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Research Paper

Study of the Removal of Toxic Anions from Contaminated Water Utilizing Natural Kaolinite Clay of Assam

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***Abstract** - Groundwaters of many parts of Assam, a state of north-east India, are contaminated with high levels toxic arsenic, fluoride. The soil of the area also shows high levels of nitrite and nitrate. The presence of arsenic and fluoride in excessive limits in drinking water along with the attendant problems prevailing in many parts of Assam in the North Eastern India is well documented. Recently Dhemaji and Karimganj districts of Assam have been recorded as arsenic affected areas. Both the World Health organization (WHO) and the U.S. Environmental Protection Agency (USPEA) have classified arsenic as carcinogen. The present study observed the effectiveness of natural clay in the removal of these anions from contaminated water. For this purpose clay samples were collected from Longai of Karimganj district of Assam. This study observed the adsorption capacity of the clay minerals with respect to the parameters, adsorbent dosage, concentration, pH and contact time. SEM-EDX characterization shows the presence of kaolinite along with significant amount of iron and quartz in both the samples. XRD and FTIR analysis also reveals the presence of kaolin minerals. The efficacy of the local clay in removing contaminating anions is discussed in the article.*

Keywords: Natural kaolinite clay,Arsenic; Assam, Anion -Exchange capacity, Adsorption, etc.

Introduction

The use of pure waters for drinking and other purposes have been the dominant concern along with the concern of better environment. The development of new technology has grown up steadily but water purification in the community level almost remains same. Water purification process will be a major challenge throughout the world. Ground water is one of the major sources of water for domestic purposes in India. In our rural areas water is considered to be pure and unpolluted if it is odorless, free from turbidity and good from aesthetic point of view. But even if the water is clear, it may be polluted. Besides that, the surface water is contaminated by the effluents from industries, municipalities and other places. A recent survey reveals that, 90% of water available contains many pollutants which cause number of health problems[1,2].The contamination of hazardous anions like fluoride, nitrate, arsenite etc in general, in ground water is a wide spread phenomenon which causes many health problem. Many domestic water purification processes are available but not suitable for rural people because they are very costly and common people cannot use them in regular basis. So in the present study natural clay was taken as the adsorbent to see its efficacy in the removal of these anions from contaminated water. Hence an attempt has been made in the present work for the removal of the above mentioned anions from water. In Assam, recently Dhemaji and Karimganj districts have been recorded as arsenic affected areas [3]. For this purpose soil samples were collected from Longai region of Karimganj district of Assam, India situated in the southern part of Assam in north east India (within 92^{o}15'-92^{o}35'long, and 24^{o}15'-25^{o}55'lat.).

After the characterization it was found that the Longai clay is the pure kaolinite clay. Various parameters such as coagulant dose, pH, contact time and concentration were studied to establish optimum conditions.

Experimental

All glassware used in the present study was manufactured by Borosil India private Ltd (Bombay). 150ml capacity "Borosil" arsine generator apparatus were used in the experiment. The soap solution utilized for cleaning up the glass apparatus was Rankleen, (Ranbaxy Laboratories Ltd., Punjab, India). All chemicals were of analytical grade and purchased from E Merck, Germany and all the working solutions were prepared in freshly prepared double distilled water and the pH of the distilled water was around 6.9.

Instruments used for characterization of clay: SEM-EDX analysis was done through LEO 1430 vp electron microscope. XRD analysis was done through Philips PW-1710 diffractometer using 001 plane. Again for FTIR analysis Perkin-Elmer Model 1605 FTIR spectrophotometer was used and the KBr pellets were placed in the path of the infrared spectra and the adsorption was recorded in between 400-4500cm.

Procedure for determining the concentration of arsenic (III) in the resultant solution:

The concentration of arsenite in the samples were measured using UV-visible spectrophotometer (Model Shimadzu spectrophotometer UV-1700) utilizing silver diethyl dithio carbamate (SDDC).(E-Merck, Germany) [4].

