

## Montmorillonite K 10: a Scavenger for Fluoride from Aqueous Solution

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**Abstract:** The objective of the present work is to assess the defluoridation capacity of montmorillonite K10. It involves batch adsorption experiments to investigate the effects of adsorbent dose, initial concentration, pH, interfering ions, adsorption kinetics, adsorption isotherms etc. The Freundlich, Langmuir and Dubinin-Raduskevich models were applied to describe the adsorption isotherms and their isotherms constants were also calculated. The Freundlich and Dubinin-Raduskevich model ( $R^2 = 0.99$ ) offered better fit to the equilibrium data than the Langmuir model. The mean adsorption energy (2.83 KJ/mol) calculated from Dubinin-Raduskevich (D-R) -isotherm indicates that fluoride removal takes place by physisorption. The kinetic sorption data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The kinetic sorption data offered excellent fit to pseudo-second-order model with a high correlation coefficient value ( $R^2 = 0.99$ ). XRD and EDAX studies were carried out in order to get better insight into the mechanism of adsorption process. The performance of the adsorbent has been tested for the field sample collected from fluoride affected areas of Dhar, Madhya Pradesh, Central India. These results demonstrate the effectiveness and feasibility of Montmorillonite K10 for the removal of fluoride from water.

**Key words:** Dubinin-Raduskevich isotherm • Energy Dispersive Analysis of X-rays (EDAX) • Fluoride removal • Montmorillonite K10 • X-Ray Diffraction (XRD).

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### INTRODUCTION

A potent toxic element which is ubiquitously distributed in soil, earth and water is fluoride. Fluoride ion exhibits unique properties in water depending upon its concentration. In minute or optimum concentration, it is beneficial especially to young children for the calcinations of dental enamel and bone formation but in excess concentration beyond the prescribed limits, it affects the metabolism of elements like calcium, phosphorus in human body which in turn leads to dental (mottling of teeth), skeletal (deformation of bones in children and adults) and also non-skeletal fluorosis in children as well as adults [1-3]. Higher concentrations of fluoride in ground water not only affects human beings but also plants and animals. Fluoride inhibits plant metabolism which results in necrosis, needle scratch and tip burn diseases while in animals, it can interfere with carbohydrates, lipids, enzymes etc. at higher dosage [4].

Higher level of fluoride in groundwater is a growing global problem, occurring in various countries of Africa

and Asia as well as USA. In India alone, more than 66 million people including 6 million children below the age of 14 years are 'at risk' of fluorosis [5]. Fluoride normally enters the environment and human body through water, food, industrial exposure, drugs, cosmetics etc. However, still drinking water is the single major source of daily fluoride intake [6]. According to the Department of Drinking Water under the Ministry of Rural Development, India, rural water supply is to a large extent dependent on groundwater (85 %). Hence, it becomes essential to reduce the fluoride concentration within permissible limit of 1.5 mg/L in order to maintain public safety and quality of life according to the guidelines for drinking water quality and standard authority of India [7].

Though, various treatment methods like coagulation or precipitation, adsorption, electrochemical and membrane based have been reported for the removal of excess fluoride from water but still a lasting solution is yet to be found. Coagulation or precipitation methods are generally effective but are unpromising in bringing down the fluoride concentration within the permissible levels.

The electrochemical methods in general require high cost in terms of both installation and maintenance. Other membrane based separations like reverse osmosis [8], nanofiltration [9], electrodialysis [10] etc. are effective and can bring fluoride concentration within permissible limit but they are relatively expensive to install and operate and are generally prone to fouling, scaling or membrane degradation [11]. Hence, the high cost of these methods may be a major drawback for implementation particularly in developing countries. Among them, adsorption is still widely accepted, ideal and appropriate pollution removal technique practiced in many fluoride affected areas of the developing world because of its simplicity in operation and cost-effectiveness. The efficiency of any adsorption method depends upon the nature of the adsorbent used. However, in recent years, scientists have devoted their attention on various types of soil adsorbents such as waste mud [12], wallastonite and china clay [13], natural materials [14], red mud [15], brick powder [16], kaolinites [17], clay adsorbent [18] etc. for the defluoridation of water and other pollutants with more or less success. Therefore, it is of paramount importance to identify materials with high rate of removal, economical, socially and technical feasible for use at both household and small community levels.

The main objective of the present work is to assess the potential of montmorillonite K10 for the removal of fluoride from water. Studies have also been carried out to determine the effect of various initial fluoride concentrations, adsorbent dose, pH, interfering ions, adsorption kinetics, adsorption isotherms etc. on the efficacy of montmorillonite K10 towards the removal of fluoride. The fluoride removal mechanism of the adsorbent was also investigated by D-R isotherm, kinetics, XRD and EDAX studies to get better insight into the mechanism of adsorption process.

