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Studies on defluoridation of groundwater by aluminium modified bentonite clay, as a potential adsorbent

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Abstract

The aim of this present study is targeted to decide the fluoride removal capacity of Aluminium modified bentonite (Al-bent) clay as well asbentonite (bent) clay material. The bentonite clay was collected and dried in an oven at 120^{0}C for 24hrs. The Al-Bent clay was prepared by 300ml of 10% solution of $Al_2SO_4.18H_2O$ was mixed with 500 gram of bentonite clay and dried in an oven at 120°C for 24hrs. The dried material of bent and Al-bent clays are powdered, sieved and preserved. The consequence of pH, contact time, adsorbent dose, temperature and adsorbent size were examined for bent and Al-bent clay materials. The removal capacity of these clay materials was declared by raising the adsorbent dose and contact time. At low pH (pH=2) the maximum amount of fluoride is adsorbed by the Al-bent clay (51%). The amount of fluoride adsorption is increased from 40% to 49% with the maximum temperature of 70°C. The physical attributes of before and after treatment of the Al-bent clay was done by XRD, FT-IR, SEM and EDAX. The results indicated that the Al-bent clay can be successfully used as an effective adsorbent for fluoride removal. It can be prepared easily, cheap, efficient and eco-friendly adsorbent of fluoride removal since aqueous solutions. We concluded that Al-bent clay is a potential adsorbent than bentonite clay for defluoridation which can be applied in fluoride-rich water in rural areas of India and other developing countries.

Keywords: Adsorption, Bentonite, Al-bent clay, pH, Groundwater, Defluoridation.

Introduction

Fluoride is the 13th most abundant element in the earth's crust. It occurs mainly as a free fluoride ion in ground water. Fluorine is highly reactive because it has a strong affinity. Fluoride originates from the weathering and leaching of fluoride-containing minerals such as fluorapatite, Biotite, Muscovite, fluorite, Hornblende, fluorospar, Syenite and cryolite exchange into the surface waters with run–off and groundwater through direct contact[1,2]. The weathering and leaching mechanisms of fluorite that determine the amount of fluoride dissolved in groundwater[3].

The migration of fluoride in groundwater may arise due to natural and anthropogenic sources. In India, nearby 80% of rural domestic water needs and 50% of urban water needs are mainly due to depend on groundwater[4]. Hence fluoride concentration is an important aspect of hydrogeochemistry, because of its impact on human health. The main potential health risks from fluoride are considered to be fluorosis[5-7]. The suggested fluoride concentration in intake water is 1.5mg/L (WHO Standards 2004)[8].

In this aspect, removal of fluoride in groundwater is quite urgent to develop more advanced and cost-effective techniques. Several defluoridation techniques of drinking water, such as ion exchange, adsorption, precipitation-coagulation, reverse osmosis, electrodialysis and nanofiltration, have been developed for fluoride removal from water[9]. Among these techniques, adsorption is the most popular purification techniques for defluoridation of water due to its availability, high selectivity, low cost, high efficiency and being a comparatively more environmental friendly technique.

Recently, researchers have focused their studies on various types of effective adsorbents such as different clays, natural herbals, activated alumina, activated charcoal and zeolites on defluoridation[10]. But, some adsorbents are not capable of eliminating fluoride water at low concentration (2mg/L). At low pH and high temperature some adsorbents remove fluoride from water effectively[11]. In this view of these serious drawbacks, there is a great need to explore locally adsorbent for defluoridation. It has to develop an effective, efficient and ecofriendly for the removal of fluoride from water.

This study, therefore, aims at developing a low cost novel adsorbent of removing fluoride groundwater using Aluminium modified bentonite (Al-bent) clay.

Materials and methods

Preparation of bentonite clay (Bent): The Bentonite clay powder was obtained in a lake from Sogathur village situated in near Dharmapuri, Tamilnadu (India). Before use, bentonite clay

was washed with distilled water and dried in an oven at 120°C for 24 hrs. The dried material was powdered and sieved to separate by micron filter 106mm size.

Preparation of Aluminium modified Bentonite clay (Al-Bent): 10% solution of $Al_2(SO_4)_3.18H_2O$ was prepared by using ultra-pure water. 300ml of this Al^{3+} solution is mixed with pure 500g of Bentonite clay and stirred uniformly. This mixture was dried in an oven at 120°C for 24 hrs. This is called Aluminium modified Bentonite clay (Al-Bent). The dried material was powdered and sieved to separate by micron filter 106mm size.

These materials were preserved for further experiments, such as various batch adsorption experiments as well as characterization studies, like SEM, EDAX, XRD and FT-IR. The bent and Al-bent clay material was used for batch adsorption experiments and for characterization studies. The bent clay and Al-bent clay material as well as fluoride treated material was used. These materials, from the adsorption experiments were dried and carefully packed in an airtight container immediately, after the defluoridation experiments were carried out.

Characterization studies, like SEM and EDAX were taken from IISc, Bangalore. XRD was taken from Alagappa University, Karaikudi. FT-IR was taken from the Instrumentation Laboratory, St. Joseph's College, Tiruchirappalli.

