

Enhanced fluoride sorption by mechanochemically activated kaolinites

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Abstract

Kaolinite clay obtained from the mines was processed and studied for its fluoride sorption capacity. The surface area of the clay mineral was increased from 15.11 m²/g (raw) to 32.43 m²/g (activated) by mechanochemical activation. Batch adsorption studies were conducted to optimize various equilibrating conditions like the effect of contact time, dosage, pH for both raw and micronized kaolinites (RK and MK). The effect of other interfering anions on the defluoridation capacity (DC) of the sorbents was studied. Sorption of fluoride by the sorbents was observed over a wide pH range of 3–11. The studies revealed there is an enhanced fluoride sorption on MK. FTIR and XRD were used for the characterization of the sorbent. The surface morphology of the clay material was observed using SEM. The adsorption of fluoride was studied at three different temperatures, viz., 303, 313 and 323 K. The sorption data obtained at optimized conditions were subjected to Freundlich and Langmuir isotherms. Sorption intensity ($1/n$) (0.770–0.810) has been evaluated using Freundlich isotherm, whereas the values of sorption capacity Q^0 (0.609, 0.714 and 0.782 mg/g) and binding energy b (0.158, 0.145 and 0.133 L/mg) at three different temperatures have been estimated using Langmuir isotherm. Adsorption process was found to be controlled by both Freundlich and Langmuir isotherms. Thermodynamic studies revealed that the sorption of fluoride on MK is endothermic and a spontaneous process. The kinetic studies indicate that the sorption of fluoride on MK follows pseudo-first-order and intraparticle diffusion models.

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1. Introduction

Fluoride in drinking water may be beneficial or may have detrimental effects on health depending on the concentration of fluoride present in it. Excessive intake of fluoride greater than 1 ppm can cause dental, skeletal and non-skeletal forms of fluorosis. Skeletal and dental problems can be prevented by maintaining fluoride concentration of about 1 ppm from dietary intake [1]. A number of defluoridation techniques have been suggested for the removal of excess fluoride. Depending upon their mode of action they are classified into three major types, viz., those based on chemical addition [2–5], adsorption pro-

cess [6–10] and ion exchange mechanism [11–13]. Membrane process such as reverse osmosis [14], nanofiltration [15], electro dialysis [16] and Donnan dialysis [17] were recently investigated to reduce fluoride concentration in water.

Recently, the attention of the scientists has been devoted to many different types of soil sorbents such as spent bleaching earth [18], wallstonite and China clay [19], zeolites [20], red mud [21], montmorillonites [22], etc. Kaolinite clay has been found to remove fluoride by sorption. However, the sorptive capacity has been rated low when compared to other clay minerals. As most of the materials remove fluoride by sorption mechanism, the surface area and number of active sites of the sorbent influence the sorption capacity. Hence surface modifications would definitely make the material most promising for sorption. This could be achieved by physical or chemical methods. In the present study, a simple physical method called

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mechanochemical activation was adopted to enhance the surface area which in turn would definitely increase the sorption capacity of the sorbent.

Mechanochemical activation is one such method which involves simple grinding of an inorganic material and this would lead to physical disintegration along with the formation of active surfaces as well as changes in the physicochemical behaviour of materials. Generally this kind of process as applied to crystalline solid produces a loss of crystallinity (amorphization) [23,24] together with the increase in surface energy and surface reactivity of the material and consequently in chemical activity [25].

Mechanochemical activation was studied in relation to the behaviour of clay minerals and many works have been reported on the effect of grinding on kaolinites [26,27]. Suraj et al. [28] observed that grinding in oscillatory disc mill proved to be more effective in reducing the size of the clay particle within a short span of time. Maximum surface was attained with 10 min grinding time after which there was a decrease in surface area due to collapse of crystal structure.

Fluoride sorptive studies using MK was not reported earlier and therefore the present work reports the defluoridation studies using MK. A detailed study on fluoride sorption capacity of MK has been presented in this paper. Mechanism of fluoride sorption has been explained on the basis of isothermic, kinetic and thermodynamic models. For the purpose of comparison, the raw kaolinite (RK) was also subjected to all the defluoridation studies.

2. Materials and methods

2.1. Sorbent

Raw kaolinite which was collected from a mine was purified and supplied by M/s English India Clays Ltd., Trivandrum, Kerala. The sample was of a fine quality paper coating clay containing >95% kaolinite of which 86% is in <2 μm fraction. The chemical composition of the sample in percentage is shown in Table 1.

