



## Mitigation of Fluoride from Groundwater by Natural Clay as an Adsorbent

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### ABSTRACT

The aim of this study was to examine the potential of clay material for the elimination of excess fluoride from groundwater. This study is based on empirical laboratory research. The Natural clay material was gathered and dried in an oven at 105°C for 24 hours. The effect of pH, contact time, adsorbent dose, temperature and adsorbent size was investigated. SEM, FT-IR and XRD were used to characterize the physical attributes (particle size, pore size and distribution, surface roughness) of the natural clay material. The removal efficiency of clay material was augmented by raising the adsorbent dose and contact time, and decreasing the initial concentration of F<sup>-</sup>. At low pH (pH=2), the maximum amount of fluoride adsorbed by the clay material (F= 1.0 mg/L). The amount of fluoride adsorbed increased from 1.0 to 1.6 mg/L, (C<sub>0</sub>=2.3 mg/L) with the maximum temperature of 343K. This seems to be the mechanism is endothermic in nature. The results indicated that clay material can be successfully used as an effective adsorbent for F<sup>-</sup> removal. We concluded that clay material can be a cheap, efficient, and environmental friendly adsorbent of F<sup>-</sup> from aqueous solutions.

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## INTRODUCTION

Fluoride is a commonly occurring element in minerals, geochemical deposits, and usual water systems and enters food chains through either drinking water or eating plants and cereals [1]. Fluoride is habitually experienced in naturally-occurring minerals and geochemical deposits. It penetrates into groundwater by innate processes, for instance by natural weathering and leaching [2]. The migration of fluoride into groundwater may occur due to natural and anthropogenic sources. In India, rural drinking water supply is mainly dependent on groundwater (85%). Hence, it becomes necessary to topple the fluoride concentration; according to various water quality standards the acceptable fluoride concentration limit is 1.5 mg/L [3].

Besides, mitigation of fluorides to groundwater fluorosis is due to ingestion of excessive amounts of fluorine or its compounds that is fluoride poisoning an chronic as dental fluorosis; therefore, it requires special attention. Common techniques employed to eradicate fluoride from drinking water; can be divided into four

categories; chemical precipitation, membrane processes, adsorption and ion exchange [4]. Among these techniques, adsorption is the most competent technique for defluoridation of water because of ease of process, lesser cost and being a comparatively more environmental friendly process.

It is interesting to note that some adsorbents are not capable of eliminating fluoride from water at low concentration (2mg/L) [5, 6]. Besides, some of them only work at extreme pH (pH≤3) and, hence, are improper in natural conditions [7]. In view of these serious drawbacks, there is a great need to develop an effective, efficient and biodegradable adsorbent for the deletion of fluoride from water.

In this study, an attempt has been made for defluoridation of groundwater, using the clay material as a natural, feasible, suitable and low cost adsorbent.

## MATERIALS AND METHODS

### Experimental

#### Synthesis of adsorbent

The clay powder for adsorption and kinetic experiments was obtained from the Mannachanallur village of Trichy

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district. Before use, all raw clay samples were dried at 90 °C for 24h. Dried mass was then grounded to fine powder, and it was sieved by micron filter 106 mm size.

It was preserved for further experiments, such as, various batch adsorption experiments as well as characterization studies, like SEM, XRD and FT-IR studies. The pure clay material was used for batch adsorption experiments and for characterization studies the raw clay as well as fluoride treated clay material was used. The clay material from the adsorption experiments was carefully packed in an airtight container immediately, after the defluoridation experiments was carried out. Characterization studies, like SEM and XRD were taken from the Soil Instrumentation laboratory, NIT, Tiruchirappalli. FT-IR was taken from the Instrumentation laboratory, St. Joseph's College, Tiruchirappalli.

## CONCLUSION

### Effect of pH

The effect of pH on fluoride uptake by adsorbent was studied at five different pH, viz., 2, 4, 6, 8 and 10 by keeping all further factors constant (clay material dose 5 g l<sup>-1</sup>, C<sub>0</sub> 2.4 mg/L, temperature 39 °C, shaking speed 100 rpm and contact time four hours). Fig. 1 shows the effect of pH on fluoride adsorption. The pH of medium was attuned using necessary quantities of decimolar hydrochloric acid and sodium hydroxide solution.