Results and discussion

Effect of pH: The effect of pH on fluoride removal (Figure-1) was studied at different pH range such as 2, 4, 6, 8 and 10. The pH of the solution is controlled by adding HCl/NaOH solution. The adsorbent dose of all the pH range is 5g and the uptake of fluoride solution is 50ml (fluoride initial concentration C_0 2.6mg/L, temperature 28°C, shaking speed 100rpm and contact time 4hrs).

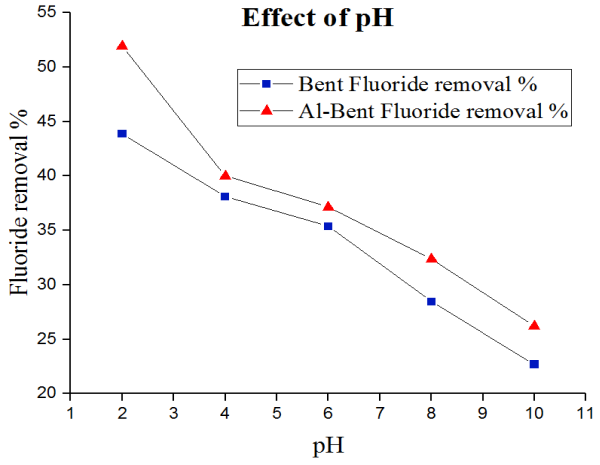

Figure-1: Effect on pH on fluoride adsorption.

The fluoride uptake was extreme at the pH value of 2.0 for both bent and Al–bent clay. But Al-bent showed good fluoride adsorbed capacity than compared bentonite clay. Fluoride adsorption was found in growth in lower pH value, because the surface of the adsorbent is highly activated in acidic medium. Therefore, in acidic condition fluoride adsorption is highly attributed. The tendency for the fluoride adsorption in basic pH range was small. It was mainly due to the competition of hydroxyl ions with fluoride ions for adsorption because of similarity in fluoride and hydroxyl ions in charge and ionic radius. The influence of fluoride adsorption of Al-bent clay assumes at low pH leads to chemisorption, and physisorption occurs at high pH range[12].

Effect of Adsorbent dosage: The effect of adsorbent dose can be observed in Figure-2. The amount of adsorbent dose significantly affects the influence of fluoride adsorption. It was studied at 28°C and the initial concentration of fluoride is 2.6mg/L by allowing a contact time of 4hrs.

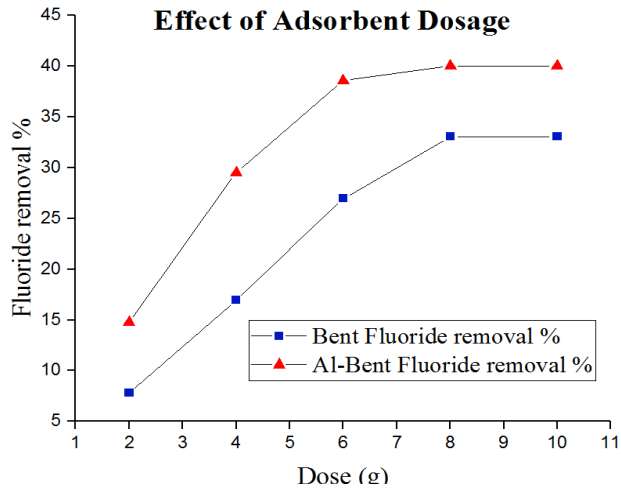

Figure-2: Effect of Adsorbent dosage on Fluoride adsorption.

The quantity of the adsorbent is increased from 2g to 10g (2g, 4g, 6g, 8g and 10g) and uptake of fluoride solution is 50ml (shaking speed 100 rpm). The effect of adsorbent dose on fluoride removal is increased from 40% to 50% with an increase of Al-bent clay dose from 2g to 10g at C_0 is 2.6mg/L. It specifies that the numbers of active adsorption spots are increased to hold fluoride ions at higher dose. So there is almost constant in the removal of fluoride, when the dosage of the adsorbent is 8g. This suggests that adsorption reaction is probable to achieve to a dynamic equilibrium.

Effect of Equilibrium time: The effect of contact time between adsorbent and fluoride ions was studied at the one hour time intervals up to 5 hours. It can be observed in Figure-3. It was studied at 28°C and the initial concentration of fluoride is 2.2mg/L by allowing a contact time via 1hr, 2hr, 3hr, 4hr and 5hrs respectively. The quantity of the adsorbent is taken to5g and uptake of fluoride solution is 50ml.The adsorbent and the fluoride ion solution are allowed to shake with a given time (shaking speed 100 rpm). The fluoride ions rapidly reached

equilibrium at three hours and high percentage of fluoride was adsorbed in both bent and Al-bent clay materials. The result shows Al-bent clay was highly adsorbed the fluoride ions than compare bent clay.