In order to increase the surface area, mechanochemical activation of the RK was carried out as detailed below: the sample was ground with oscillatory disc mill (Siebtechnik, Germany). This device works through friction and the impact caused by oscillatory rings and a cylinder (discs) inside a casing containing the sample and the grinding was extremely rapid. Thirty grams

of sample was ground for 10 min, cooled for 30 min and the sample was named as MK which is used for defluoridation studies. Surface area measurements were obtained using Micrometrics Gemini 2360, surface area analyzer and there was an enhancement of surface area from 15.11 m^2/g (RK) to 32.43 m^2/g (MK).

2.2. Sorption studies

Sorption studies of fluoride were carried out by batch equilibration method as follows: in a typical case 1 g of the clay which was fixed as the optimum dosage for all fluoride initial concentrations was added to 50 ml of sample with 3 mg/L of fluoride as initial concentration. The contents were shaken thoroughly using a shaker rotating at a speed of 125 rpm. The solution was then filtered and the fluoride ion concentration was measured. Besides determining the defluoridation capacities, the effects of variables like contact time for maximum defluoridation, dosage, pH of the medium and the influence of co-anions which are normally present in water were also investigated. The adsorption of fluoride ions on clay was also studied at different initial concentrations (2–10 mg/L) in the temperature range of 303, 313 and 323 K.

2.3. Characterization of MK

The surface morphology of the MK before and after treatment with fluoride was visualized by SEM with HITACHI-S-3000H model. The raw and treated clay samples were also scanned using SEM, in order to examine the possible morphological changes in the surface. The powdered diffractograms of the samples were obtained using X'pert PRO (PANalytical make) diffractometer coupled to a copper-anode X-ray tube and the FTIR measurements were taken using JASCO-460 plus model at ambient conditions using KBr as diluent to determine the functional groups on the clay adsorbents.

2.4. Methods of analysis

Fluoride determination was done using expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (all Orion USA make). The pH measurements were done with the same instrument with pH electrode. The concentrations of NO_3^- and SO_4^{2-} ions were determined using UV–vis spectrophotometer (Perkin-Elmer, Lambda 35). pH_{zpc} (pH of zero point charge) was determined by pH drift method [29]. All other water quality parameters were analyzed using standard methods [30].

Computations were made using Microcal Origin (Version 6.0) software. The goodness of fit was discussed using regression correlation coefficient (r) and standard deviation (S.D.).

3. Results and discussion

3.1. Effect of contact time

Fig. 1 shows the variation of DC with contact time for both RK and MK. It was observed that maximum concentration of

Table 1
Chemical constituents of kaolin

| Chemical composition | Percentage |
|------------------------------------|------------|
| SiO_2 | 47.05 |
| Al_2O_3 | 36.98 |
| Fe_2O_3 | 0.78 |
| TiO_2 | 0.53 |
| Na_2O | 0.12 |
| K_2O | 0.08 |
| LOI ^a (1025 °C for 1 h) | 14.31 |

^a Loss on ignition.

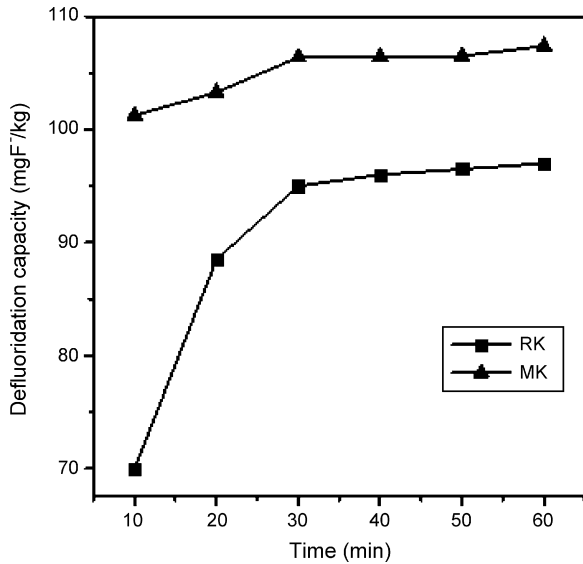


Fig. 1. Effect of contact time.

fluoride removal was attained within 30 min and there after it almost remained static for both modified and raw kaolinites. So 30 min was fixed as the period of contact for further studies. The DC of the MK is 106 mg F⁻/kg whereas for RK it is only 96 mg F⁻/kg at 30 min.