Procedure for determining the concentration of nitrate in the resultant solution:

Phenol-disulphonic acid method: In this method 25 ml of the sample was taken in a porcelain basin and evaporated on a hot water bath.0.5 ml of Phenol-disulphonic acid was added to the residue to dissolve it and then 5ml of distilled water and 1.5 ml of KOH was added through stirring. One yellow color solution was formed and the absorbance was taken at 410nm on a spectrophotometer [5].

Procedure for determining the concentration of fluoride in the resultant solution:

The fluoride concentration in the eluent was determined spectrophotometrically using **Zirconium-alizarin method.** In this method 0.0175g of sodium alizarin mono sulphonate, 0.075g of zirconium oxychloride, 25ml of concentrated HCl and 8.25ml of concentrated H_2SO_4 solutions were mixed thoroughly and volume made up to 250ml with water. The reagent changed in colour from red to yellow in an hour. In this method fluoride reacts with Zr-Alizarin S lake to form ZrF_6^{2-} and the colour of the dye lake becomes progressively weak with the increase in the amount of F^- [5].

Results and Discussion

Characterization of the clay

The powder X-ray diffraction pattern of the clay sample is done through X-ray powder Diffraction, SEM-EDX and through FTIR Techniques. XRD analysis (Fig-1) was done through Philips PW-1710 diffractometer using 001 plane at 0 to 110^o using Fe-filtered Co-Kα radiation. The pattern obtained was compared with standard data set of the Joint Committee for powder Diffraction Standards (JCPDS), USA [6].

SEM-EDX analysis of the clay fraction (Fig-2) shows pseudo hexagonal arrangement of layers of kaolinite with broken edge. The chemical analysis of the clay sample indicates one titaniferrous mineral associated with the sample. The clay was found to be contained SiO_2, 45.86 ; Al_2O_3, 39.36; Fe_2O_3, 5.62; CaO,0.17; TiO 1.59; K_2O, 0.03; MgO, 0.41 and water content 7.29.After chemical analysis it is found that the clay contains high amount of Iron in its Fe^{3+} state.

For FTIR analysis (Fig-3) the clay fractions were ground in an agate mortar and then mixed with KBr. The small amount of the mixture was placed in the path of the infrared spectra and %Transmission was recorded in between 200-4000cm$^-$. The occurrence of a band at 790-920 cm$^-$ and at 1010 cm$^-$ suggests the presence of Kaolinite minerals. The IR-band near 441 cm$^-$ and a medium band near 914cm$^-$ are also significant band of Kaolinite. The IR-band near 3700cm$^-$ is the characteristic and a diagnostic IR band of kaolin minerals.This band is diagnostic even for very small amounts of kaolinite [7, 8, 9].

Adsorption study

After characterization it was confirmed that the clay sample contains kaolinite mineral ($Al_2Si_2O_5(OH)_4$). Since kaolinite only has negative hydroxyl sites at the edge of the mineral, the cation exchange capacity is low, (3-15 meq/100g) [10]. This makes the soil easy to acidify as its ability to hold on the basic cations is low. Therefore in the present study the clay sample is utilized to remove some of the toxic anions from the contaminated water. To study the removal efficiency of natural clay six standard solutions of arsenic (III), nitrate and fluoride having different concentration of 1,3,5,7,9 and 10ppm were prepared. The present study is concerned with the evaluation of the effect of the following parameters through batch experiments since previously through column experiment the same process was performed.

- Effect of adsorbent dosage
- Effect of contact time
- Effect of concentration.
- Effect of pH

Effect of adsorption dosage

To observe the effect of adsorbent dosage 5ppm solutions of anions arsenite, fluoride and nitrate were prepared. These solutions were kept in contact with different amount of clay samples ranging from 5gL^{-1} to 30gL^{-1}. Each container contains 50ml solutions of different concentrations and were stirred using magnetic stirrer for 6hrs. The solutions were filtered and the concentrations in the resultant solutions were determined spectrophotometrically. It is observed that with the increase in the amount of adsorbent dosage removal efficiency increases and the optimum condition appears at $30gL^{-1}$ (Fig-4). Maximum removal is observed in case of fluoride and the arsenite removal is least under these conditions and attains the equilibrium condition almost at the same stage.