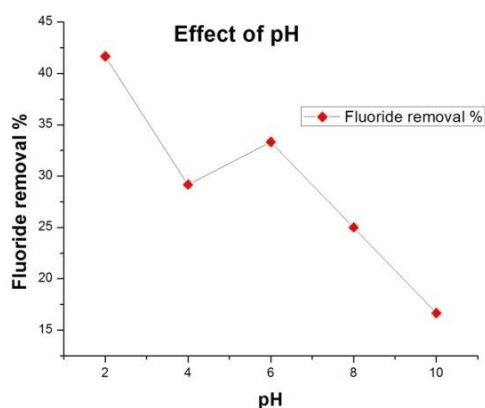


Figure 1. Effect of pH on fluoride removal

The fluoride uptake was maximum at the pH value of 2.0. Fluoride removal was found to increase at lower pH, because the surface is highly protonated in an acidic medium and therefore, in acidic medium maximum fluoride removal is attributed. The trend for the fluoride elimination in alkaline pH range was low; that was due to competition of hydroxyl ions with fluoride for adsorption sites owing to resemble in fluoride and

hydroxyl ions responsible and ionic radius. The influence of pH on the pronounced adsorption of fluoride on the surface of the clay material at low pH ranges leads to the assumption that chemisorption dominates in this range and chemisorption along with physisorption occurs at the higher pH ranges [8].

### Effect of adsorbent dose

The influence of adsorbent dosage on fluoride deletion was studied at 40 °C and at initial fluoride ion concentration of 2 mg/L by permitting a contact time of 4 hours. The amount of adsorbent appreciably influences the amount of fluoride adsorptions. As the quantity of the adsorbent is augmented from 5 to 20 g/l, there is an apparent rise as the percentage of fluoride removal (Fig. 2). It was observed that percent fluoride removal increased from 40 to 50 % with an increase in clay adsorbent dose from 5 to 10 g/l at C<sub>0</sub> 2 g/l. This specifies that the number of active adsorption spot at a higher dose is more than sufficient to hold fluoride ions. Nevertheless, there is almost constant in the removal of fluoride, when the dosage of the adsorbent is above 10 g/l. This implies that adsorption reaction is probable to attain to a dynamic equilibrium.

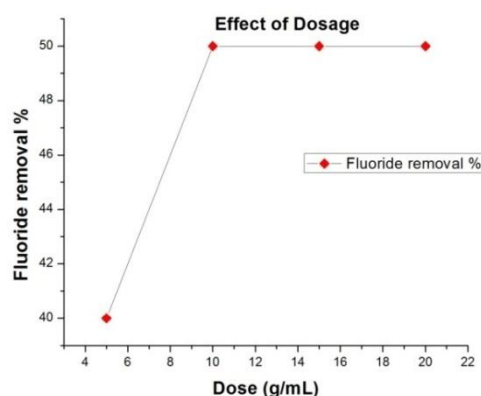


Figure 2. Effect of adsorbent dosage on fluoride removal

### Effect of equilibration time

The effect of contact time between the adsorbent and fluoride ions was studied at the one hour time intervals up to 6 hours. The effect of contact time between the adsorbent and fluoride ions can be observed in Fig. 3. Even though at the commencement the proportion of detached fluoride augmented with longer contact times, it approached a flat terrain after a few minutes. Presumably, the equilibrium time is the time at which the curves appear almost asymptotic to the time axis. In this case, the equilibrium was attained at three hours; the sorption percentage altered from 25% at one hour to 41.66 % at three hours, at which point it raised ground. This perhaps owing to the fact that once a certain

amount of fluoride ions gets doped onto these composites within a given time, no more doping occurs afterwards, i.e. the doping level might have attained [9]. Further, the achievement of highest doping level within three hours proposes that a minimum contact time is adequate enough for the taking away of fluoride from water by these composites. The  $F^-$  rapidly reached equilibrium at three hours, and 41.66 % of  $F^-$  was adsorbed, after that there is no more fluoride uptake takes place. Hence, three-hour contact time was chosen as the optimum time for the sorbents for further inspection.

