cation of zeolite thereafter, attraction of its hydrophobic end. After 24 hours zeolite was filtered and washed with deionized water, the surfactant modified zeolite was allowed to dry naturally.

Sorption analysis

All chemical used were of analytical grade and double distilled water was used for studies. When solution of vanadate is treated with naphthalene 1, 5

diamine at pH 4-5.5 a red violet complex obtains. The complex is stable for more than 6 days and shows maximum absorbance at 578 nm. The data obtained from batch studies was used to calculate the percentage adsorption and equilibrium metal adsorption capacity. Adsorption studies of was carried out under identical conditions at pH-4-5. Sorption studies were carried out by batch equilibrium technique. 25 ml of vanadate solution were kept with SMZ (surfactant modified zeolite) 24 hours to equilibrium. After equilibrium solution is filtered and filtrate was used for analysis. All concentration was determined using.

Result and Discussion

Characterization

1. XRD -During powder diffraction the samples are compressed on a sample holder.

The sample and the rotation of the sample holder during exposure guarantee that all crystallite orientations are present. Powder X-ray diffraction pattern of synthesized and modified materials was recorded at room temperature on X-Ray Diffractometer Philips Holland/X Pert MPD. Samples were scanned using Cu-K α radiation of wavelength 1.54056 Å and the diffract grams were recorded in the range $2\theta = 0^\circ - 65^\circ$ at the scanning speed of 1 step / second and Powdered XRD were obtained from SICART Gujarat. Different features of powdered diffraction pattern can be exploited in the characterization of materials. Powdered diffraction data is most commonly used a finger print in identification of material. Powder X Ray diffraction pattern of synthesized zeolite are shown in fig 1.