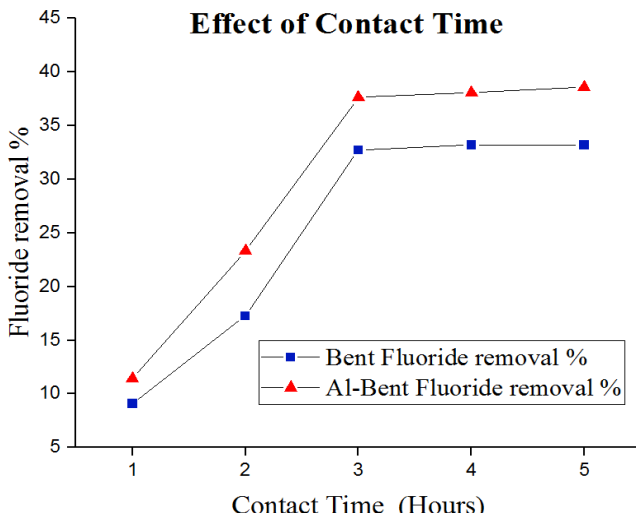

Figure-3: Effect of Contact time on fluoride adsorption.

Effect of Adsorbent Particle Size: The effect of adsorbent particle size was investigated using the average particle size (53, 106, 300 and 500 microns). The increase in adsorbent particle size from 53 to 500 microns reduced the adsorption level. It may be due to the small particle size resulted larger surface area and it has enlarged the adsorption ability of fluoride ions[13].

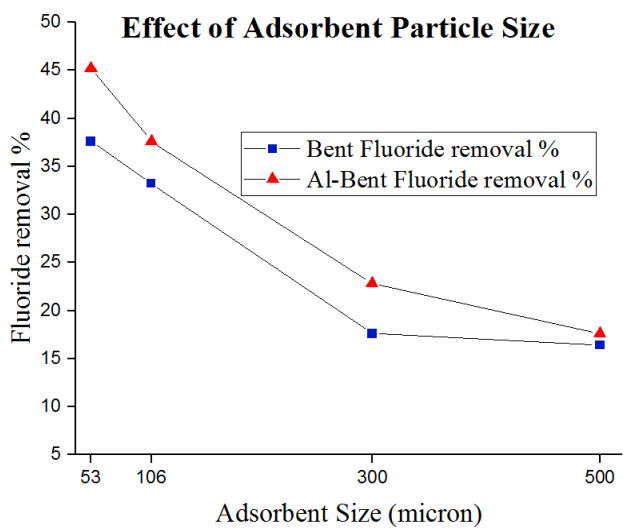

Figure-4: Effect of Adsorbent particle Size.

For larger particles, the amount of fluoride adsorption was less. Because the larger particle have less surface area and it has the spreading resistance to mass transfer is high. So the majority of the internal surface of the particle is may not be used for adsorption. Thus the amount of fluoride adsorption was lesser than smallest particle.

$$\text{adsorbent Particle size (mm)} \quad \alpha \frac{1}{\text{Surface area}} \alpha \frac{1}{\text{Adsorption}}$$

It also believed that the larger particles breaking up to form smaller particles and it was opened some tiny adsorption area, which might be available for adsorption. So the larger particles have less sorption than the smaller particles. This observation specifies that fluoride ion sorption occurs by a surface mechanism.

Effect of temperature: The effect of temperature on fluoride removal by bent and Al-bent clay was observed at 30, 40, 50, 60 and 70°C respectively. Figure-5 shows the outcomes of such investigations. The contact time during the experiment was four hours (C_0 is 2.3mg/L, shaking speed 100rpm and the uptake fluoride solution is 50ml).

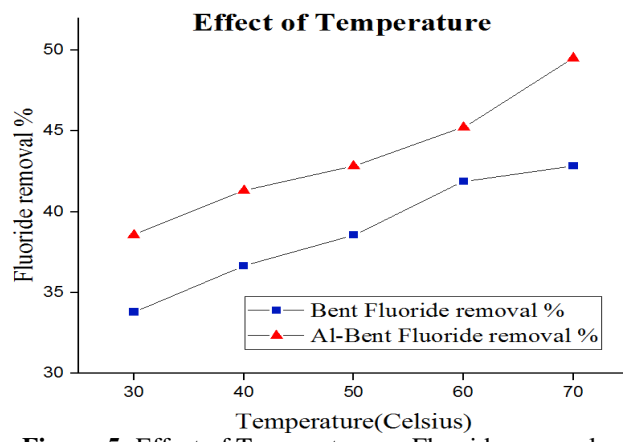

Figure-5: Effect of Temperature on Fluoride removal.

This experiment is more experienced than the adsorption of Al-bent clay material by fluoride ions was higher than the bent clay material. The adsorption potential of both materials was increased with increases temperature. This observation expresses that the interaction between fluoride ions and adsorbent is endothermic in nature, and the temperature seems to the important parameter for removal of fluoride from water.

Characterization studies: XRD Pattern for adsorbents: The XRD pattern of untreated and fluoride treated Aluminium modified bentonite clay (Al-bent) materials are shown in Figure-6A and Figure-6B. The XRD model of adsorbent after fluoride treated material showed considerable changes in the intensity of peak subsequent to the 2 theta values at 11, 20, 22, 26, 34 and 61. It gives an indication of small changes over the crystal cleavages, which might have formed due to the reaction of fluoride with adsorbent[14]. This proves the strong adsorption of fluoride with the surface of the adsorbent. Moreover, after fluoride adsorption, the appearance of some peaks confirms that the adsorption manner is purely chemical adsorption. This suggests that the uptake of fluoride ions through the adsorbent is from chemisorption, which accordingly modifies the chemical arrangement of the adsorbent.