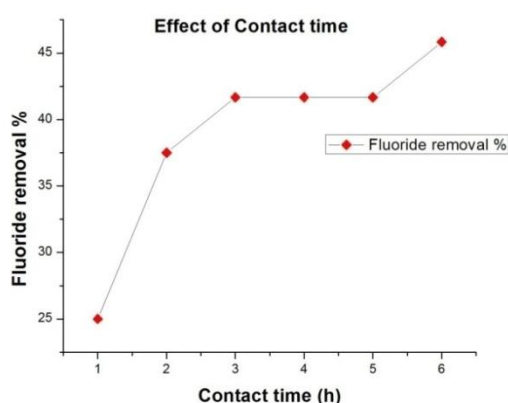


Figure 3. Effect of contact time on fluoride removal

### Effect of temperature

The effect of temperature on fluoride elimination by clay material was examined at four different temperatures (311, 323, 333 and 343 K). Fig. 4. Presents the results from such tests. It is more experienced than the adsorption potentials of clay material for fluoride increases from 0.3 to 0.7, 0.5 to 1.0, 0.8 to 1.3 and 1.0 to 1.6 mg/L as an adsorbent dosage of 1g, 2g, 3g and 4g with increasing temperatures from 311 to 343 K as the initial fluoride concentration of 2.3 mg/L respectively. The contact time during the experiment was three hours. The maximum amount adsorbed increased from 1.0 to 1.6 mg/L (at 2.3 mg/L, initial fluoride concentration, and Contact time 3 hours). The observation shows that the interaction between adsorbate and adsorbent is endothermic in nature, and the temperature seems to be a significant parameter.

### Effect of particle size

In the present work, the effect of adsorbent particle size was investigated using the average particle size (53, 106 and 300 microns) (Fig. 5). Increase in particle size from 53 to 300 microns reduced the adsorption level from 47.82 to 21.73%. It might be due to the smaller particle size of adsorbent resulted a large surface area; that has increased the adsorption capacity [10]. This is because

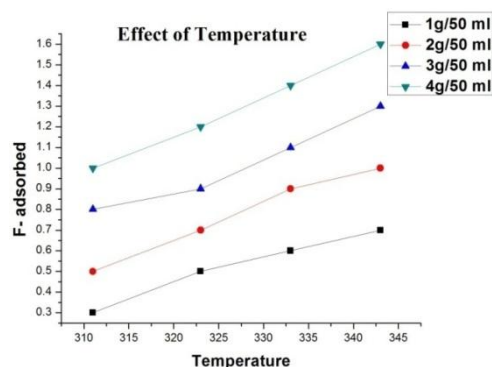


Figure 4. Effect of temperature, on fluoride adsorption

the smaller particles have more surface area and access to the particle pores is facilitated when the small size of particles. For larger particles, the dispersion resistance to mass transfer is high and the majority of the internal surface of the particle may not be used for adsorption, and thus the amount of fluoride ions adsorbed was less.

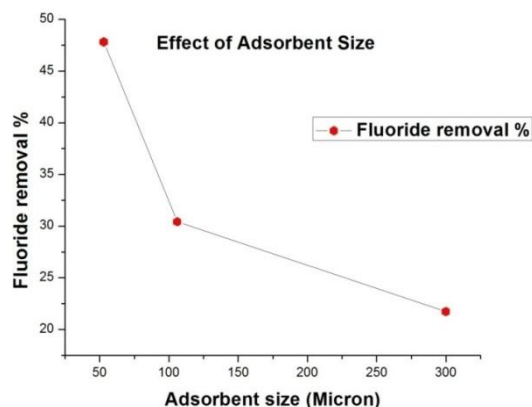


Figure 5. Effect of adsorbent size on fluoride removal

It is also believed that the breaking up of large particles, to form smaller ones opens some tiny sealed channels, which might then become available for adsorption, and so the sorption by smaller particles is higher than that the larger particles. These observations indicate that fluoride ion sorption occurs by a surface mechanism.

### Characterization studies

#### SEM morphology for fluoride adsorption

The scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of clay material. Figs. 6a. and 6b show the SEM images of clay material before and after adsorption of fluoride. The surface of clay material appeared to be rough and more porous. In this case, the sponge-like structure with some bright spots confirms the presence of the fluoride

on clay material [Fig. 6b]. The flake structure after adsorption [Fig. 6b] may be the fluoride coverage on top of the surface of the clay material. A close inspection of SEM photograph indicated the density difference before and after adsorption of fluoride ions confirming the uptake of fluoride ions.