Effect of contact time

$30gL^{-1}$ of the clay sample was kept in contact with 5ppm solution and the removal efficiency was determined after 15min, 30 min, 60 min, 120 min, 240 min and 360min. It is observed that the equilibrium state is achieved after 2hrs (Fig-5).

Effect of Concentration

To observe the effect of concentration $30gL^{-1}$ of the clay samples were kept in contact with different concentrated solution ranging from 1ppm to 10ppm. Solutions were stirred through magnetic stirrer for 6hrs. After observations it is seen that the adsorption capacity decreases with the increase in the concentration (Fig-6).

Effect of pH

To observe the effect of pH solutions were prepared at different pH value taking $100gL^{-1}$ of adsorbent dose in 50ml of 5ppm solutions in different container and the retention time was of 6hrs. After several observations it was found that in case of arsenite at low pH adsorption capacity was high which decreases gradually and then starts increasing from pH 7 to pH 9. In case of fluoride and nitrate the adsorption on clay sample shows uniform behavior. Percentage removal of fluoride and nitrate decreases with the increase in the pH value, this may be due to the increase in the positively charged sites at low pH level (Fig-7).

Conclusions

From the above discussion it is clear that the clay sample collected from the Longai region of Karimganj district of Assam India is iron-rich kaolinite clay containing very small amount of titanium and magnesium. The XRD study of the clay fraction revealed dominant association of kaolinite along with quartz and calcite. In the XRD traces the 001 diffraction maximum of kaolin minerals at 10-16 degrees 2<theta> is conclusive for kaolinite [11].

During the observation it is found that adsorption increases with the increase in the adsorbent dose and attains the optimum condition after $25gL^{-1}$.Adsorption capacity also increases with increase in the retention time and attains the state of equilibrium after 1hr and the process was continued for 6hrs to observe any variation. Among all the three anions fluoride was highly adsorbed 45-50% of fluoride can be removed utilizing the clay. And in other two cases about 35-40% can be removed with this adsorbent. After observing the effect of concentration on adsorption it is seen that adsorption decreases with the increase in the concentration of the contaminated water. At lower value of pH of the reacting solution maximum adsorption was observed in all the cases and adsorption capacity decreases with the increase in the pH level except arsenic, here adsorption first decreases and again starts increasing from pH 7 - pH 9.

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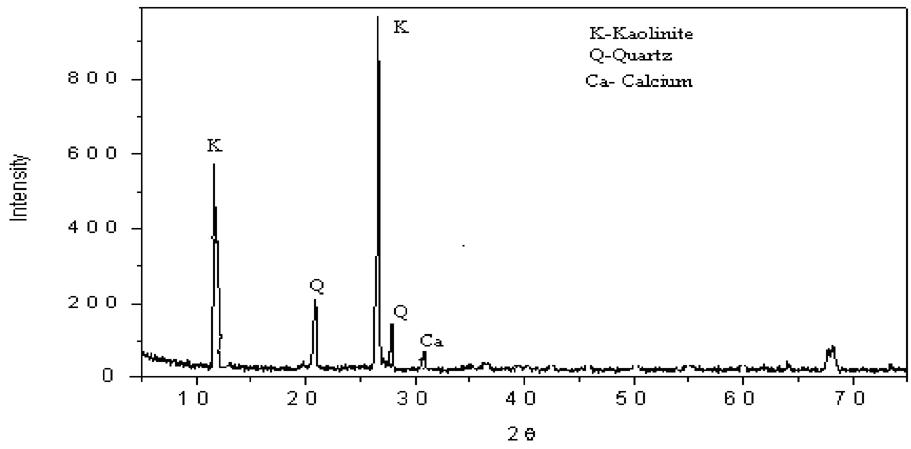