3.2. Effect of dosage

In order to fix the minimum dosage for maximum fluoride removal, experiments as a function of dosage was carried out. The percent removal of both RK and MK samples at different dosages (0.5–2.5 g) was measured. It was observed as shown in Fig. 2 that the percent removal increases by increasing sorbent dosage from 0.5 to 1.0 g and stayed almost constant after 1 g of the sample in both RK and MK samples. Hence for further experiments the sorbent dosage was optimized as 1 g. The increase

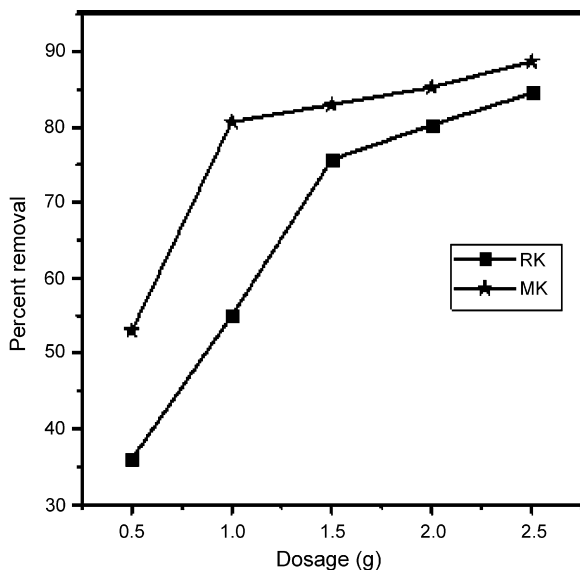


Fig. 2. Effect of dosage.

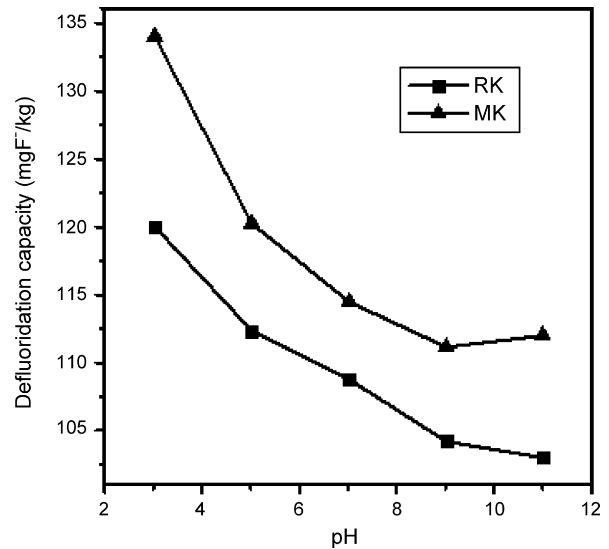


Fig. 3. Effect of pH on fluoride adsorption.

in sorption capacity with increase in dosage is obvious, because any adsorption process depends upon the number of active sites. The same explanation holds good for the increased DC of MK than RK.

3.3. Effect of pH

The removal of fluoride ions from aqueous solution was highly dependent on the solution pH in many cases as it altered the surface charge on the sorbents [31]. Any solid surface can develop charge by adsorption of ions, where the solid acts as an electrode (e.g., H⁺ and OH⁻ on the surface of clays). In clay aqueous systems the potential of surface is determined by the activity of ions (H⁺ or pH) which react with the mineral surface. So pH plays an important role and it controls the adsorption of the fluoride at the clay–solution interface. Such interface on acid–base dissociation develops positive and negative charges of the surface [32]. Defluoridation studies were carried out with both RK and MK at various pH ranging from 3 to 11. The plot of DC at various pH ranges as given in Fig. 3 clearly indicates that the DC of both RK and MK were influenced by pH of the medium. The DC of the sorbents was found to be more at lower pH than at higher pH levels. It was found that the higher fluoride removal of 134 mg F⁻/kg was noticed at pH 3 and the efficiency decreased with the increase in pH. At neutral pH the capacity being 114 mg F⁻/kg and at pH 11 it was only 112 mg F⁻/kg for the MK whereas in RK maximum DC noted at pH 3 was 120 mg F⁻/kg. Similar trend was observed by Karthikeyan et al. [33] when alumina was used as the adsorbent for fluoride removal where the DC of the alumina was maximum at pH 3 which was nearly double than it was at pH 7. Higher adsorption at lower pH ranges leads to the assumption that chemisorption dominates in this range and physisorption occurs at higher pH ranges. The p*H*_{zpc} for both the clays are around 4 [34] suggesting that above this pH the sorption is mainly due to physisorption.