### XRD Pattern for Adsorbents

The XRD patterns of untreated and fluoride treated clay materials are given in Fig. 7. The XRD patterns of adsorbent after fluoride adsorption showed significant changes. XRD model of the adsorbent material after the fluoride treatment showed considerable changes in the intensity of peak subsequent to the  $2\theta$  values at 20, 52 and 68. The XRD Figs. of the treated clay material give an indication of small alteration over the crystal cleavages. This proves the strong adsorption of fluoride lying on the surface of the adsorbent. Furthermore, after fluoride adsorption, the appearance of some peaks confirms that the adsorption process is purely chemical adsorption. This suggested that the uptake of fluoride ions through the adsorbent is by chemisorptions, which accordingly modify the structure of the adsorbent.

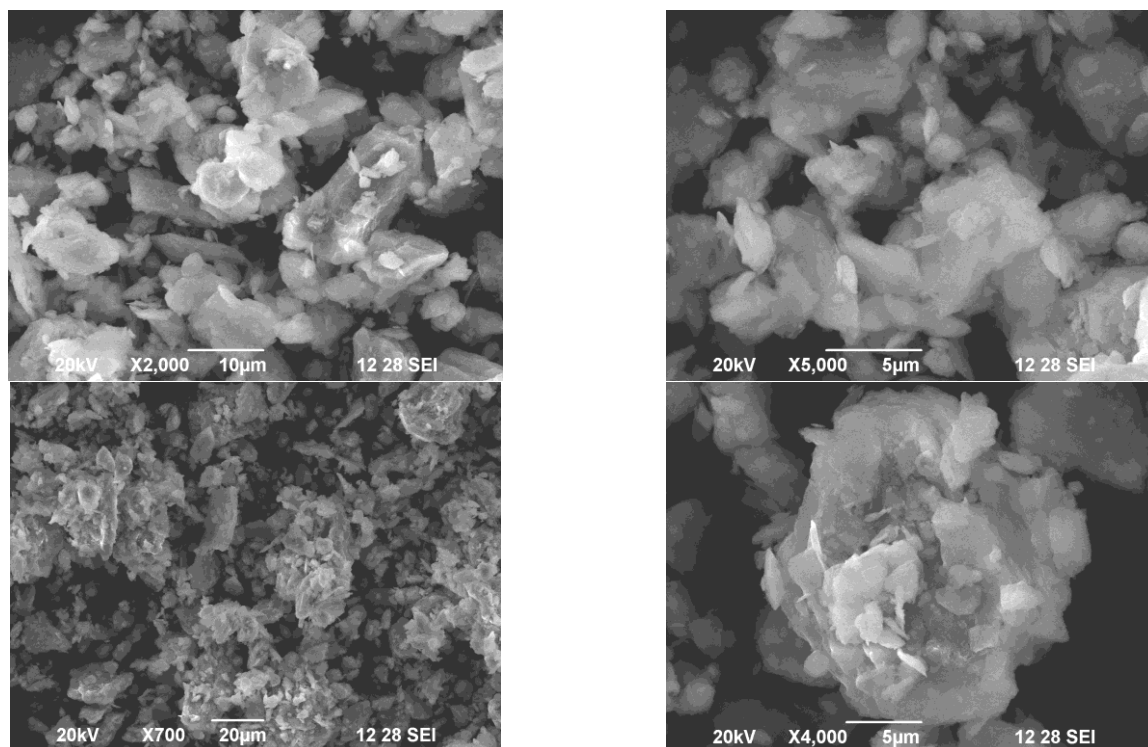
### FT-IR Spectrum for Fluoride adsorption

The FT-IR spectrum of clay material was characterized and illustrated in Fig. 8. The shift in stretching frequency from 3620 to 3423  $\text{cm}^{-1}$  is assigned to the