Fig 1a

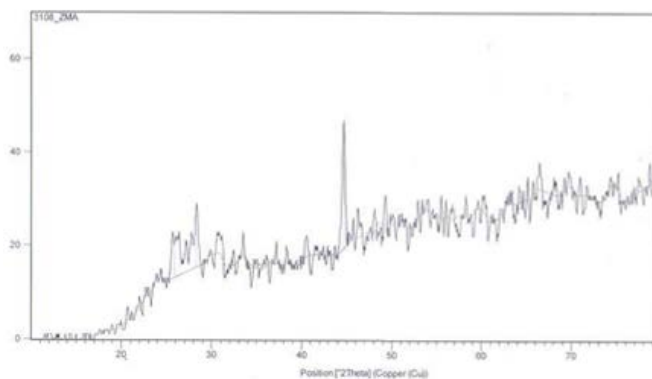


Fig 1b

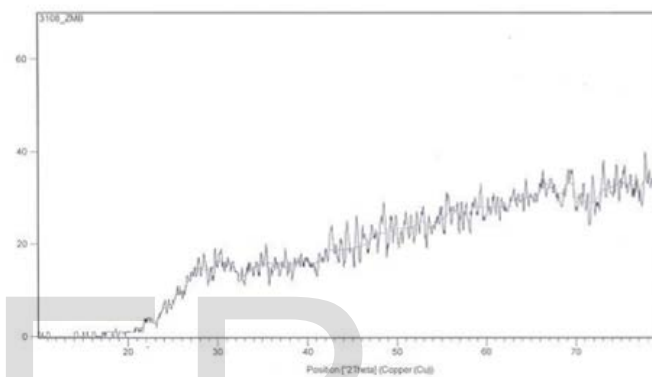


Fig 1c

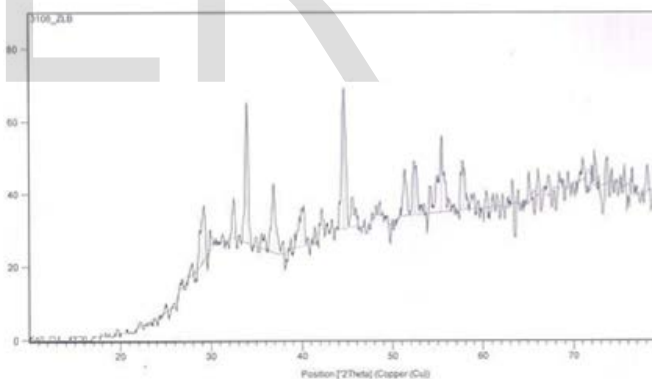


Fig 1d

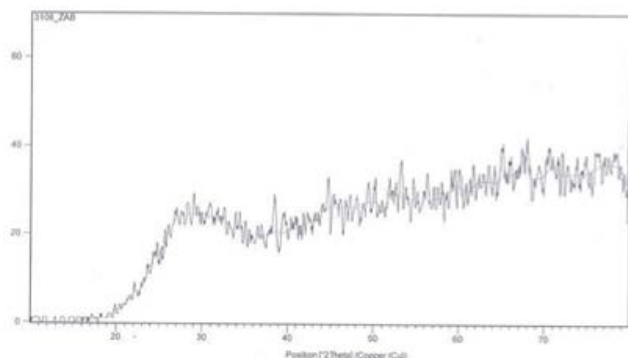
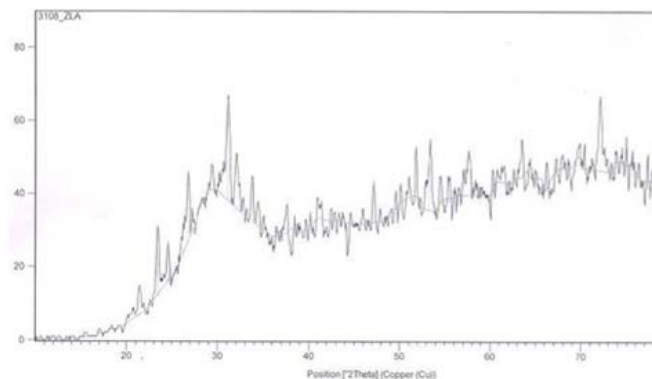


Fig 1e

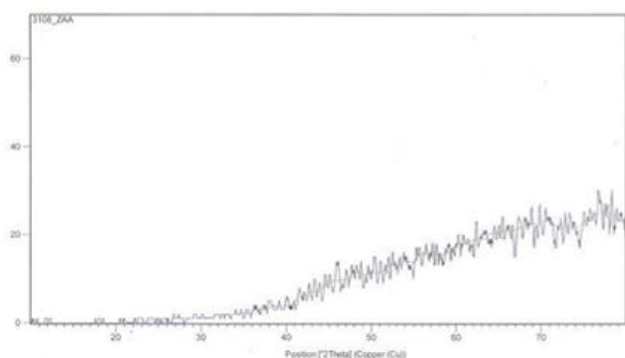


Fig 1f

2.FTIR- The FTIR spectra of the compound were recorded on a KBr 400-4000 cm^{-1} using Perkin Elmer spectrophotometer. Zeolite exhibits a typical infra red spectroscopy pattern. The spectra can be grouped in two classes. The first is due to internal vibration of $\text{TO}_{4/2}$. Tetrahedron. It is found in a range 950 -1250 cm^{-1} and 420-950 cm^{-1} and is assigned to banding modes which are sensitive to Si/Al composition of the frame work. The second type of vibration is sensitive to the overall structure and the joining of individual tetrahedral in secondary structural unit as well as existence in the large pore openings. The hydroxyl band (OH) stretch near 3550 cm^{-1} in the spectra indicates the bimodal absorbance. The band at 3346-50 cm^{-1} is attributed to loosely bound water molecules attached to zeolite frame work and shows strong characteristic structure sensitive bands due to water, banding vibration at 1648 cm^{-1} . Thereby sorption and desorption (Hydration and dehydration) may be easily monitored by IR observing the change occurred in these vibration bands.