## MATERIALS AND METHODS

**Materials:** Montmorillonite K10 used for the present study was obtained from Lancaster synthesis, India Ltd. All chemicals and reagents used in the present study were of analytical grade purchased from E-Merck India Ltd. Mumbai, India. All synthetic stock solutions of fluoride and other anions such as chloride, sulphate, nitrate, carbonate bicarbonate etc. were prepared by dissolving known weight of corresponding sodium salts in double distilled water and the desired working solutions were prepared from stock solution by appropriate dilution.

**Preparation of the Adsorbent:** About 10g of montmorillonite K10 obtained from the commercial sources was washed with deionised water till filtrate gave negative test for chloride ion with 0.1M silver nitrate solution. The resulted residue or clay was further dried in an oven at 120°C for overnight, then ground in a mortar and pestle to obtain a finely divided powder which was further used for subsequent adsorption studies.

**Batch Adsorption Studies:** Batch adsorption studies were performed by adding known weight of the adsorbent to 100 ml of the desired fluoride solution taken in a 250 ml Tarson conical flask. The contents of flasks were then shaken (150 rpm) thoroughly on a horizontal rotary shaker (Model No. CIS-24, Remi Instruments, Mumbai, India) at room temperature ( $30 \pm 2^\circ\text{C}$ ) for 24 h in order to attain equilibrium. The solution was then filtered and the residual fluoride ion concentration was measured. Besides determining the defluoridation capacities, similar procedure was followed to study the effect of other variables such as adsorbent dose, initial concentration, pH, interfering ions etc. The specific amount of fluoride adsorbed was determined from the following equation:

$$q_e = \frac{C_o - C_e}{W} \times V \quad (1)$$

where;  $C_o$  and  $C_e$  are the initial and equilibrium fluoride concentration in the solution (mg/L), respectively,  $V$  is the volume of the aqueous solution (L) and  $W$  is the weight of the adsorbent (g) used in the present experiments.

**Methods of Analysis:** Fluoride determination was carried out by using fluoride ion selective electrode (Orion number 9409 on a sargent Welch pH/activity meter model PAX 900). The pH measurements were also done with the same instrument with pH electrode. Heavy metals if any released by the adsorbent after equilibrium studies were determined (ICP-AES, Model OPTIMA-4100DV) by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model OPTIMA-4100DV). All other water quality parameters were analysed using standard methods [19].

**Physical Characterization:** Untreated montmorillonite K10 and the treated one with fluoride ion solution were characterized using XRD and SEM coupled with Energy Dispersive Analysis of X-rays (EDAX). A representative experiment was carried out under the given conditions: 30°C, initial fluoride concentration = 100 mg/L, shaking speed = 150 rpm and contact time = 6 h respectively, for

the preparation of XRD and SEM samples. The X-ray diffraction patterns were recorded using X-ray diffractometer, Model (Philips, "X" Pert). The samples were scanned for  $2\theta$  range from  $5^\circ$  to  $80^\circ$ . The SEM coupled with energy dispersive analysis of X-ray (EDAX) has been recorded using Analytical Scanning Electromicroscope, JSM – 6380A, Jeol, Japan.

## RESULTS AND DISCUSSION

**Physical Characterisation:** The XRD patterns of montmorillonite K10 before and after treatment with fluoride solution are shown in Figure 1. The results reveal that there is no major change in the crystal structure of the adsorbent except slight decrease in crystallinity after fluoride sorption. Similar results were also reported by earlier workers [18, 20]. SEM coupled with energy dispersive analysis of X-rays (EDAX) was studied to analyse the elemental constituents of the untreated and treated adsorbent as shown in Figure 2 (a & b). EDAX analysis shows the presence of small amount of fluoride in the spectrum along with other principal elements Si, Al and O and also some other minor elements. It also provides direct evidence for the superficial adsorption or physical adsorption of fluoride on the adsorbent. Similar observations were also reported by earlier workers [21, 22].

**Effect of Adsorbent Dose:** The effect of adsorbent dose on the fluoride removal was studied by using different amounts of adsorbent at a fixed initial fluoride concentration of 5.15 mg/L, pH = 6.7, shaking speed = 150

rpm and contact time = 24 h respectively, as shown in Figure 3. It was noticed that the percentage removal of fluoride increased slightly from 0.5 g/L to 0.9 g/L and then significantly from 1.0 g/L to 5.0 g/L respectively. However, an adsorbent dose of 4 g/L is sufficient to reduce the fluoride concentration below 1.5 mg/L. The increase in fluoride removal with increase in adsorbent dose was obviously due to increase in the availability of fluoride binding active sites [23]. So, it was considered as optimum dose for all the subsequent experiments.

