REMOVAL OF ARSENATE BY SURFACTANT MODIFIED LINDE TYPE A ZEOLITE.

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Abstract

In the present work, the potential use of modified linde type a zeolite for removal of arsenic (V) has been examined. The predominant oxidation states of arsenic are As (III) and As (V). A simple & effective method has been proposed to reduce the arsenic from environmental sample. Linde TypeA zeolite was synthesized hydrothermally & characterized by X-ray and FTIR, SEM, PSA. Synthesized zeolite was modified with hexadecyl trimethyl ammonium (HDTMA) to make it capable to exchange Anions. Molar absorptivity of Arsenic was determined at various concentrations by adding 0.25 mg of surfactant modified zeolite using Batch process. Concentration of the solution was determined by molybdenum method having an absorption maximum at 840 nm. All studies were carried out at room temperature result obtained shows that Arsenate ion absorbed effectively up to 70% by surfactant modified zeolite (SMM). Which is comparable or sometimes better than the previous proposed material. Studies were also carried out by using different amount of surfactant modified Zeolites at conc. 50 µg / ml. The optimum condition reached when 0.25 gm of modified zeolite was used. From the study of time dependence of sorption by synthesized modified zeolite it was found that sorption 72 % increase up to about 6-7 hr and then it remains more or less constant.

Introduction:

The presence of arsenic in water is due to the dissolution of minerals from subterranean strata or from an anthropogenic origin such as the leaching of manmade arsenic compounds from smelting of metal ores, agricultural pesticides, desiccants and wood preservatives. The presence of arsenic in water supplies has been linked to arsenical dermatitis, skin cancer [1], neurological effects, enlargement of liver, heart disease and internal cancers [2].

Arsenic contamination and its consequence is an emerging issue for public health with respect to social aspects in India and other country. Scientific evidence of arsenic contamination and socioeconomic condition of a society has direct linkage with health hazards and behavioral attitude. Consequently, most of the countries in Asia have been reported to suffer from this problem most especially in Bangladesh (3-9).

It was estimated that 97% people living in rural areas used As-contaminated water for drinking and irrigation purposes (10)

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The presence of toxic metals in groundwater sources is a serious problem in water and wastewater management. Arsenic is a ubiquitous element widely distributed in the earth’s crust. It is released in drinking water supply by either natural sources or industrial processes [11]. Arsenic can cause serious health issues such as cancers of the skin, lungs and bladder. Epidemiological evidence indicates that arsenic concentration in drinking water exceeding 50 μg/L is detrimental to public health. Toxicity of arsenic varies greatly according to its oxidation state. Naturally occurring inorganic arsenic generally exists in two oxidation states, arsenite As(III) and arsenate As(V). Arsenic commonly present in water is a pH dependent species of arsenic (H₃AsO₄) and arsenate (H₃AsO₃) acid systems. In natural water and drinking water, it is mostly found as As(III) and As(V) [12,13]. As(III) is sixty times more toxic than As(V) [14,15].

The maximum permissible concentration of arsenic, according to World Health Organization (WHO), United States Environmental Protection Agency (US EPA), in drinking water is 10 μg/L [16]. However, arsenic concentrations, about hundred times more than the permissible limit. Several treatment methods have been investigated for arsenic contaminated drinking water and the main mechanism used for removal of arsenic from ground water are solvent extraction, chemical precipitation etc [17, 18]. Other techniques include reverse osmosis, adsorption, ion exchange methods and permeable reactive barriers[19, 20]. All methods and techniques are associated with disadvantages such as efficiency of metal removal, high cost of reagents and energy requirement [15-20]. Adsorption has emerged as an alternate to these traditional methods due to its simplicity and safety, ease of operation, maintenance and handling, sludge free operation, potential for regeneration and possibility of the use of low cost adsorbent. So far, various adsorbents for arsenic removal have been developed that include materials such as activated carbon, activated alumina, activated carbon impregnated with ferric hydroxide and tartaric acid, metal-loaded coral lime stone [21-24].