The bands at 550 -580 cm^{-1} can be associated with the structural order such as ring of the tetrahedral and/ octahedral. Especially, this assigned peak of stretching frequencies of 6 coordinate's aluminum. 4 member ring deformation mode of the network is observed around 730 cm^{-1} along with the other modes. The peaks below 550 cm^{-1} are generally due to O-T-O banding and rotation mode.

The peaks between 700-900 cm^{-1} and 1000-1150 cm^{-1} are assigned to symmetric and anti symmetric TOT stretching vibration. The IR peaks observed for pure

zeolite and modified zeolite are presented as transmittances spectra's and are given in fig 2a, 3a &4a.. The major peaks appeared in unmodified zeolite were compared with that of modified zeolite and found almost similar with each other indicating the structure stability of the sample. Modified zeolite in contrast to unmodified zeolite has two intense bands around 2850 cm^{-1} and 3500 cm^{-1} which are assigned to asymmetric and symmetric stretching vibration of C- CHO of the alkyl chain, respectively. The intensities of these peaks increase with increasing surfactant loading. The structure sensitive bands are not affected by the surfactant treatment. The strong band appearing at 1250-1400 cm^{-1} due to the banding mode of water is weaker for modified zeolites than for unmodified zeolites. The weakening of this band can be ascribed to an intensification of the hydrophobic characteristic of modified zeolite sample which is in agreement with the result for the absorption of water vapor. It was found that there was a strong peak between 900-1700 cm^{-1} which was absent in unmodified analogue of zeolite that is attributed to N- Br bond in modified zeolite by Hexadecyltrimethylammonium (HDTMA) given in fig.