**Effect of Initial Concentration:** The effect of initial fluoride concentration on the percentage removal of fluoride was studied at different initial fluoride concentrations ranging from 5-50 mg/L respectively, by keeping all other parameters constant such as adsorbent dose = 4 g/L, pH = 6.7, shaking speed = 150 rpm and contact time = 24 h. It was apparent from Figure 4 that the percentage of fluoride removal decreases while adsorption capacity increases with increase in initial fluoride concentration. It may be because when initial fluoride concentration is low, the ratio of surface binding active sites to total fluoride is high and hence all fluoride ions could interact with adsorbent sufficiently [24]. But however, when the initial fluoride concentration is high, the numbers of active binding sites are insufficient to interact with all the fluoride ions [25].

**Effect of pH:** The pH of the aqueous solution is an important variable which controls the sorption between the sorbent and water interface. The percentage of fluoride removal by the adsorbent was studied at different

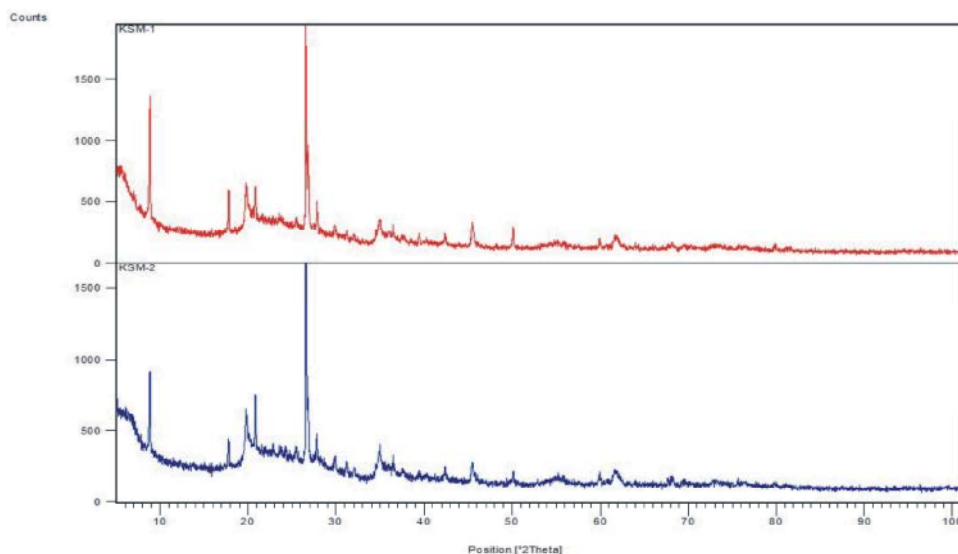


Fig. 1: XRD of untreated and treated montmorillonite K10

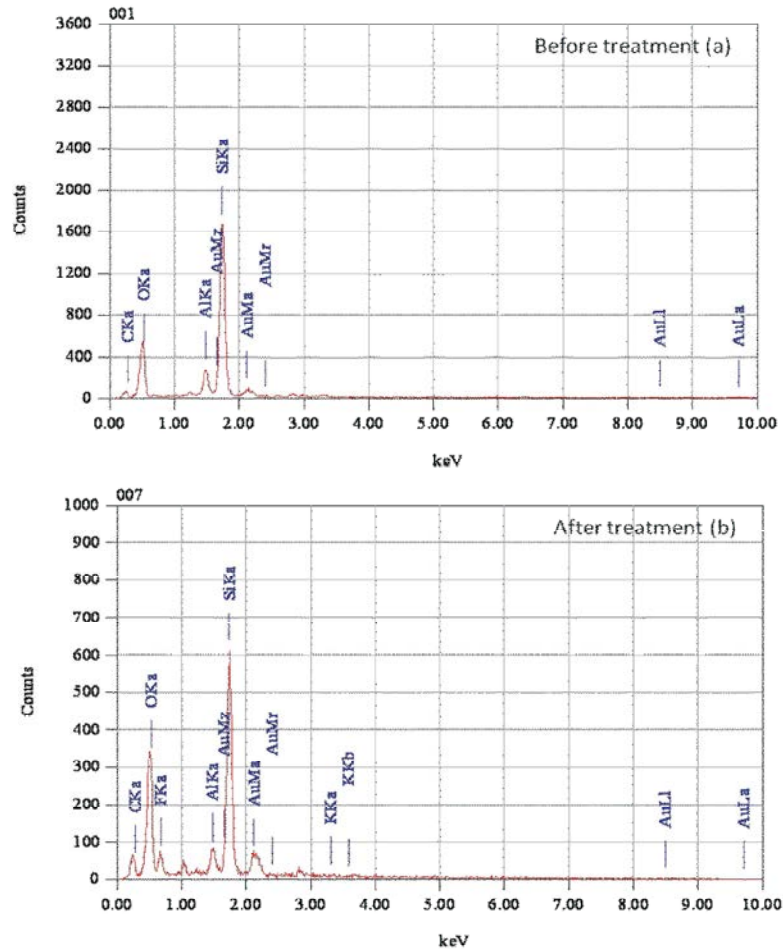


Fig. 2 (a&b): EDAX of montmorillonite K 10 before and after treatment