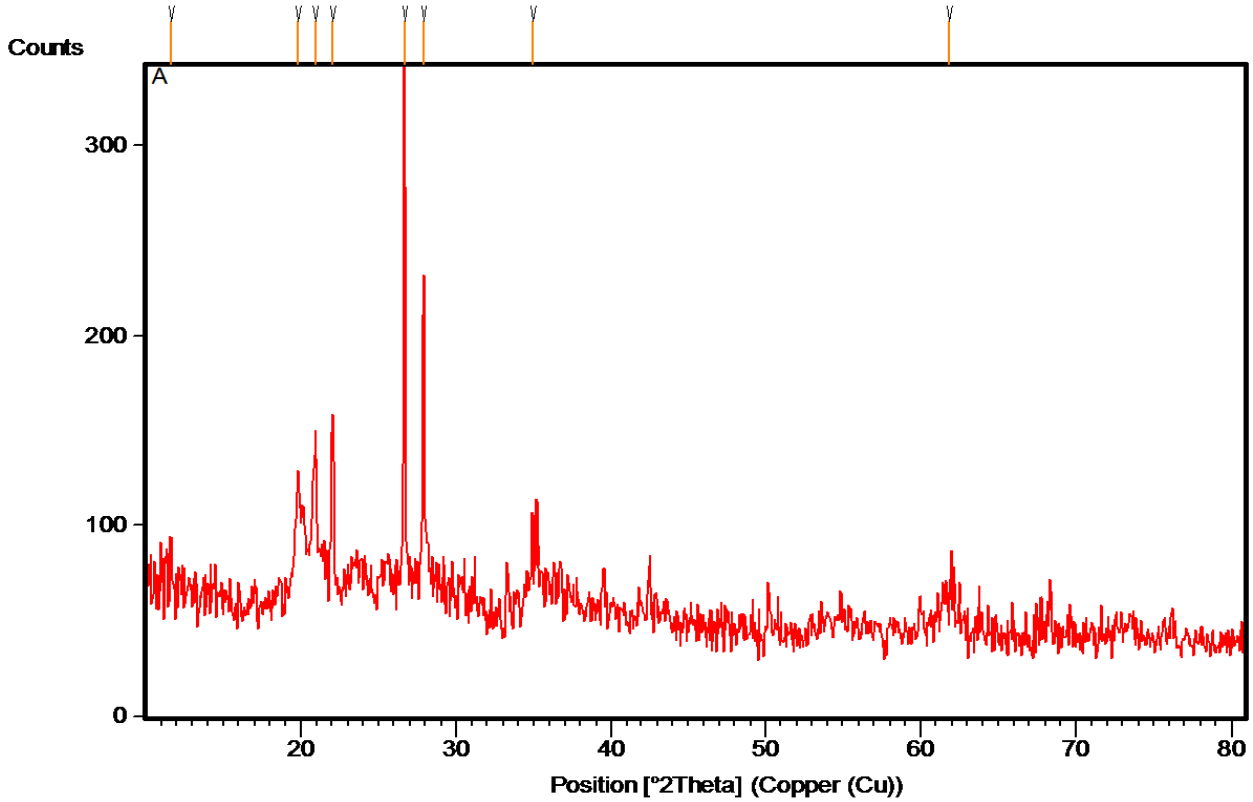

Figure-6A: X-ray Diffraction pattern of Al-Bent Clay material before fluoride adsorption.