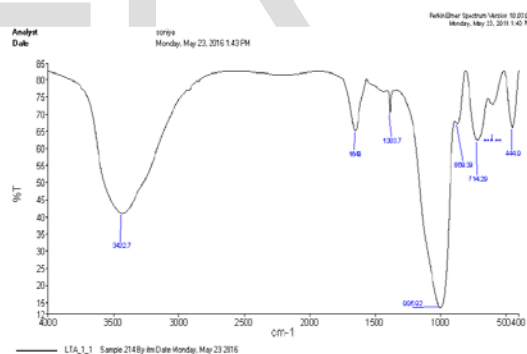


Fig 2a: Unmodified Linde type A

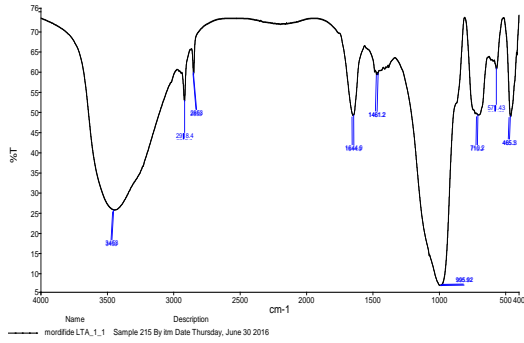


Fig 2b: Modified Linde type A

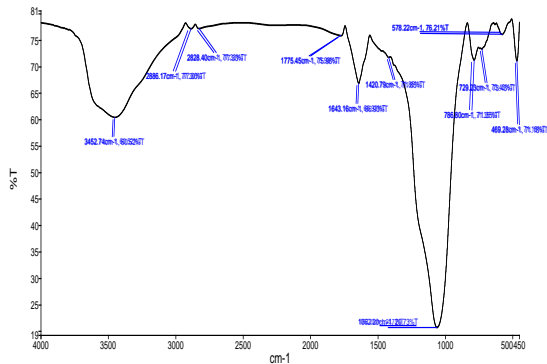


Fig2c: Unmodified Mordenite

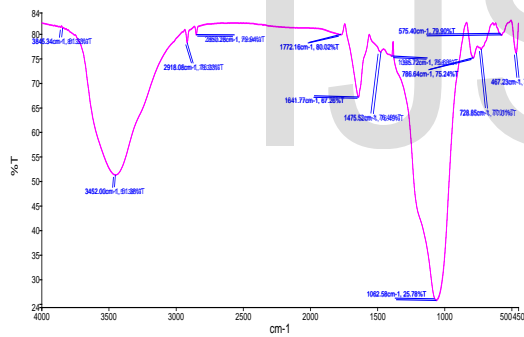


Fig2d: Modified Mordenite

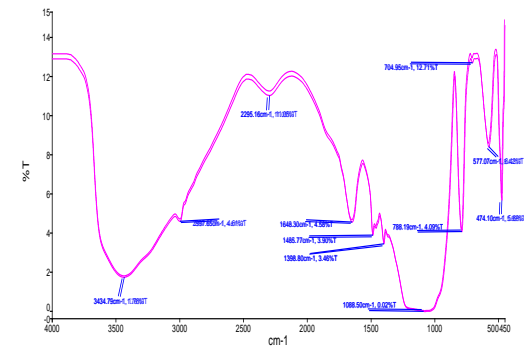


Fig 2e: Unmodified Alpha

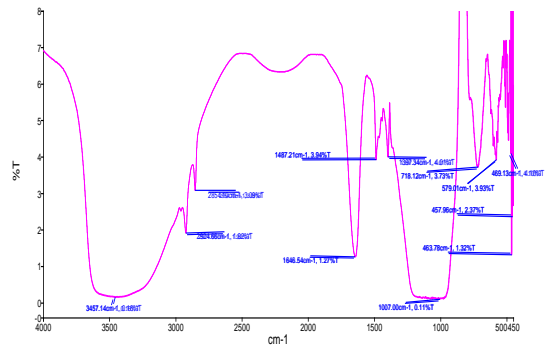


Fig.2f: Modified Alpha

Particle size analysis-The size of the particles is very important for the sorption . The exchange surface has to be the largest to improve the reaction. But a too small size does not make it possible to catch the molecules which have to be treated, and then not to start the sorption (figure 3). Smaller are the particles, bigger is the reaction surface (specific surface).