Fig. 1: X –ray diffraction study of the clay

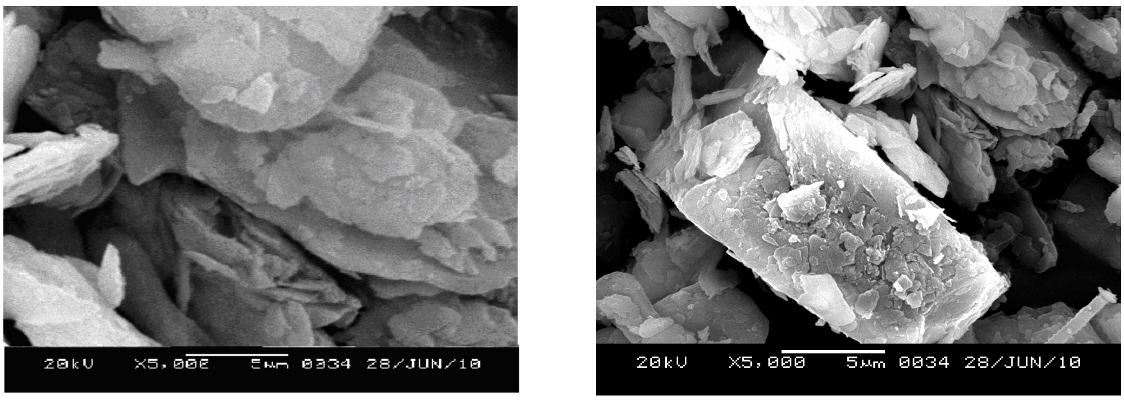

Fig.2 (a): SEM morphology of the clay showing pseudohexagonal image

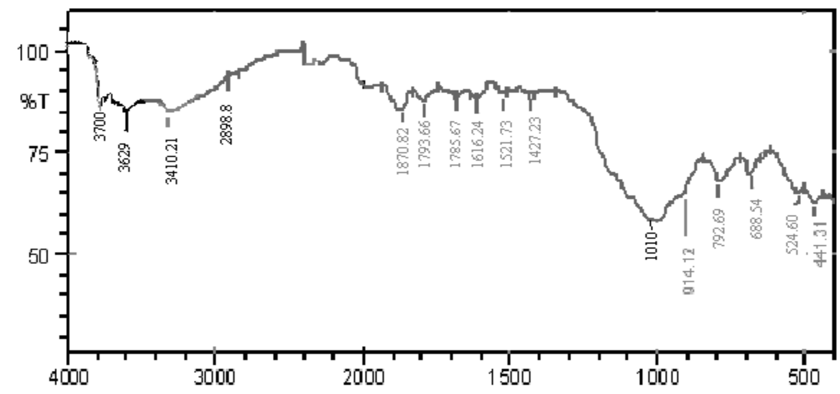

Fig.3: FTIR diffraction study of the clay

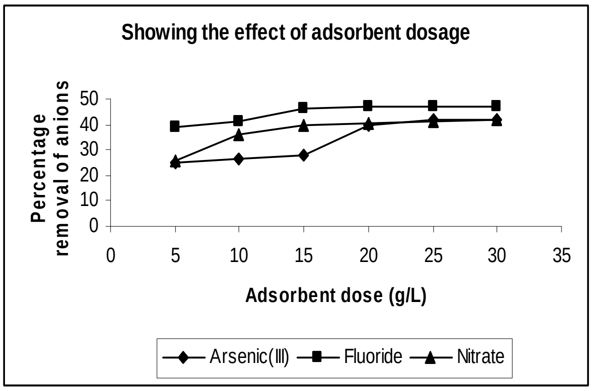

Fig.4: Showing the effect of adsorbent dosage

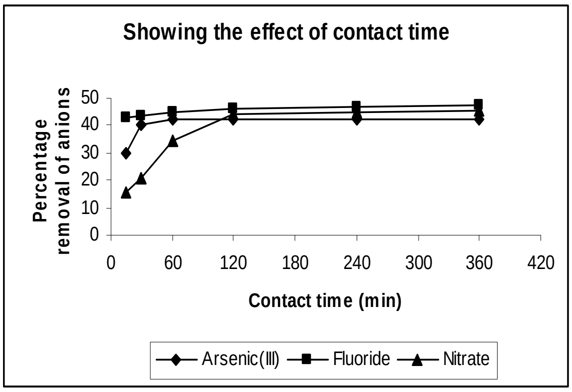