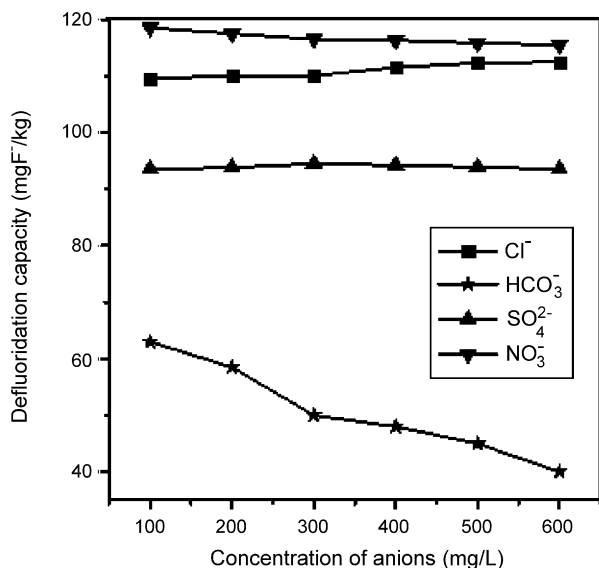


Fig. 4. Effect of other anions on DC onto MK.

3.4. Effect of other anions

Though both RK and MK follow the same trend, MK has a slightly higher DC and hence for further studies only MK was employed. The DC of MK was experimentally verified in the presence of other common anions like Cl⁻, SO₄²⁻, NO₃⁻ and HCO₃⁻. Fig. 4 depicts the influence of other anions on the DC of the MK. There is no significant influence on the DC in the presence of sulphate, chloride and nitrate ions, but the DC decreases by 50% in the presence of 100 mg/L bicarbonate ion and further decreases by 70% as the concentration of bicarbonate are increased to 600 mg/L. A similar interfering role on the DC was earlier reported in the defluoridation property on activated alumina [33]. This is due to competition of bicarbonate ions with the fluoride ions at the active site on the surface of the adsorbent. Selectivity of fluoride by the sorbent depends on the factors, viz., size, charge, polarizability, electronegativity difference, etc. The preference of adsorption of anions by this sorbent may be in the following order, F⁻ > HCO₃⁻ > Cl⁻, SO₄²⁻ and NO₃⁻.

3.5. Adsorption isotherms

The Freundlich equation is commonly used to explain the adsorption of pollutants from aqueous medium empirically [35]. The Freundlich equation is expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{1}$$

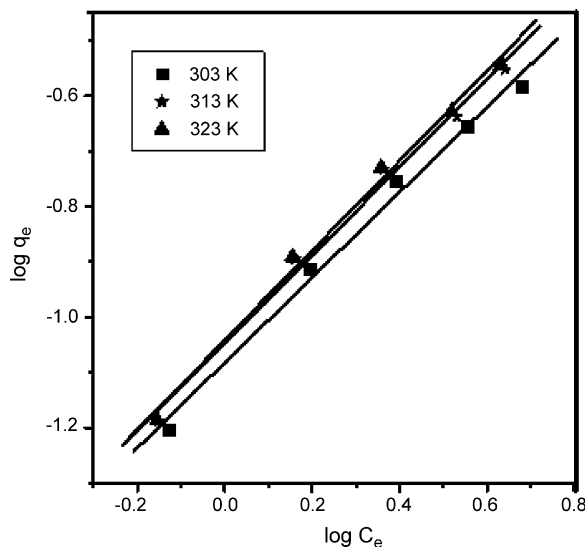


Fig. 5. Freundlich isotherm of MK.

where k_f and n are adsorption capacity and intensity of adsorption. Fig. 5 shows the linear plots of $\log q_e$ versus $\log C_e$ indicating that the adsorption follows Freundlich isotherm. The values of Freundlich constants k_f and n given in Table 2 are derived from the intercepts and slopes, respectively. Values of $1/n$ are lying between 0.1 and 1.0 and the n value lying in the range of 1–10 confirms the favorable conditions for adsorption [36].

The applicability of Langmuir isotherm was also tested on fluoride adsorption on MK. The Langmuir equation [37] was applied in the form

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{2}$$

where Q^0 and b are Langmuir constants indicating the adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e versus C_e (cf. Fig. 6) with high r values indicates the monolayer adsorption on MK. The values of Q^0 and b were calculated from the slopes and intercepts of the plots, respectively, and are presented in Table 2.

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter [38,39]:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

Table 2
A comparison of the Freundlich and Langmuir isotherm parameters obtained at different temperatures

| Temperature (K) | Freundlich isotherm parameters | | | | | Langmuir isotherm parameters | | | |
|-----------------|--------------------------------|-------|---|-------|-------|------------------------------|----------|-------|-------|
| | 1/n | n | k _f (mg/g) (L/mg) ^{1/n} | r | S.D. | Q ⁰ (mg/g) | b (L/mg) | r | S.D. |
| 303 | 0.770 | 1.299 | 0.083 | 0.995 | 0.027 | 0.6097 | 0.1587 | 0.995 | 0.318 |
| 313 | 0.793 | 1.261 | 0.089 | 0.996 | 0.068 | 0.7147 | 0.1455 | 0.987 | 0.384 |
| 323 | 0.810 | 1.235 | 0.091 | 0.996 | 0.025 | 0.7822 | 0.1333 | 0.989 | 0.313 |