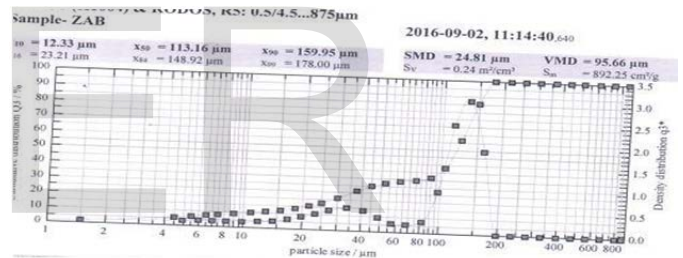


Fig3a

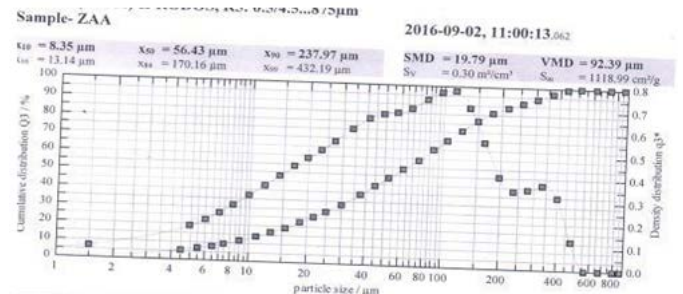


Fig3b

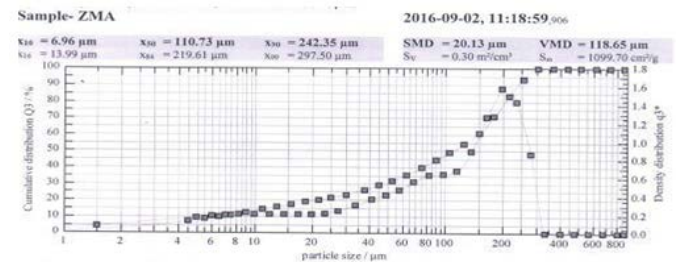


Fig3c

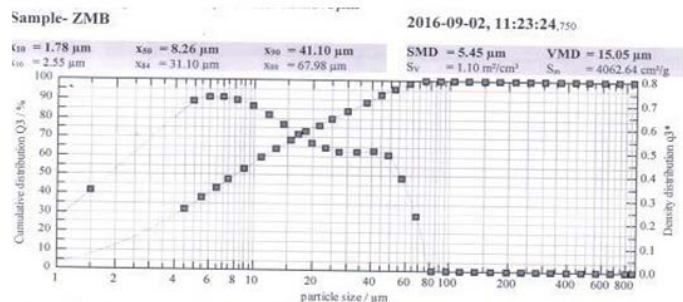


Fig3d

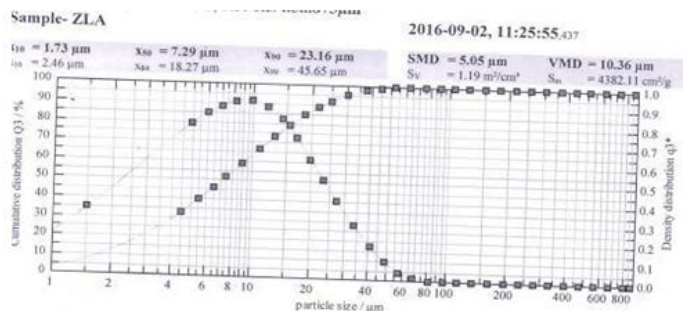


Fig4e

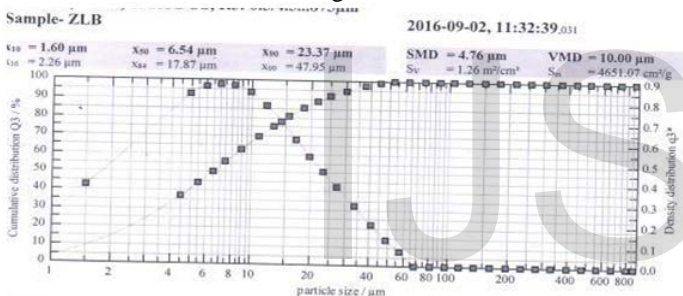


Fig3f

SEM analysis

The morphology and crystal size of the synthetic material was examined by ESEM XL 30 scanning electron microscopy (SEM). Samples were analyzed by using Microscope and the imaged obtained shows the morphology of the materials. Powders of the sample and coated surface were characterized to obtain information about the size and morphology using scanning electron microscope, which provides topological and elemental information about the sample. The SEM images (Fig. 4) of the synthetic modified zeolite show various morphologies of the mesostructured materials depending on the crystallization conditions. Photomicrographs of the synthetic modified zeolite exhibited well defined narrow shape with excellent crystal edges.