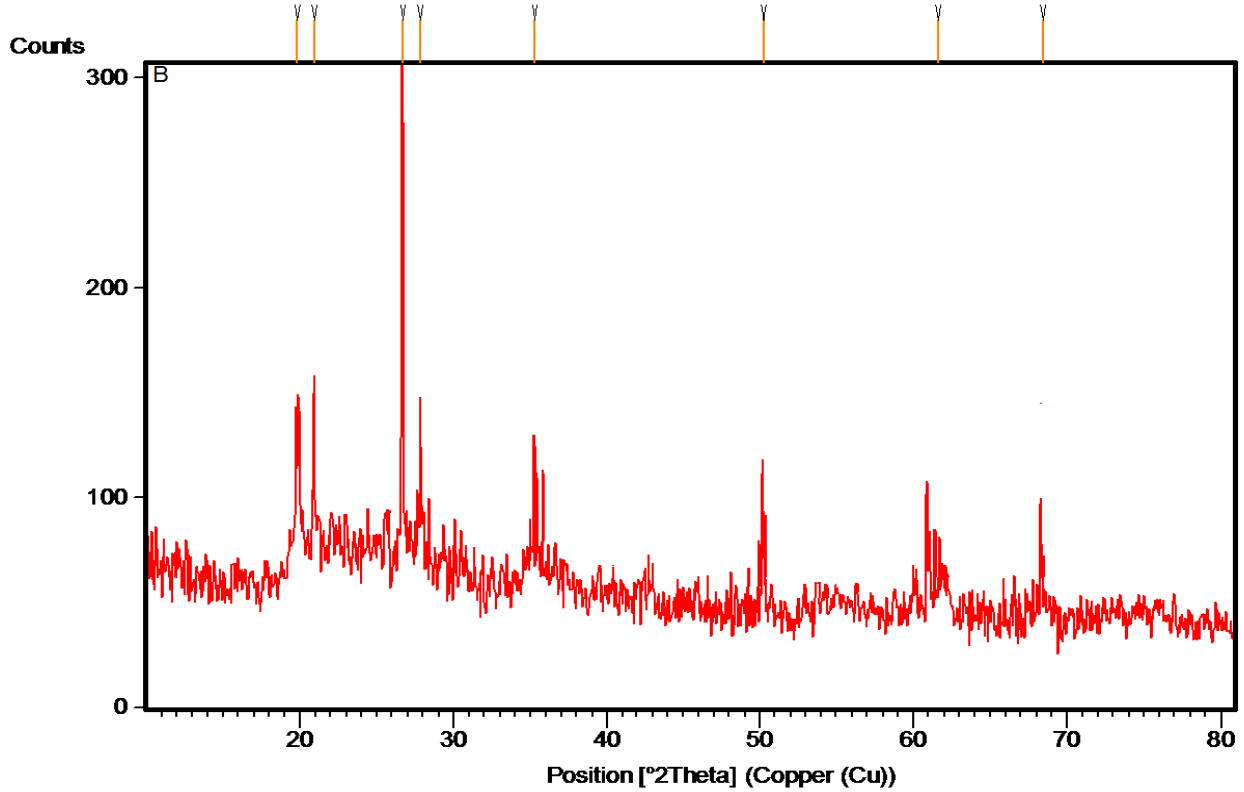

Figure-6B: X-ray Diffraction Pattern of Al-bent clay material after fluoride adsorption.

FT-IR Spectrum for Fluoride adsorption: The FT-IR Spectrum of Aluminium modified Bentonite clay material was illustrated in Figure-7A and 7B. The stretching frequency 3464 and 3420cm^{-1} and the shift of stretching frequency from 3420 to 3407cm^{-1}is assigned to the involvement of hydroxyl groups.

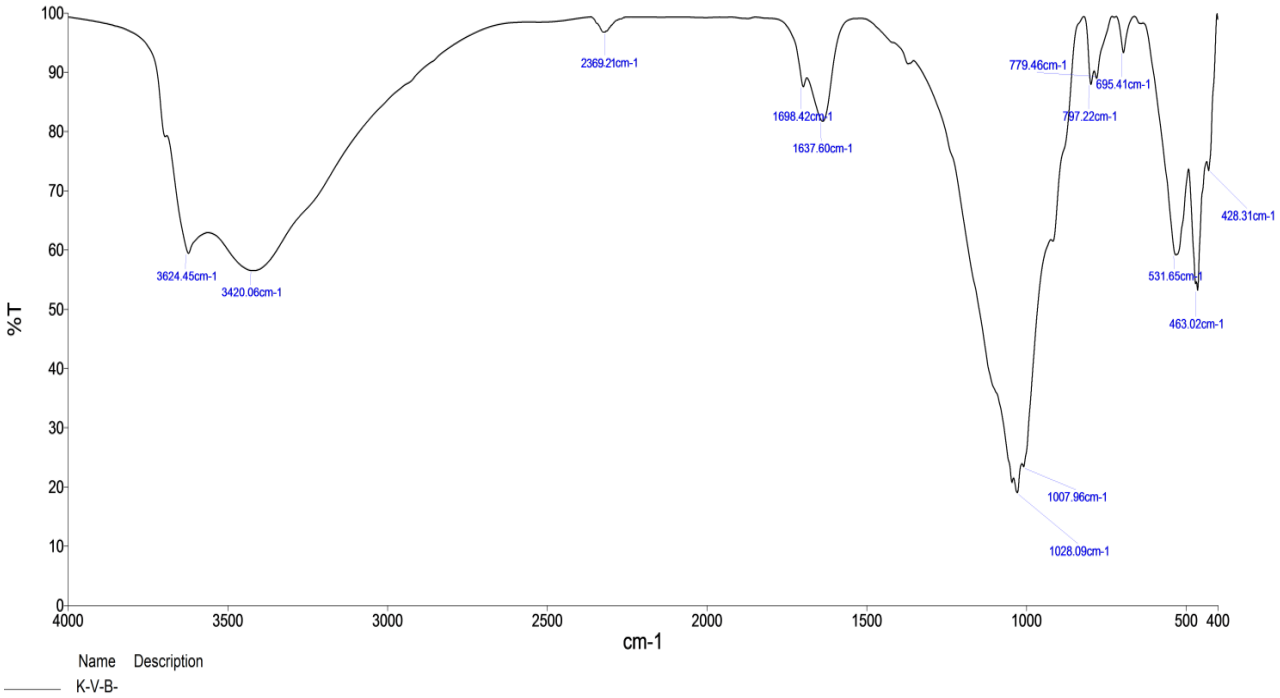

Figure-7A: FT-IR Spectrum of Al- Bent clay material after fluoride adsorption.