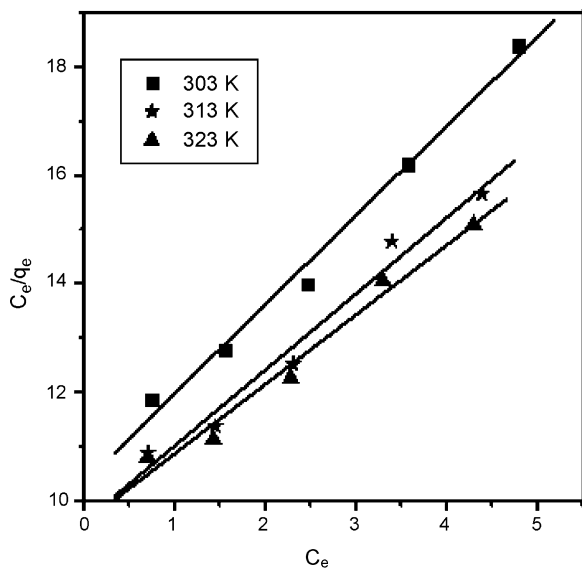


Fig. 6. Langmuir isotherm of MK.

where b is the Langmuir isotherm constant and C_0 is the initial concentration of fluoride (mg/L). The R_L value at different temperatures studied were calculated and are given in Table 3. The R_L values between 0 and 1 indicate favorable adsorption for all the initial concentrations and temperatures studied. So adsorption confirms to both Langmuir and Freundlich isotherms.

3.6. Chi-square analysis

To identify a suitable isotherm model for the sorption of fluoride on MK this analysis has been carried out. The chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement is

$$\chi^2 = \sum \left(\frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (4)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the experimental data of the equilibrium capacity (mg/g). If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number. Therefore, it is necessary also to analyze the data set using the non-linear chi-square test to confirm the best-fit isotherm for the sorption system [40].

Table 4
Thermodynamic parameters for the fluoride sorption by MK

| Temperature (K) | K_o | ΔG° (kJ/mol) | ΔH° (kJ/mol) | ΔS° (kJ/mol K) |
|-----------------|-------|------------------------------|------------------------------|--------------------------------|
| 303 | 0.110 | -5.553 | 4.05 | 31.66 |
| 313 | 0.106 | -5.826 | | |
| 323 | 0.100 | -6.181 | | |

The χ^2 values are calculated using Eq. (4) and are given in Table 3. The χ^2 values of both the isotherms are comparable and hence the adsorption of fluoride on MK follows both Freundlich and Langmuir isotherms and better fits to Langmuir as its χ^2 value is slightly less than that of Freundlich model.

3.7. Thermodynamic parameters

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated using the following expressions

The free energy of sorption process, considering the sorption equilibrium constant K_o , is given by the equation

$$\Delta G^\circ = -RT \ln K_o \quad (5)$$

where ΔG° is the free energy of sorption (kJ/mol), T the temperature in Kelvin and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The sorption equilibrium constant K_o for the sorption reaction was determined from the slope of the plot $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating to zero C_e according to the method suggested by Khan and Singh [41].

The sorption equilibrium constant may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature.

$$\ln K_o = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{RT} \quad (6)$$

where ΔH° is the heat of sorption (kJ/mol) and ΔS° is the standard entropy changes (kJ/mol K).

The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_o$ against $1/T$. The values of K_o , ΔG° , ΔH° and ΔS° are presented in Table 4.

The negative values of standard free energy and positive value of entropy change indicate the spontaneity of the sorption of fluoride. The value of enthalpy change was positive, indicating that the sorption process is endothermic.

Table 3
The R_L and chi-square values of MK

| Temperature (K) | R_L values | | | | | χ^2 values for isotherms | |
|-----------------|--------------|--------|--------|--------|---------|-------------------------------|----------|
| | 2 mg/L | 4 mg/L | 6 mg/L | 8 mg/L | 10 mg/L | Freundlich | Langmuir |
| 303 | 0.759 | 0.612 | 0.512 | 0.441 | 0.387 | 4.74 E-4 | 4.17E-5 |
| 313 | 0.775 | 0.632 | 0.534 | 0.462 | 0.407 | 7.39E-4 | 5.98E-4 |
| 323 | 0.790 | 0.652 | 0.556 | 0.484 | 0.429 | 1.75E-3 | 1.47E-3 |