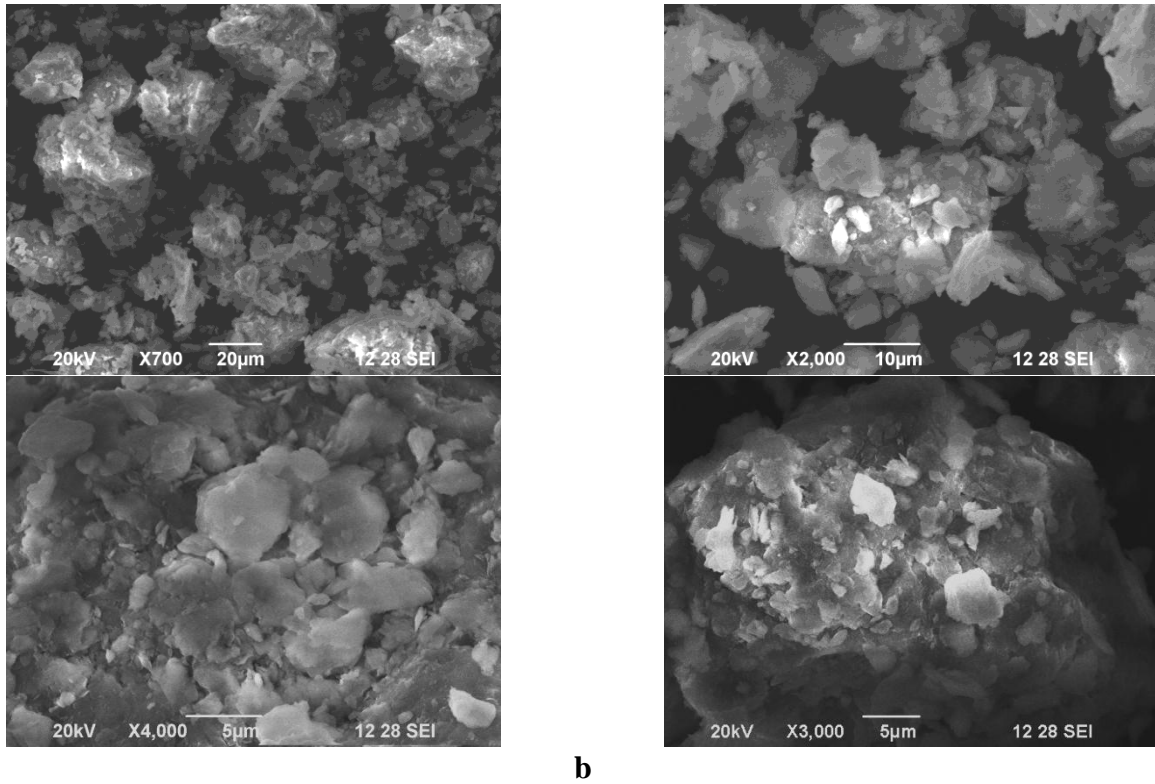
involvement of hydroxyl groups. The peak at 2360  $\text{cm}^{-1}$  is associated with the Hydrogen bonded O-H stretching group (Fig 8b). The adsorption bands in between 3300 to 3600  $\text{cm}^{-1}$  show the characteristics of -OH group [11]. FT-IR spectrum revealed that the hydroxyl groups on the adsorbent surface were involved in the sorption of fluoride. Anion exchange and electrostatic interaction were suggested as the main mechanisms involved in the sorption of fluoride on the adsorbent. The changes of stretching frequency of Fluoride treated clay material compared to natural clay material confirm the chemical modification.