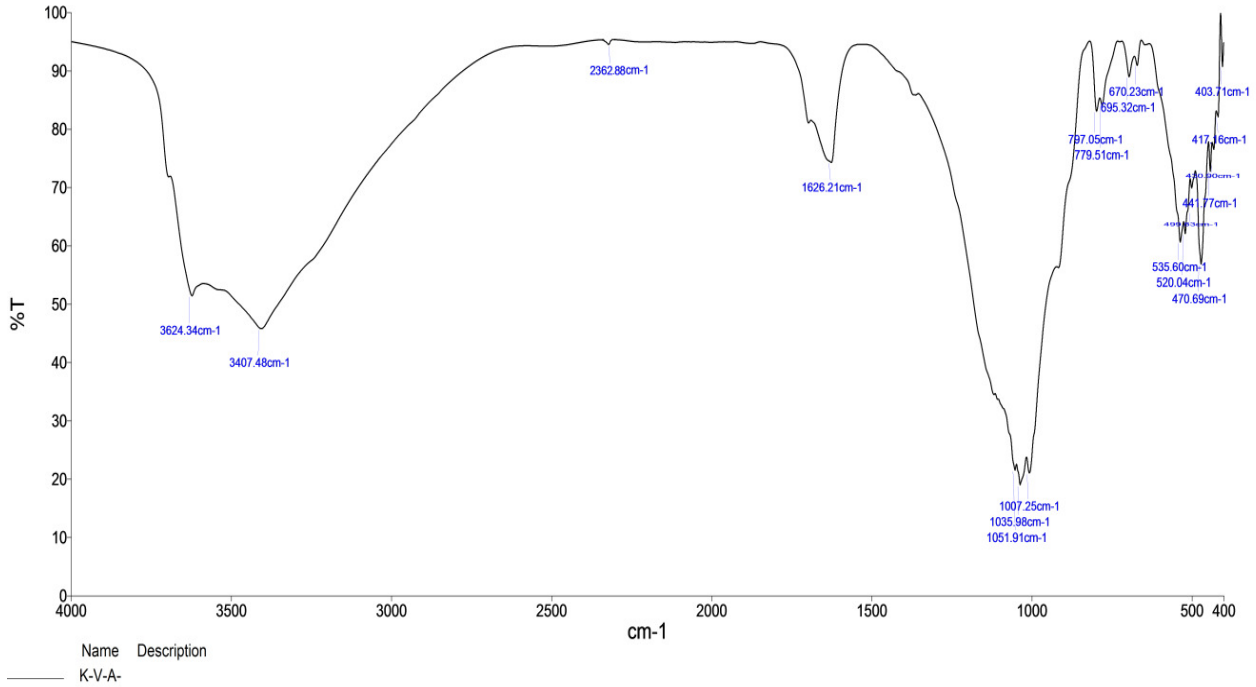

Figure-7B: FT-IR Spectrum of Al- Bent clay material before fluoride adsorption.

The peak at 2369cm^{-1} is associated with the hydrogen bonded O-H stretching group (Figure-8B). The adsorption bands in between 3300 to 3700cm^{-1} shows the characteristics of –OH group[15]. It exposed that the –OH groups on the adsorbent surface were involved in the sorption of fluoride. Electrostatic interaction and anion exchange were recommended as the main mechanisms involved in the chemisorption of fluoride on the adsorbent. The changes of stretching frequency of fluoride treated aluminium modified bentonite clay material confirm the chemical modification.

EDAX Spectra for fluoride adsorption: The EDAX Spectra was performed to notify the elemental components present. The Figures-8A and 8B shows EDAX Spectra of Al-Bent clay material before and after adsorption of fluoride.

It showed that the presence of fluoride in small amount appeared in the spectrum other than the principal element's O, Fe, Al and Si (Figure-8B) in the case of fluoride sorbed Al-bent clay material, whereas there is no fluoride peak in the Sterile Al-bent clay material[16].

SEM morphology for fluoride adsorption: The SEM (Scanning Electron Microscopy) technique was used to observe the surface physical morphology of Al-bent clay material.