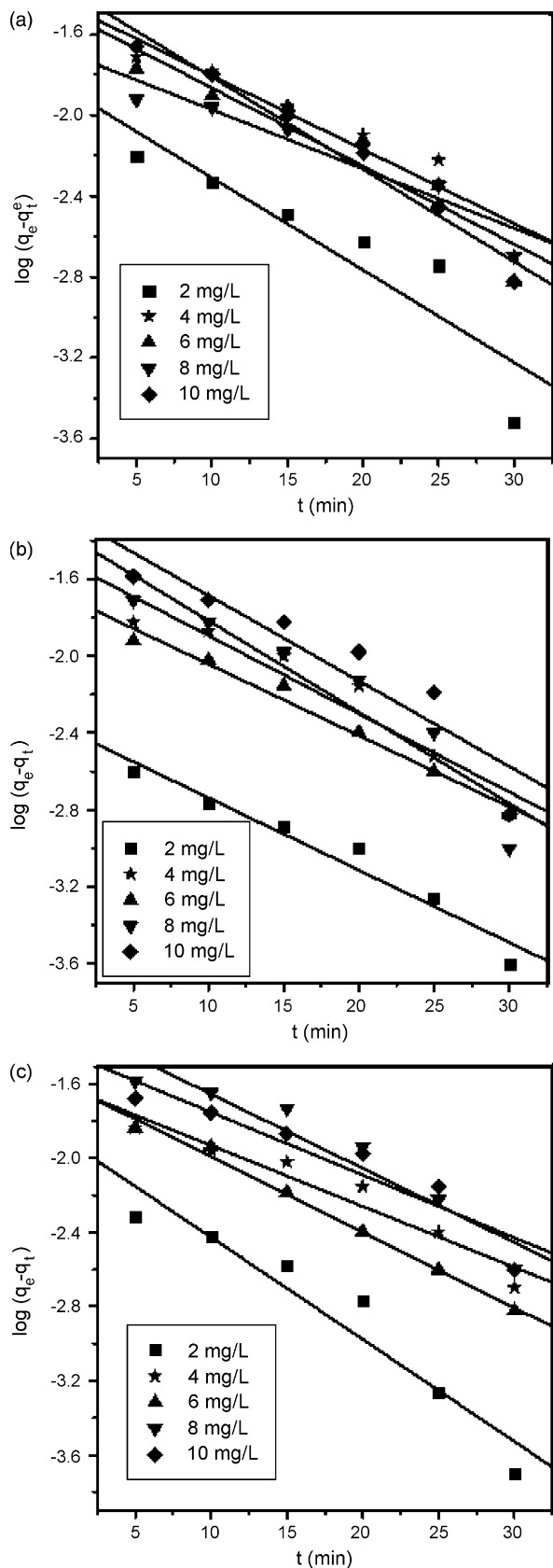


Fig. 7. Lagergren plots of MK at (a) 303 K, (b) 313 K and (c) 323 K.

Table 5

Lagergren constants for fluoride sorption on MK at various temperatures

| C_o (mg/L) | Mass (g) | k_{ad} (min^{-1}) | | |
|--------------|----------|--------------------------------|---------|---------|
| | | 303 K | 313 K | 323 K |
| 2 | 1.0 | 4.5 E-2 | 4.4 E-2 | 5.5 E-2 |
| 4 | 1.0 | 2.9 E-2 | 4.7 E-2 | 3.3 E-2 |
| 6 | 1.0 | 3.8 E-2 | 3.7 E-2 | 4.1 E-2 |
| 8 | 1.0 | 3.6 E-2 | 4.0 E-2 | 4.0 E-2 |
| 10 | 1.0 | 4.5 E-2 | 3.7 E-2 | 3.4 E-2 |

3.8. Adsorption kinetics

The rate constants for adsorption, k_{ad} for the removal of fluoride by mechanochemically activated kaolinites at three different temperatures (303, 313 and 323 K) were determined by the following pseudo-first-order rate expression given by Lagergren:

$$\log(q_e - q_t) = \log q_e \left(\frac{k_{ad} t}{2.303} \right) \quad (7)$$

where q_e and q_t are the amount of fluoride adsorbed at equilibrium and at various time interval t , respectively. The Lagergren plots of $\log(q_e - q_t)$ versus t for various temperatures are given in Fig. 7a–c. The linearity indicates that the system obeys pseudo-first-order kinetics. The values of k_{ad} at three different temperatures were calculated from the slopes of the respective linear plots and are given in Table 5.