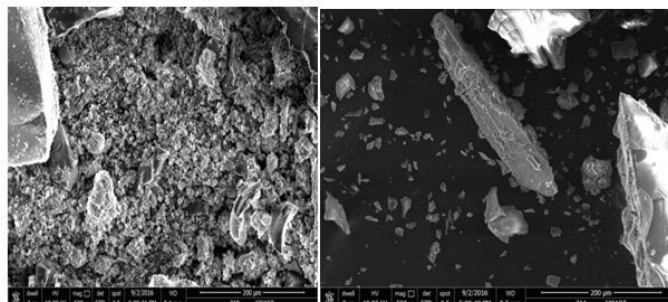


Fig 4a: Alpha zeolite before modification

Alpha zeolite after modification

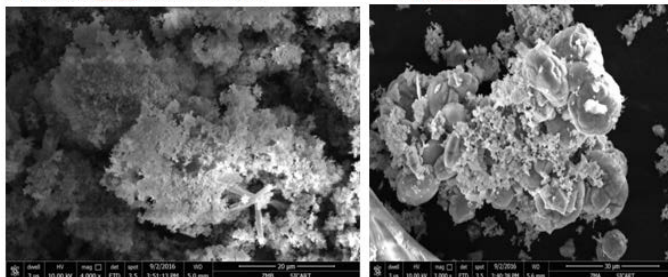


Fig4b: Mordenite zeolite before modification

Mordenite zeolite after modification

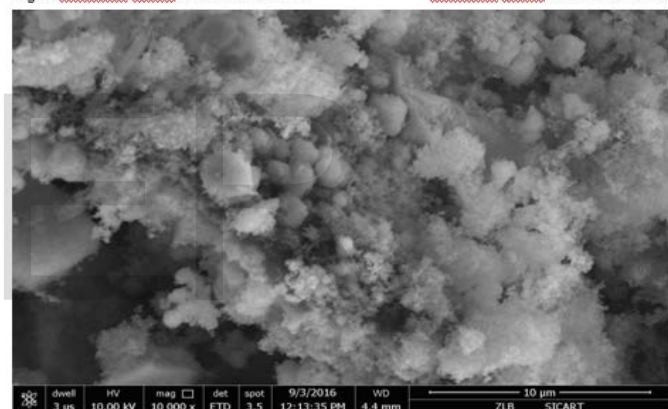


Fig4c: Linde Type A zeolite before modification

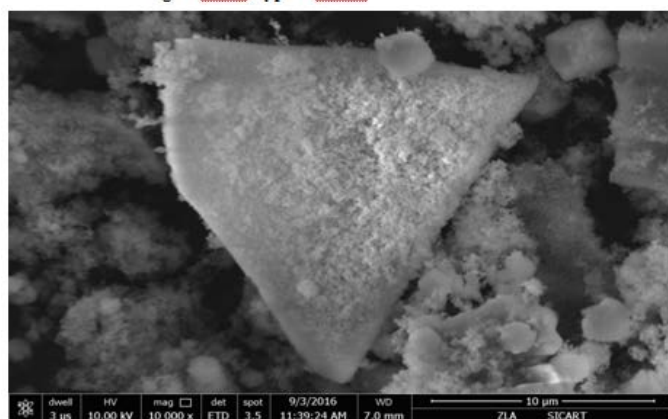


Fig4d: Linde Type zeolite after modification

Sorption studies Results on Analogue of surfactant Modified Linde Type A, Mordenite, Alpha Zeolite

The experimental data for sorption of vanadate on surfactant modified zeolite suggests the following result.

1. Effect of contact time on sorption

In order to accomplish the kinetics study the effect of contact time experiments on vanadate sorption by surfactant modified Linde Type A, Mordenite, Alpha Zeolite- were carried out with 50µg/ml concentration., ranging from 1 hour to 24 hours. The plots of vanadate sorption percentage against contact time are shown in fig. which indicate that vanadate sorption increases with time and attain equilibrium in hours. This trend emphasizes that the time of sorption have an important effect on the sorption efficiency which increases significantly with increasing contact time with vanadate solution. This is the consequence the ability of surfactant modified Linde Type A, Mordenite, Alpha Zeolite to sorb vanadate is due to the anion exchange at the positive sites brought about by the reversed charged resulting from the HDTMA DOUBLE layer on to zeolite surface. The fig suggest that surfactant modified Linde Type A is more efficient in removing V (V) species from aqueous solution than the surfactant modified sorbed vanadate upto 98% .