### ACKNOWLEDGEMENT

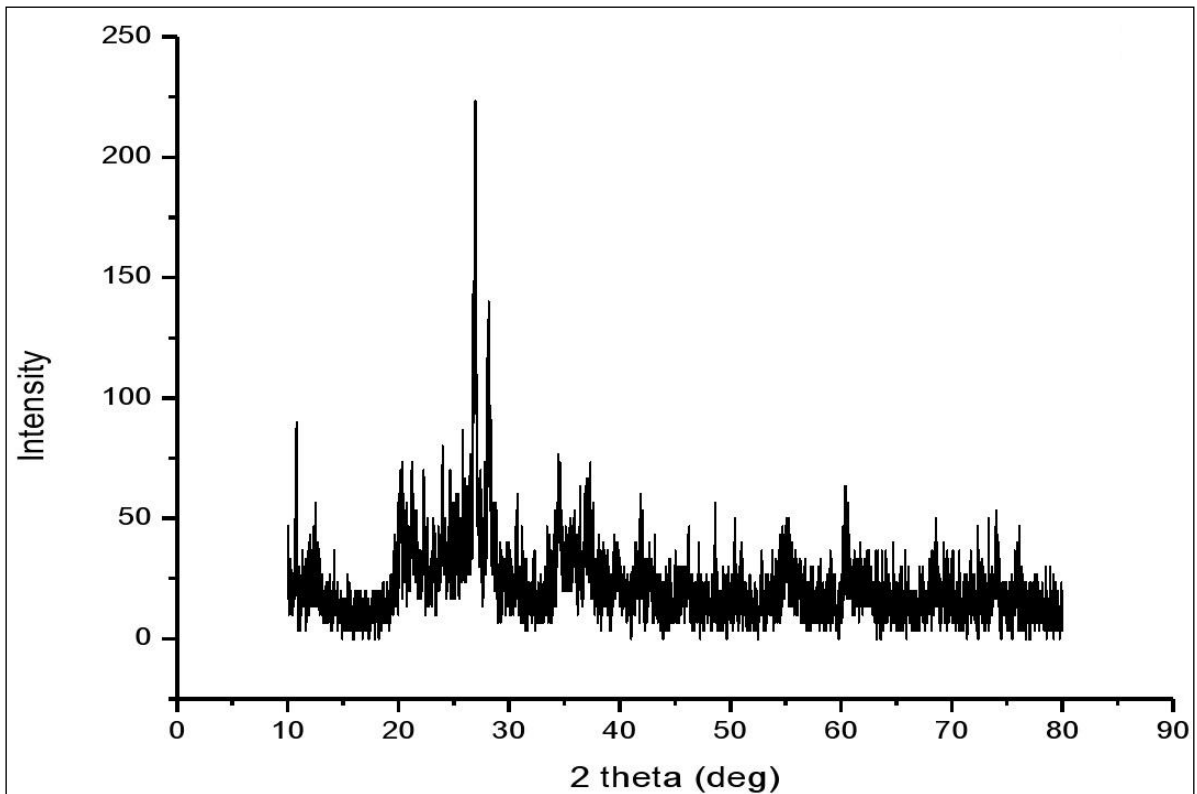
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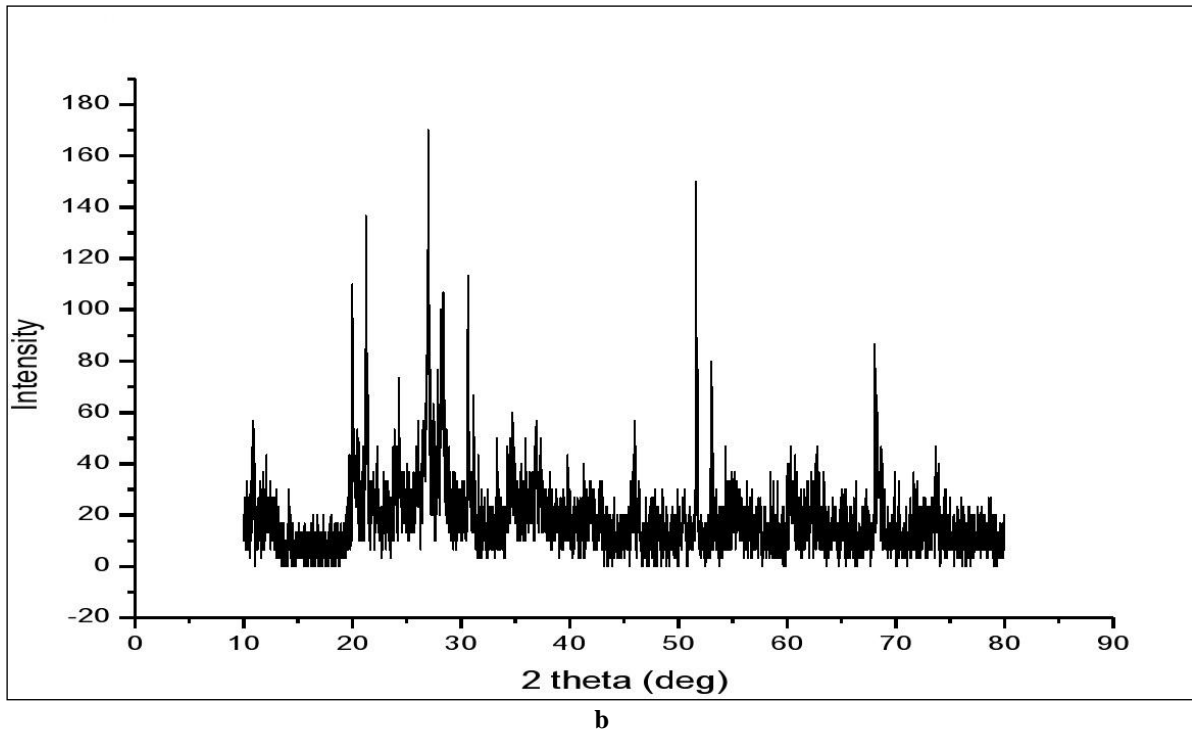
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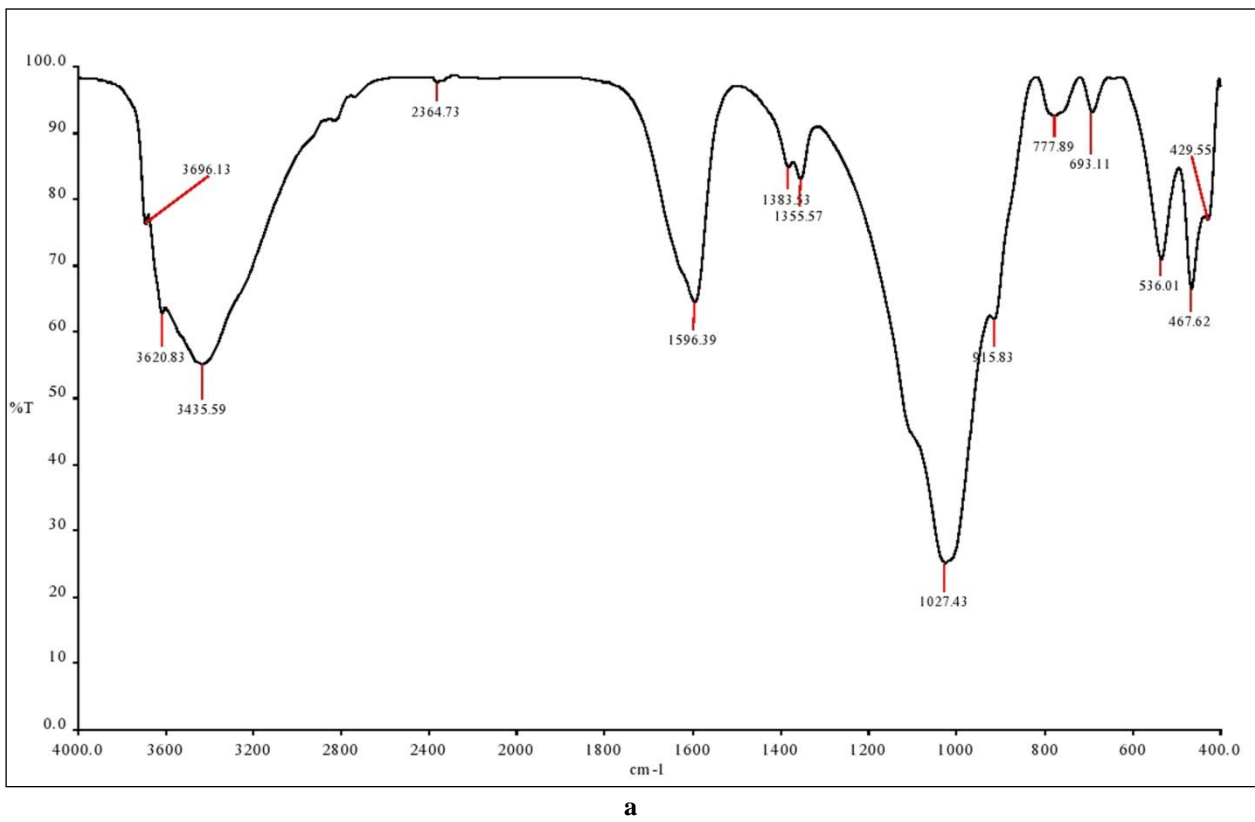
**Figure 6.** a. SEM image of clay material before fluoride adsorption, b. SEM image of clay material after fluoride adsorption