3.9. Intraparticle diffusion model

The contact time experimental data was used to study rate determining step in the adsorption process as shown by Weber and Morris [42]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume the mass transfer from the bulk liquid to the particle external surface which does not limit the rate. One might then postulate

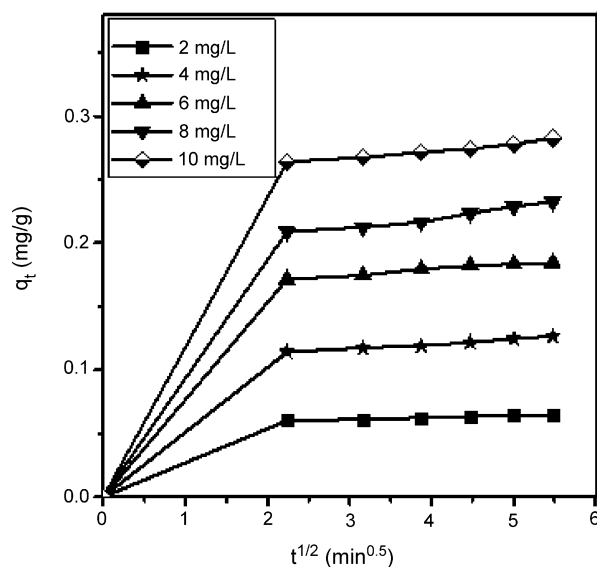


Fig. 8. Validation of Weber–Morris equation for fluoride sorption onto MK.

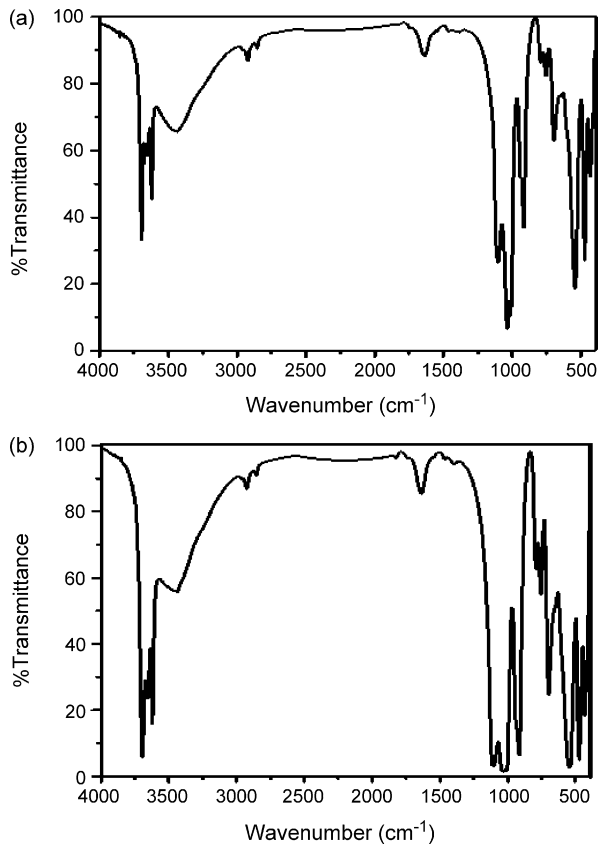


Fig. 9. FTIR spectra of MK: (a) before fluoride sorption and (b) after fluoride sorption.

that the rate determining step may be either film or intraparticle diffusion.

In batch reactors due to rapid agitation, there is a possibility that the adsorbate ions can diffuse from solution to the adsorbent pores and this may form the rate determining step [43]. The plot of q_t versus $t^{1/2}$ is shown in Fig. 8. All the plots have the same general features of initial curved portion followed by linear portion and a plateau. The initial portion is attributed to the bulk

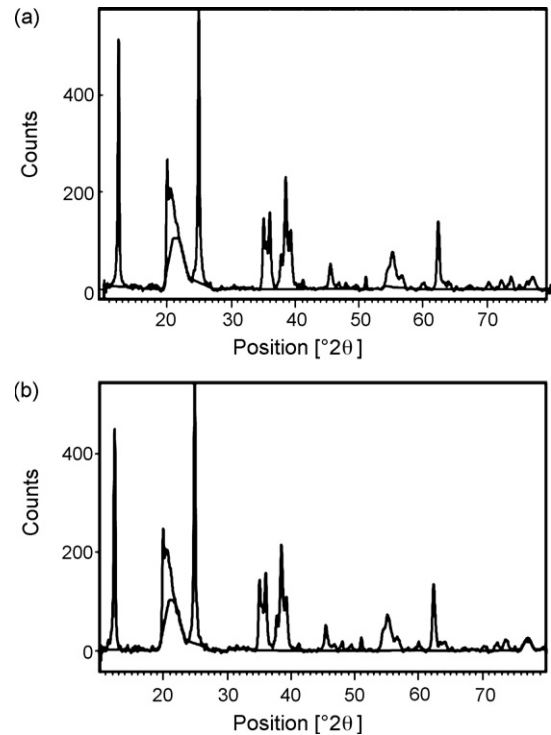


Fig. 11. XRD spectra of MK: (a) before fluoride sorption and (b) after fluoride sorption.

diffusion and subsequent linear portion is attributed to the intraparticle diffusion. The fitness of particle diffusion model gives further evidence that the fluoride removal is a surface process under the studied experimental conditions.