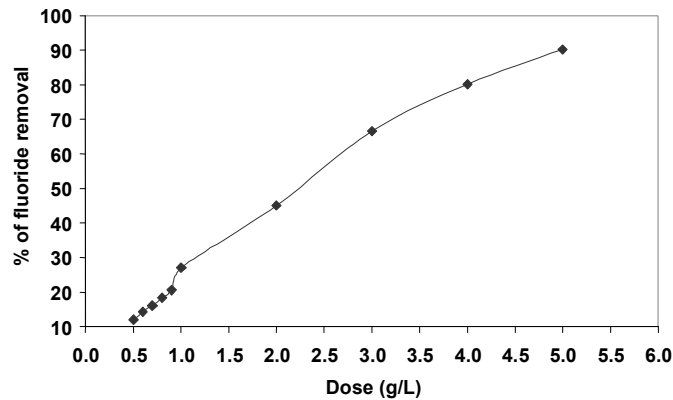


Fig. 3: Effect of adsorbent dose for fluoride removal (Initial concentration = 5.15 mg/L, pH = 6.7, shaking speed = 150 rpm contact time = 24 h)

pH ranging from 3- 8 as shown in Figure 5. It was apparent from Figure 5 that the percentage of fluoride removal remains nearly constant within the pH range of 4 - 7 while decreasing sharply beyond it. The significant decrease in fluoride removal beyond pH = 7 may be

possibly due to the electrostatic repulsion between the negatively charged surface and fluoride ion and also because of the competition between the fluoride and excess amount of hydroxyl ions for active sites [24, 26].

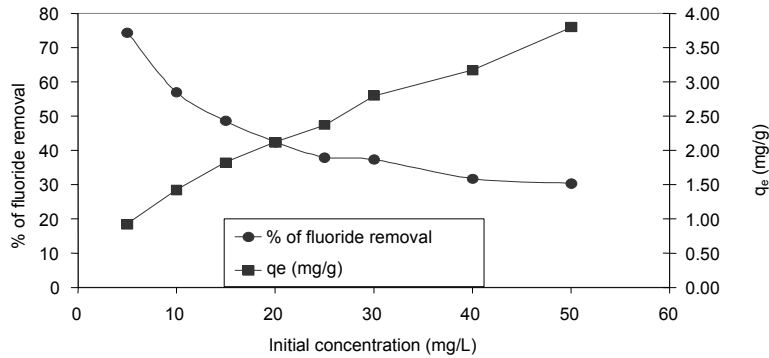


Fig. 4: Effect of initial  $F^-$  concentration for fluoride removal (Adsorbent dose = 4 g/L, pH = 6.7, shaking speed = 150 rpm and contact time = 24 h)

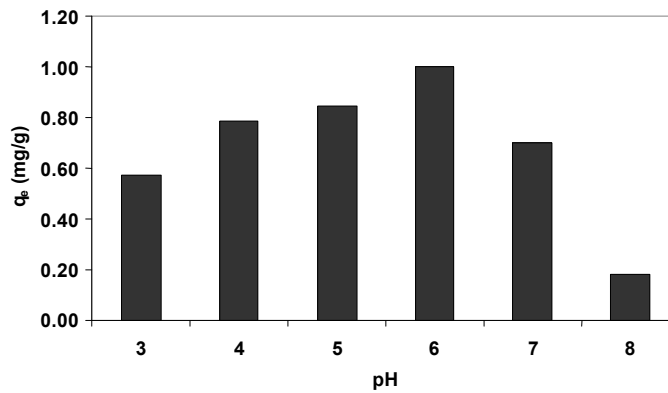


Fig. 5: Effect of pH for fluoride removal (Initial fluoride concentration = 5.22 mg/L, dose = 4 g/L, shaking speed = 150 rpm and contact time = 24 h)

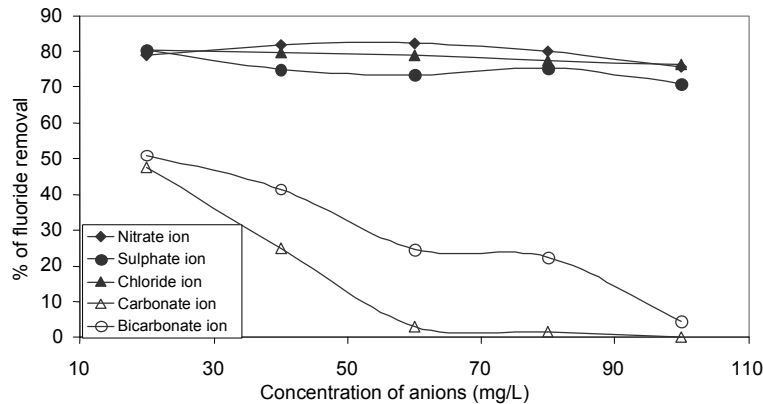


Fig. 6: Effect of interfering ions for fluoride removal (Initial concentration = 5.49 mg/L, dose = 4 g/L, shaking speed = 150 rpm and contact time = 24 h)