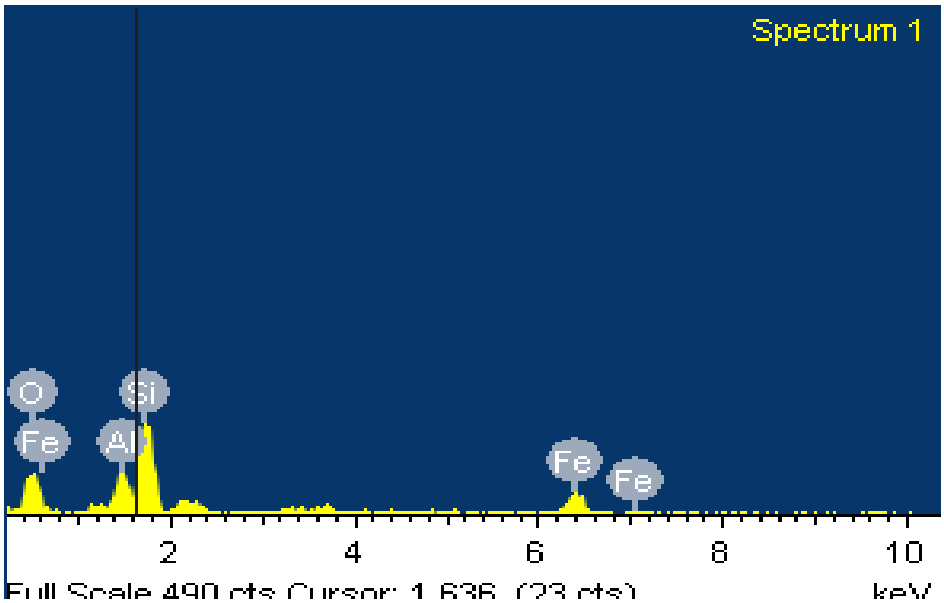

Figure-8A: EDAX Spectrum of Al-Bent clay material before fluoride adsorption.

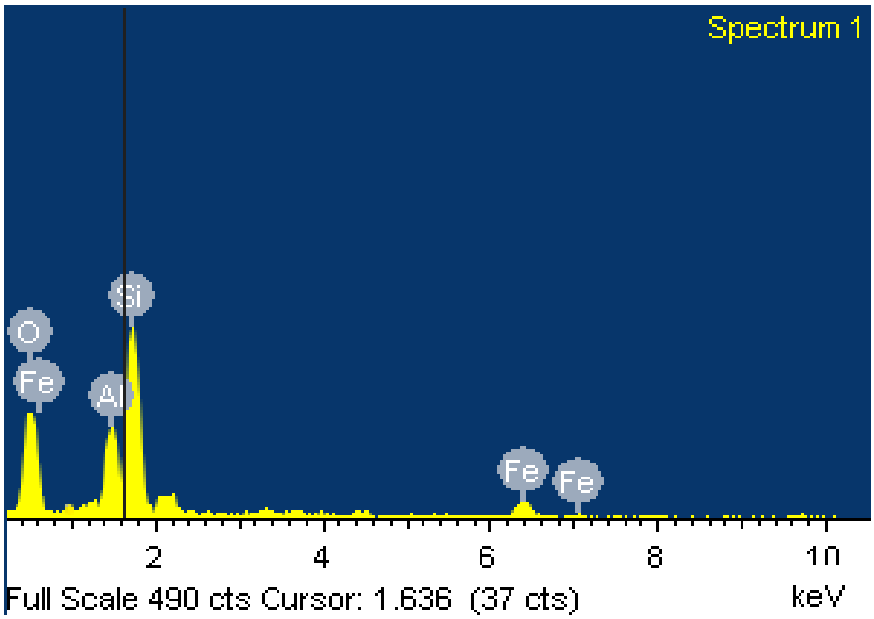

Figure-8B: EDAX Spectrum of Al-bent clay material after fluoride adsorption.

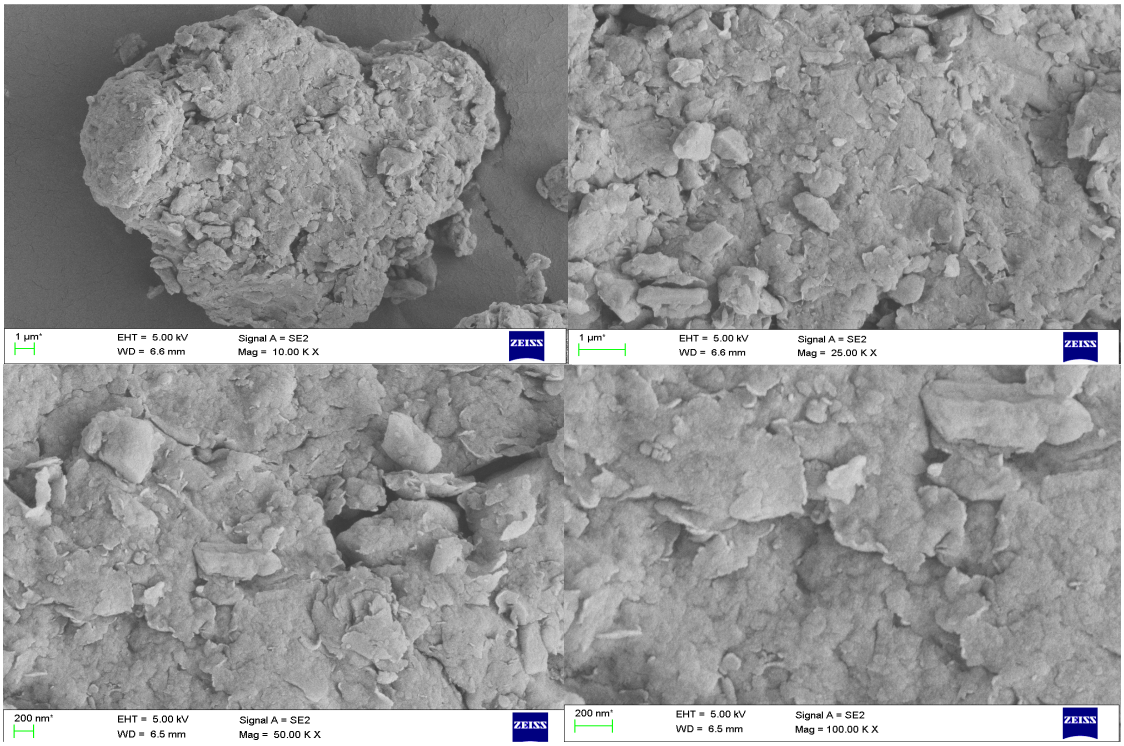

Figure-9A: SEM image of Al-bent clay material before fluoride adsorption.