3.10. Instrumental studies

In order to understand the nature of fluoride sorption on MK sample FTIR, SEM and XRD studies were performed using the fluoride treated and untreated samples. FTIR spectra of MK and fluoride sorbed MK are presented in Fig. 9a

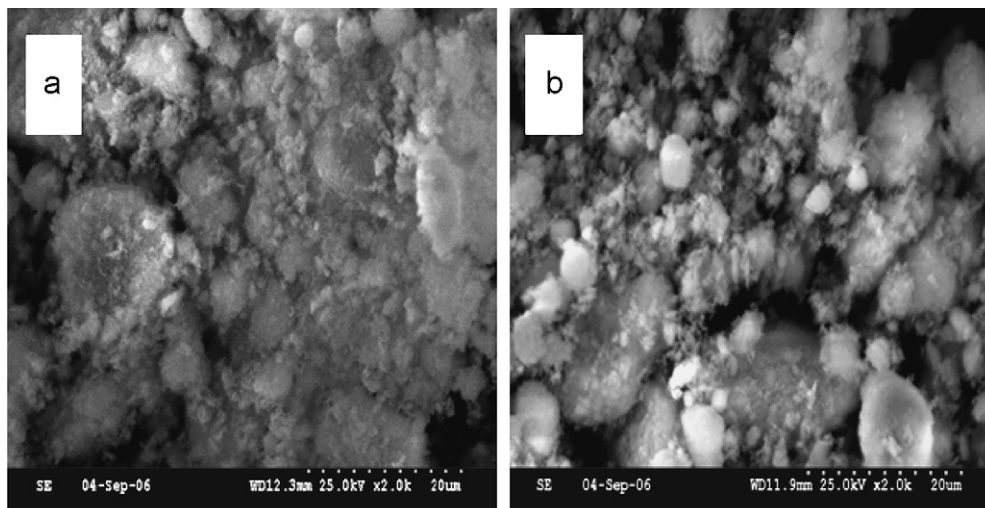


Fig. 10. SEM images of MK: (a) fresh and (b) fluoride-sorbed.

and b, respectively. FTIR spectra shows usual kaolinitic peaks at 3694 cm^{-1} for inner surface —OH stretching, 3626 cm^{-1} for inner —OH stretching, 1110 and 1033 cm^{-1} for Si—O bending, 695 cm^{-1} for Si—O stretching, 471 and 433 cm^{-1} for Si—O bending, 789 and 753 cm^{-1} for $\text{Si—O—Al}^{(\text{VI})}$ compounded vibrations, 541 cm^{-1} for $\text{Si—O—Al}^{(\text{IV})}$ compounded vibrations and 433 cm^{-1} , 471 cm^{-1} for Si—O vibrations. The decrease in the intensity of transmittance in fluoride treated MK at 3694 and 3620 cm^{-1} indicates the exchange of OH from its surface [28]. This data confirms the fact that fluoride removal also follows ion exchange mechanism in addition to adsorption.

The SEM photographs of untreated and fluoride treated MK is provided in Fig. 10a and b, respectively. The difference in the surface morphology of these samples clearly confirms the fluoride sorption on fluoride treated MK. The respective XRD patterns of MK samples before and after fluoride sorption are presented in Fig. 11a and b. The results reveal that there is no major change in the crystal structure after fluoride adsorption at this low concentration level. Similar results on XRD patterns on fluoride adsorption were reported by Diaz-Nava et al. [44] while studying the DC of water using zeolite.

4. Conclusions

The experimental results reveal that there is an enhancement in the DC of MK when compared with RK. The adsorption follows both Langmuir and Freundlich isotherms and best-fit to Langmuir model. FTIR studies indicate the participation of surface OH group in the fluoride exchange. Hence, to some extent fluoride ions are also removed by ion exchange process. The kinetics of adsorption of fluoride on MK follows pseudo-first-order model and intraparticle diffusion pattern. The spontaneity of the process is indicated by values of thermodynamic parameters. The material is cheap and indigenous. The activation method is also very simple, does not cause any pollution, hence eco-friendly. Hence, MK could be employed as a low cost defluorinating agent.

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