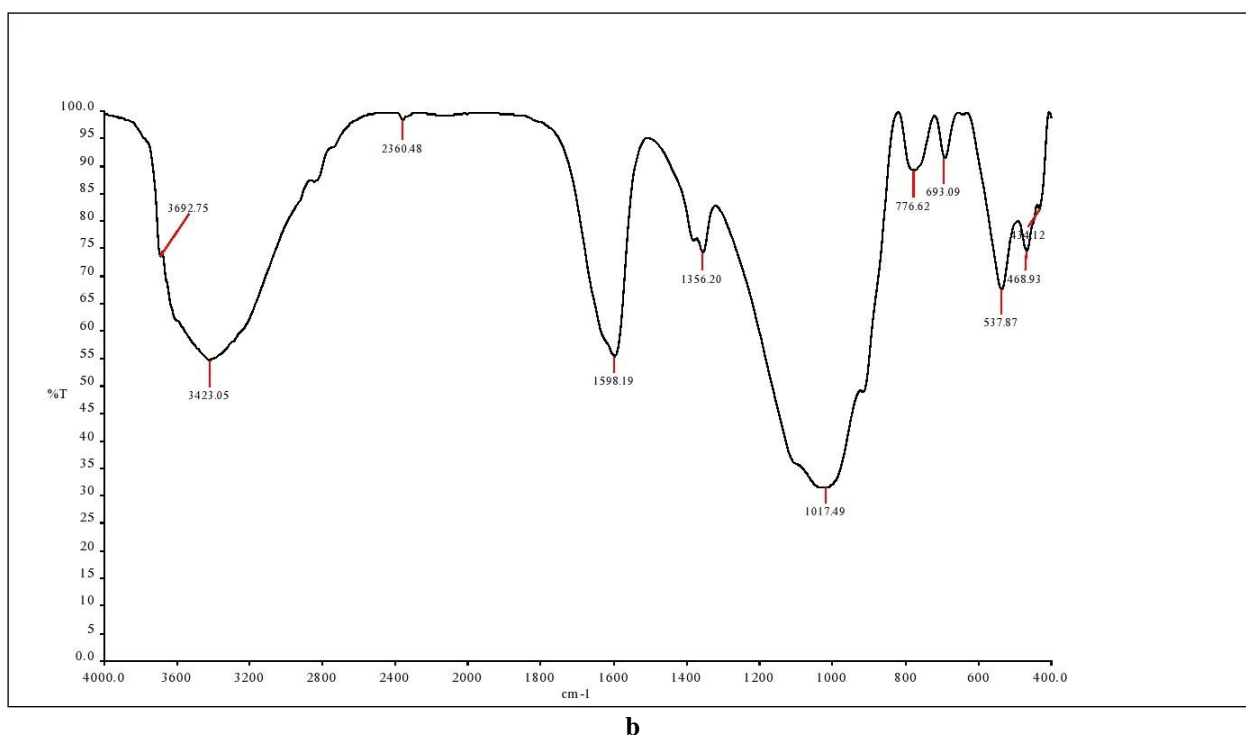
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**Figure 7. a.** X-ray diffraction pattern of clay material before fluoride adsorption, **b.** X-ray diffraction pattern of clay material after fluoride adsorption