**Effect of Interfering Ions:** The influence of interfering ions such as chloride, nitrate, sulphate, carbonate and bicarbonate in addition to fluoride that are usually present in ground water was studied by varying their initial concentrations from 20-100 viz., 20, 40, 60, 80 and 100 mg/L, respectively, with an adsorbent dose = 4 g/L, initial fluoride concentration = 5.49 mg/L, shaking

speed = 150 rpm and contact time = 24 h, respectively. It was apparent from Figure 6 that carbonate and bicarbonate ions showed significant decrease in fluoride removal while other ions such as sulphate, chloride and nitrate showed little or negligible effect on fluoride removal within the concentration range tested. However, the significant reduction of fluoride removal by carbonate

and bicarbonate ions may be due to the change in pH as well as the competing effect of these interfering ions for the active binding sites of the adsorbent [27].

**Adsorption Modelling:** The analysis of equilibrium data for the adsorption of fluoride onto montmorillonite K10 has been done by the linear forms of three important adsorption models, namely Freundlich, Langmuir and Dubinin-Radushkevich (D-R) isotherm models.

**Freundlich Isotherm:** The Freundlich isotherm is used for modelling the adsorption on heterogeneous surfaces [28]. The linear form of the Freundlich isotherm is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (1)$$

where;  $q_e$  is the equilibrium fluoride concentration on the adsorbent (mg/g),  $C_e$  is the equilibrium fluoride concentration of the solution (mg/L),  $K_F$  and  $1/n$  are Freundlich constants related to the adsorption capacity and adsorption intensity, which varies with the heterogeneity of the material. The Freundlich constants  $K_F$  and  $1/n$  or  $n$  can be calculated from the slope and intercept of the linear plot of  $\log q_e$  against  $\log C_e$  and were found to be 1.0147 mg/g and 0.2 or 6.34 respectively, with correlation coefficient ( $R^2$ ) of 0.99. Since the value of  $1/n$  is lying between 0.1 and 1 and also the value of  $n$  is within the range of 1 – 10 which indicates favourable conditions for the fluoride removal by montmorillonite K10 at the studied conditions [18, 29]. The results are also summarized in Table (1).

**Langmuir Isotherm:** The Langmuir isotherm assumes that the fluoride removal on a homogenous surface is by monolayer adsorption without any interaction between adsorbed ions [30]. The linear form of the Langmuir isotherm is expressed as follows:

$$\frac{1}{q_e} = \frac{1}{q_o \times b} \times \frac{1}{C_e} + \frac{1}{q_o} \quad (2)$$

where;  $q_e$  is the equilibrium fluoride concentration on the adsorbent (mg/g),  $C_e$  is the equilibrium fluoride concentration of the solution (mg/L),  $q_o$  and  $b$  are the monolayer capacity of montmorillonite K10 and Langmuir adsorption constant which indicates the affinity of the fluoride towards montmorillonite K10. The Langmuir parameters,  $q_o$  and  $b$  can be calculated from the slope and intercept of the linear plot of  $1/q_e$  against  $1/C_e$  and were found to be 1.35 mg/g and 4.08 L/mg respectively, with correlation coefficient ( $R^2$ ) of 0.93. The results are also summarized in Table (1).

Furthermore, the favourability of fluoride removal by montmorillonite K10 was tested using the essential features of the Langmuir isotherm, expressed in terms of a dimensionless constant called equilibrium parameter ( $R_L$ ) which is expressed as follows [12]:

$$R_L = \frac{1}{1 + bC_o} \quad (3)$$

where;  $b$  and  $C_o$  are the Langmuir constant and initial fluoride concentration respectively. The value of  $R_L$  for an initial fluoride concentration of 5.15 mg/L was found to be less than unity indicating that this system is favourable for fluoride adsorption.

**Dubinin-Raduskevich Isotherm:** Eventhough, Freundlich and Langmuir isotherm models are widely used, these models does not give any idea about the nature of adsorption mechanism (i.e. physical or chemical). Therefore, in order to understand the nature of adsorption mechanism, the equilibrium data was tested with Dubinin-Raduskevich isotherm model (D-R isotherm) [31]. The Dubinin-Raduskevich model predicts the sorption nature of the adsorbate on adsorbent and it is also used to calculate the mean adsorption energy.