In most studied areas it was seen that high-arsenic groundwater was not related to areas of high arsenic concentration in the source rock. Two key factors were identified: first, there should be very specific biogeochemical triggers to mobilize arsenic from the solid/sorbed phase to groundwater, and second, the mobilized arsenic should have sufficient time to accumulate and not be flushed away, that is, it should be retained in the aquifer (25). In other words, arsenic released from the source should be quick, relative to the rate of groundwater flushing. There are number of processes for mobilization of arsenic in groundwater namely, (i) mineral dissolution, (ii) desorption of arsenic under alkaline and oxidizing conditions, (iii) desorption and dissolution of arsenic under reducing conditions, (iv) reduction of oxide mineral surface area, and (v) reduction in bond strength between arsenic and host mineral surface (25).

During long-term exposure to high levels of inorganic arsenic (e.g. through drinking-water), the first changes are usually seen in the skin; pigmentation changes and then skin lesions and hard patches on the palms of the hands and soles of the feet. Other effects of long-term exposure to high inorganic arsenic levels include peripheral neuropathy, gastrointestinal symptoms, conjunctivitis, diabetes, renal system effects, enlarged liver, and bone marrow depression, destruction of erythrocytes, high blood pressure and

In this work synthetic linde type A were successfully synthesized from sodium aluminates, sodium hydroxide, silicate solution. zeolite molecular structure is a frame work containing chain of five membered rings of linked silicate and aluminate trahedra. Its high ratio of silicon to aluminium atoms makes it more resistant to attack by acids than most other zeolite. zeolite were modified by using hexadecyltrimethyl ammonium (HDTA). Modified linde type A zeolite was investigated for their ability to absorb arsenate, and cardiovascular disease.
Experimental Section:

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.

Synthesis of Analogue of Zeolite Linde type A:-

\[ \text{Na}_{12} \left[ (\text{AlO}_2)(\text{SiO}_2)_{12} \right]:27\text{H}_2\text{O} \]

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 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 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.

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 arsenate is treated with ammonium molbdate and hydrazinium sulphate solution a blue complex obtain sat 840 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. Sorption studies were carried out by batch equilibrium technique. 25 ml of arsenate 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-Kα radiation of wavelength 1.54056 Å and the diffract grams were recorded in the range 2θ = 0° – 65° 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.
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 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 the 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.
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).
Fig 3a

Fig 3b

Fig 3c

Fig 3d

Fig 3e
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.
Sorption studies Results on Analogue of surfactant Modified Linde Type A.
The experimental data for sorption of arsenate on surfactant modified zeolite suggests the following result.

**Effect of contact time on sorption:**
In order to accomplish the kinetics study the effect of contact time experiments on sorption sorption by surfactant modified Linde Type A, Zeolite were carried out with 50µg/ml concentration. ranging from 5min. to 24 hours. The plots of arsenate sorption percentage against contact time are shown in fig.5 which indicate that arsenate 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 arsenate solution. This is the consequence the ability of surfactant modified Linde Type A, 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 As(V) species from aqueous solution than the surfactant modified sorbed arsenate5upto 80% .

**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 arsenate concentration was 50 µ/ml. As expected the percentage of arsenate sorption increased with increasing surfactant modified LTA, in fig.6
The increase in arsenate 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 arsenate solution.

**Effect of metal concentration on sorption:**
Variation 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.

![Graph showing the effect of metal concentration on sorption](image)

**Conclusion:**
Exposure to arsenic may come from natural source, from industrial source, or from administered Acute poisoning. Chronic arsenical dermatosis arises from consuming arsenic contaminated drinking water for long time. Ingestion via food or water is the main pathway of arsenic into the organism. Humans are more sensitive to arsenic than animals. Weak and malnourished people can be easily affected by arsenic contaminated water or fume or dust or contact at the skin. Melanosis may disappear by using medicine but keratosis can not alter though further complication may be prevented. No medicine was found effective once complication developed.

Arsenic free water or environment or decrease in arsenic concentration level is only the solution of arsenic, since the proposed method was applied for the quantitative determination of arsenic, this method is simple, rapid and common metal ion such as Fe³⁺, Al³⁺, Pb²⁺, Na⁺, K⁺ do not interfere. The proposed methods are more sensitive than some reported method in the literature, so that Arsenate ion absorbed effectively up to 70 -80% by surfactant modified zeolite Linde Type A.

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**References:**