**Figure 8 a:** FT-IR Spectrum of clay material before fluoride adsorption **b:** FT-IR Spectrum of clay material after fluoride adsorption

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## Persian Abstract

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### چکیده

هدف از این پژوهش بررسی کارایی خاک رس برای حذف فلوراید اضافه از آب های زیر زمینی است. این پژوهش براساس نتایج تجربی آزمایشگاهی انجام شده است. مواد رسی طبیعی جمع آوری شده و در آون و در دمای  $105^{\circ}\text{C}$  به مدت ۲۴ ساعت خشک شدند. تاثیر pH، زمان تماس، غلظت جاذب، دما و سایز جاذب مورد بررسی قرار گرفت. به منظور تعیین خصوصیات فیزیکی مواد رسی (اندازه ذره، سایز حفرات، پراکندگی، ناهمواری سطحی) تست های SEM، FT-IR و XRD انجام شد. بازده حذف توسط خاک رس با افزایش غلظت جاذب، زمان تماس و کاهش غلظت اولیه  $\text{F}^{-}$  افزایش می یابد. در pH های پایین ( $\text{pH}=2$ )، بالاترین مقدار جذب توسط مواد رسی اتفاق می افتد ( $\text{F}^{-}=1\text{ mg/L}$ ). میزان جذب فلوراید با افزایش دما تا دمای ماکزیمم  $343\text{ K}$  از  $1/0\text{ mg/L}$  تا  $1/6\text{ mg/L}$  افزایش می یابد ( $\text{C}_0=2/3\text{ mg/L}$ ). این قضیه نشان می دهد که این فرآیند در طبیعت یک فرآیند گرماگیر است. نتایج نشان می دهد که مواد رسی می توانند به خوبی برای حذف فلوراید مورد استفاده قرار بگیرند. از این تحقیق می توانیم نتیجه بگیریم که مواد رسی ارزان، کارآمد بوده و جاذبی موافق با طبیعت برای جذب فلوراید از محلول های آبی است.