The linear form of the D-R isotherm equation is expressed as follows:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (4)$$

where  $q_e$  is the amount of fluoride ions adsorbed per unit weight of the adsorbent (mol/g),  $q_m$  is the maximum adsorption capacity (mol/g),  $\beta$  is the activity coefficient related to mean adsorption energy ( $\text{mol}^2/\text{KJ}^2$ ) and  $\epsilon$  is the polanyi potential ( $\epsilon = RT \ln(1+1/C_e)$ ). D-R isotherm constants,  $\beta$  and  $q_m$  can be calculated from the slope and intercept of the linear plot of  $\ln q_m$  against  $\epsilon^2$  and were found to be 0.0628  $\text{mol}^2/\text{KJ}^2$  and 4.90 mg/g respectively, with correlation coefficient ( $R^2$ ) of 0.99. The results are also summarized in Table (1). The mean adsorption energy ( $E$ ), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid or adsorbent from infinity in solution which can be calculated from the equation [23] given below:

$$E = \frac{1}{\sqrt{2\beta}} \quad (5)$$

From the magnitude of  $E$  value, the nature of adsorption mechanism such as physical or chemical can be determined. The  $E$  value ranges from 1.0 to 8.0 KJ/mol for physical adsorption and from 9.0 to 16.0 KJ/mol for

Table 1: Isotherm parameters for the fluoride removal by montmorillonite K10

Freundlich constants	Langmuir constants	Dubinin - Radushkevich constants
KF = 1.0147 mg/g	q <sub>max</sub> = 1.35 mg/g	q <sub>m</sub> = 4.90 mg/g
1/n = 0.16	b = 4.08 L/mg	E = 2.83 KJ/mol
n = 6.25	RL = 0.05	R <sup>2</sup> = 0.99
R <sup>2</sup> = 0.99	R <sup>2</sup> = 0.93	

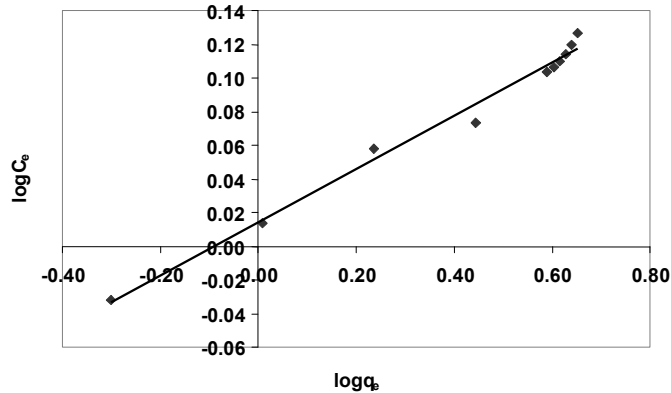


Fig. 7: Freundlich plot for fluoride removal (Initial concentration = 5.15 mg/L, pH = 6.7, shaking speed = 150 rpm and contact time = 24 h)

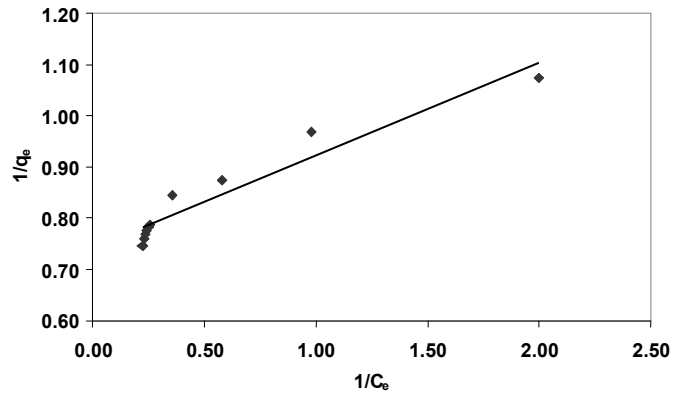


Fig. 8: Langmuir plot for fluoride removal (Initial concentration = 5.15 mg/L, pH = 6.7, shaking speed = 150 rpm and contact time = 24 h)

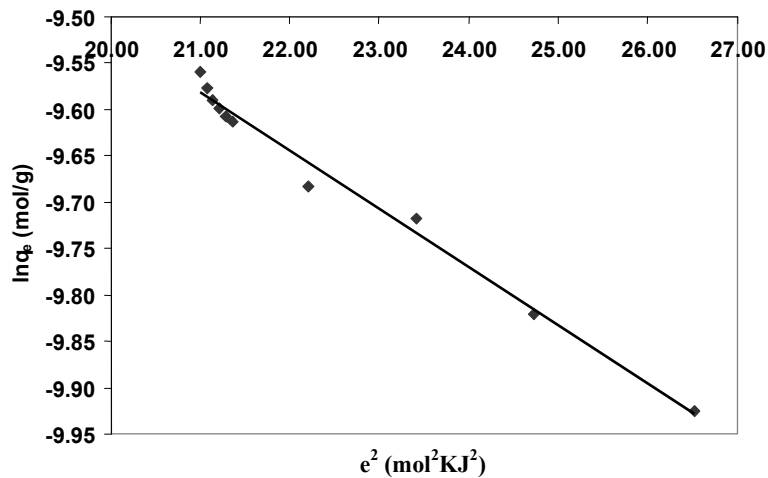


Fig. 9: Dubinin-Radushkevich plot for fluoride removal (Initial concentration = 5.15 mg/L, pH = 6.7, shaking speed = 150 rpm and contact time = 24 h)

chemical adsorption [32]. The value of  $E$  for the present study was found to be 2.83 KJ/mol which suggests that the mechanism for the adsorption of fluoride on montmorillonite K10 is physical in nature.