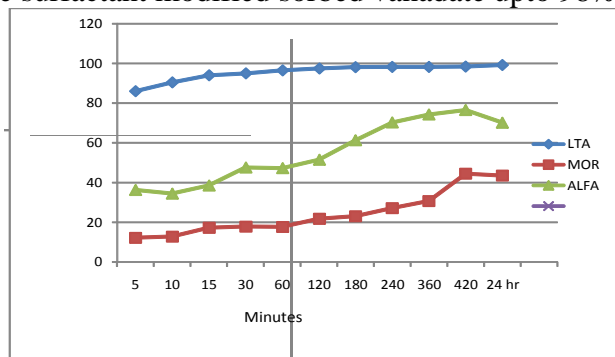


Fig5

2. Effect of sorbent dose on sorption

To determine the effect of sorbent dosage on sorption, the sorbent dose were varied from 0.1 gm to 0.5 gm while $V_2O_5^-$ concentration was 50 µ/ml. As expected the percentage of vanadate sorption increased with increasing surfactant modified LTA,

MOR, ALF. As seen from fig

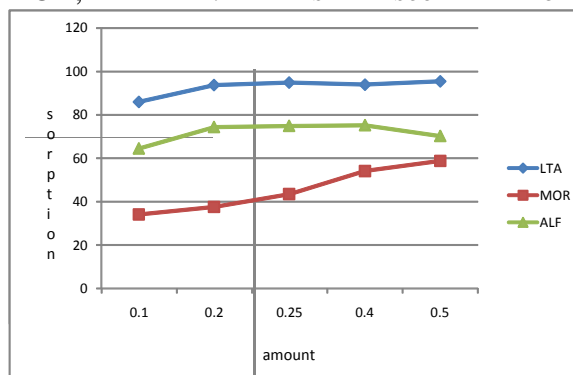


Fig6

The increase in vanadate sorption with sorbent dose can be attributed to increased surface area and the sorption sites. The data shows that with increase in weight of exchanger from 0.1 to 0.5 gm sorption percentage increases. Zeolite Linde Type A shows maximum percentage for vanadate solution.

3. Effect of metal concentration on sorption

Variontaion in ion concentration as been analysed as an important factor in sorption. By changing the concentration from 50µg/ml to 5µg/ml, it was found that sorption percentage decrease. This is due to the increasing number of metal ion that compete for a infinite number of binding sites on the sorbent surface.

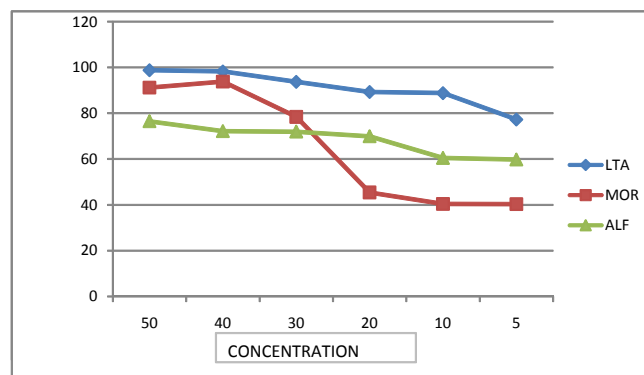


Fig7

Conclusion

The present work deals with the synthesis their surface modification cherecterization of analouge of zeolites, mordenite, zeolite alpha, Linde Type A

zeolite, and there use as sorbent for removal vanadate.

The reaction parameters such as reaction time, temperature, concentration amount of various modified zeolite were optimized. It was observed that after modification the pore size of zeolite becomes larger and facilitate the reactant to get entered into it and promoted the adsorption of vanadium (V_2O_5)

It was observed the after modification Surfactant HDTMA formed double layer by exchange of its cation with the cation of zeolite. It was also observed that after modification the removal of vanadate from 25 ml. of solution having 0.25 gm of SMZ gives the competitive capacity achieved through functionalization this material can be considered as a potential candidate for treatment of vanadium from contaminated wastewater.

Result shows that 0.25 gm of modified zeolite is sufficient to remove vanadate from 25 ml. of 50 μ g/ml solution. Kinetics study shows that process aqre equilibria in 5-7 hours, studies also reveal that modified LTA shows maximum sorption efficiency up to 98% for the ion under study.

Acknowledgement

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