Fig.5: Showing the effect of contact time

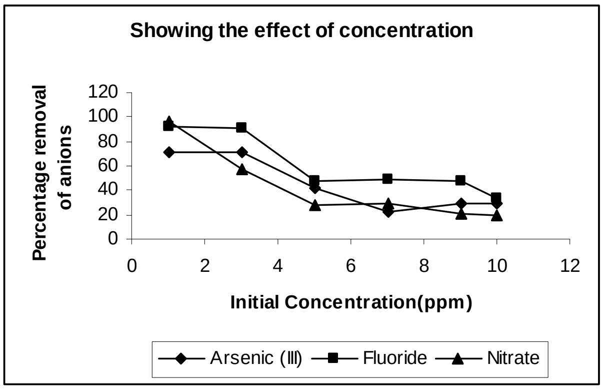

Fig.6: Showing the effect of concentration

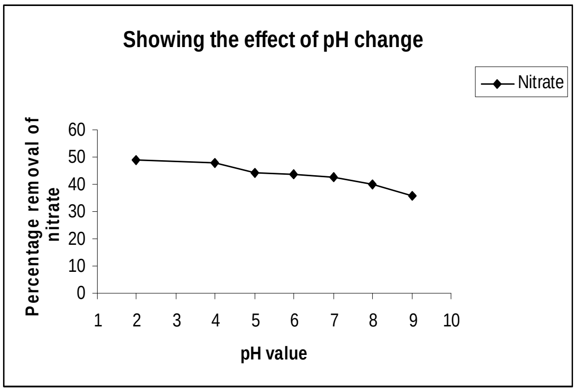

Fig.7A): Nitrate

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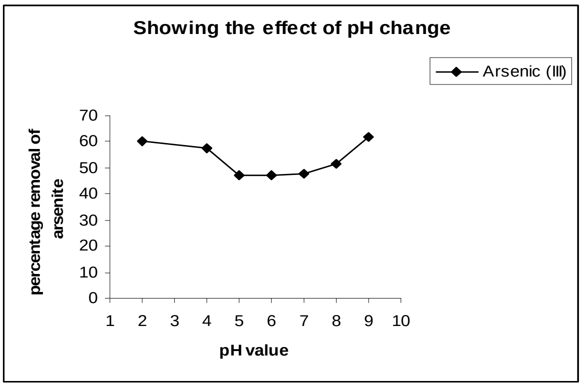

Fig. 7: (B) Arsenite

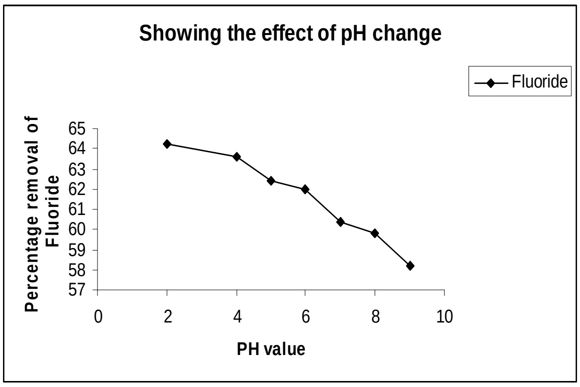

Fig.7: (C) Fluoride