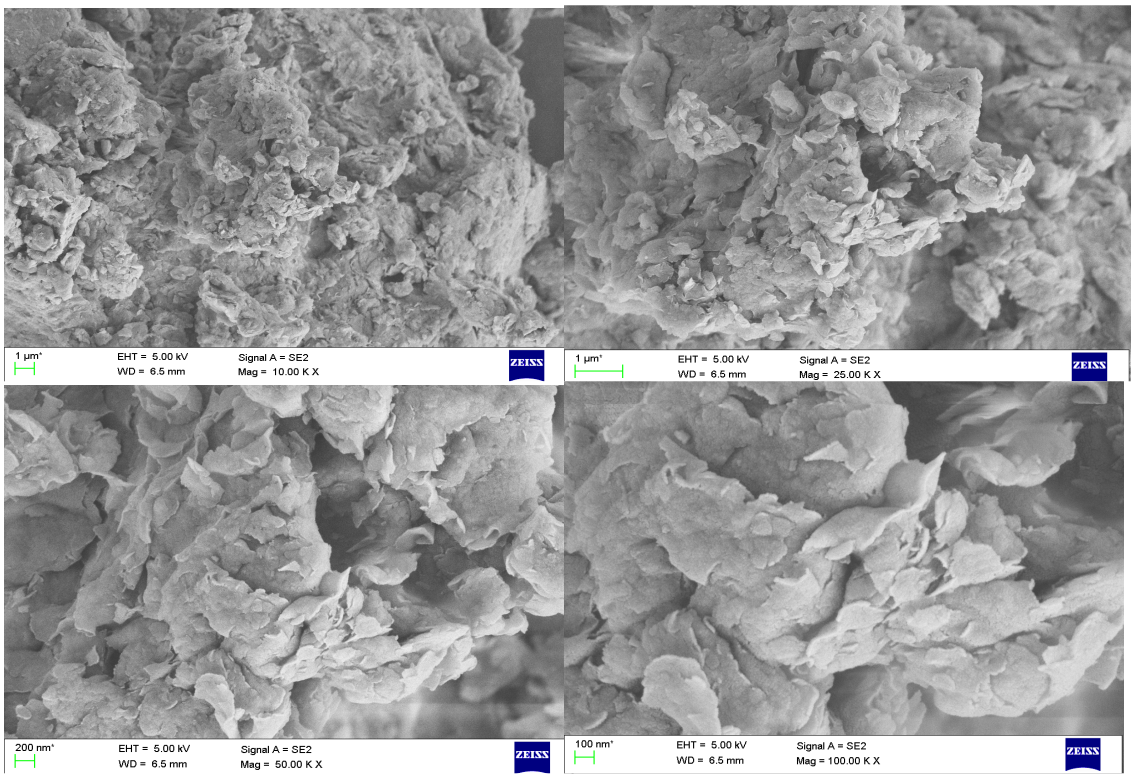

Figure-9B: SEM image of Al-bent clay material after fluoride adsorption.

Figures-9A and 8B shows the SEM images of Al-Bent clay material before and after adsorption of fluoride. The surface of Al-bent clay material appeared to be rough and more porous. In this case, the sponge-like structure with some bright spots confirms the presence of fluoride on Al-bent clay. The flake structure after adsorption may be the fluoride coverage on top of

the surface of the adsorbent. A close inspection of SEM image indicated the density difference before and after adsorption of fluoride ions confirming the uptake of fluoride ions.

Conclusion

In this study, the Chemical modification of bentonite clay with Al^{3+} significantly enhanced the adsorption capacity of fluoride removal than compared unmodified bentonite clay. At low pH (pH=2) the maximum amount of fluoride is adsorbed by the Al-bent clay (51%). The amount of fluoride adsorbed almost constant in the removal of fluoride, when the dosage of the adsorbent is 8g and it has rapidly reached equilibrium at three hours and high percentage of fluoride was adsorbed. The amount of fluoride adsorption in the larger particles has less sorption than the smaller particles, because the larger particles have less surface area. Generally fluoride adsorption increased from 40% to 49% with the maximum temperature 70°C. The results indicated that the Al-bent clay can be successfully used as an effective adsorbent for fluoride removal. It can be prepared easily, inexpensive, efficient and eco-friendly adsorbent of fluoride removal from aqueous solutions. We concluded that Al-bent clay is a potential adsorbent than bentonite clay for defluoridation which can be applied in fluoride-rich water in rural areas of India and other developing countries.

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