The Freundlich, Langmuir and Dubinin-Raduskevich adsorption constants were determined from their corresponding isotherms as shown in Figures 7, 8 and 9 at 30°C with their regression correlation coefficients as listed in Table (1). As seen from this table, Freundlich and Dubinin-Raduskevich model have shown high regression correlation coefficient ( $>0.99$ ) which indicates that Freundlich and Dubinin-Raduskevich model are best suitable for describing the sorption equilibrium of fluoride by montmorillonite K10.

**Adsorption Kinetics:** The adsorption kinetics was studied to explain the fluoride removal mechanism of montmorillonite K10. The fluoride removal is characterised by initial rapid phase followed by a slow phase. However, around 60 % of the fluoride removal takes place just within first 5 min itself after which the rate is slowed down with negligible removal after 6 h indicating the attainment of equilibrium. The initial rapid fluoride removal may be due physisorption or surface bound sorption followed by the slow and gradual removal in the second phase which may be due to long-range diffusion of fluoride ions into interior pores of the adsorbent. The results obtained from the experiments were used to study the rate - limiting step. In order to study the rate-controlling mechanism of fluoride removal by montmorillonite K10, kinetic equations such as Lagergren's pseudo-first order, Ho's pseudo-second order and the intraparticle surface diffusion model of Weber and Morris were used to examine the experimental data.

The pseudo-first order kinetic equation of Lagergren is generally expressed as follows [33]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (1)$$

where;  $q_e$  and  $q_t$  (both in mg/g) are the amount of fluoride adsorbed per unit mass of the adsorbent at equilibrium and time " $t$ ", respectively and  $K_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant. The pseudo-first-order rate constant ( $K_1$ ) was calculated from the slope of the linear plot of  $\log(q_e - q)$  against  $t$  as shown in Figure (10). The values of  $K_1$  and their correlation coefficients  $R^2$  for the initial fluoride concentrations of 5.67, 10 and 14.9 mg/L are given in Table (2). It can be observed from Table (2) that the correlation coefficients of the pseudo-first-order kinetic model obtained at all the studied concentrations

are low. This clearly suggests that pseudo-first-order model is not suitable to describe the present sorption process.

The pseudo-second order equation [34] based on equilibrium adsorption is generally expressed as follows:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2)$$

where;  $K_2$  and  $h = Kq_e^2$  are the pseudo-second-order rate constant and the initial sorption rate respectively. The values of  $K_2$  (g/mg/min) and  $h$  (mg/g/min) of the pseudo-second-order equation can be calculated experimentally by plotting  $t/q_t$  against  $t$  as shown in Figure (11). The values of  $K_2$ ,  $h$  and their correlation coefficients  $R^2$  for the initial fluoride concentrations 5.67, 10 and 14.9 mg/L respectively, are given in Table (2). However, from this table, it was observed that the correlation coefficient values of the second-order kinetic equation are almost equal to unity at all the studied initial fluoride concentrations, indicating the applicability of second-order kinetic equation to describe the present sorption process.

As the above two kinetic equations were unable to identify the diffusion mechanism, the intraparticle diffusion model based on the Weber and Morris theory [35] was thus studied to identify the diffusion mechanism. According to this theory, the intraparticle diffusion model is generally expressed as follows

$$q_t = K_p t^{1/2} + C \quad (3)$$

where;  $K_p$  ( $\text{mg/g/min}^{1/2}$ ) is the intraparticle diffusion rate constant and  $C$  (mg/g) is a constant which gives an idea about the thickness of the boundary layer i.e., larger the 'C' value, greater is the boundary layer effect [11]. The  $K_p$  and  $C$  values can be calculated from the slope and intercept of the plots of  $q_t$  against  $t^{1/2}$  and their values along with correlation coefficient for the initial fluoride concentrations of 5.67, 10 and 14.9 mg/L, respectively, are given in Table (3). Though, the plot of  $q_t$  versus  $t^{1/2}$  as shown in Figure (12) renders a straight line, indicating the importance of intraparticle diffusion in the adsorption process but it fails to pass through the origin, suggesting that intraparticle diffusion is not only the rate-limiting step but other kinetic factors may also control the rate of adsorption, in addition to some degree of boundary layer control [36, 37] as indicated by the  $C$  value. This observation along with the biphasic nature of the sorption kinetics further indicates that the fluoride removal by this adsorbent is complex with more than one mechanism limiting the rate of sorption.



Table 2: Kinetic parameters for the fluoride removal by montmorillonite K 10

Initial Fluoride Concentration (mg/L)	$K_1(\text{min}^{-1})$	$q_e$ (mg/g)	$R^2_1$	$K_2(\text{g/mg/min})$	$q_2$ (mg/g)	$R^2_2$
5.67	0.0088	0.581	0.9399	0.1104	1.0752	0.9983
10	0.0051	0.794	0.8230	0.2851	1.4631	0.9997
14.9	0.0074	0.898	0.9751	0.2216	1.9257	0.9998

Table 3: Intraparticle diffusion parameters for the fluoride removal by montmorillonite K 10

Initial fluoride concentration (mg/L)	$K_p$ (mg/g/min <sup>1/2</sup> )	C (mg/g)	$R^2_p$
5.67	0.0139	0.8088	0.97
10	0.0088	1.3094	0.80
14.9	0.0104	1.7423	0.94

Table 4: Detailed characteristics of field water before and after treatment with montmorillonite K 10

Sample No.	Parameters	Values of Field water before treatment of Montmorillonite K 10	Values of Field water after treatment with Montmorillonite K 10
1	Nitrate (mg/L)	0.60	3.0
2	Total hardness as CaCO <sub>3</sub> (mg/L)	56.00	22.0
3	Chloride (mg/L)	140.00	142.00
4	Fluoride (mg/L)	13.2	1.00
5	Sulphate (mg/L)	56.96	60.00
6	Alkalinity as CaCO <sub>3</sub> (mg/L)	44.00	18.0
7	Total dissolved solids (mg/L)	510.00	548
8	pH	7.78	6.0
9	Cadmium (mg/L)	<0.01	<0.01
10	Chromium (mg/L)	<0.05	<0.05
11	Lead (mg/L)	<0.01	<0.01
12	Manganese (mg/L)	<0.1	<0.1
13	Iron	<0.11	<0.03
14	Arsenic (mg/L)	<0.01	<0.01
15	Aluminium (mg/L)	<0.03	<0.03

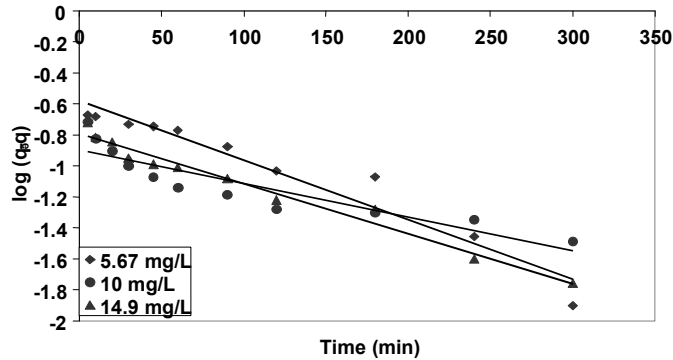


Fig. 10: Lagergren pseudo-first order plot for fluoride removal

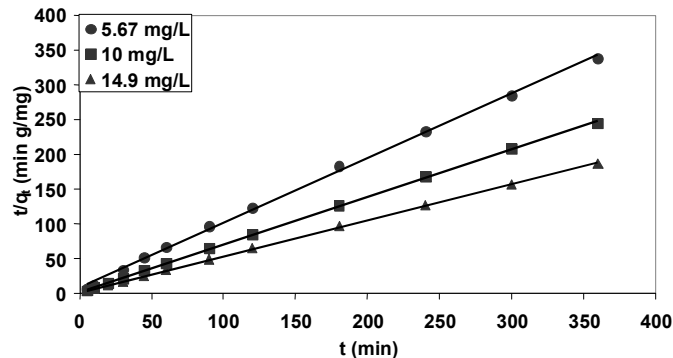


Fig. 11: Ho's pseudo-second order equation plot for fluoride removal

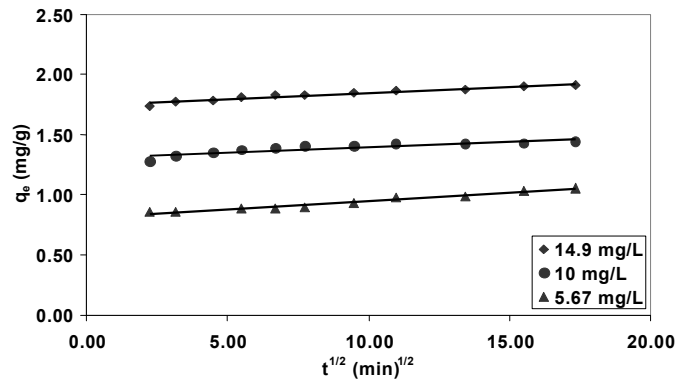


Fig. 12: Intraparticle mass transfer curves for fluoride removal

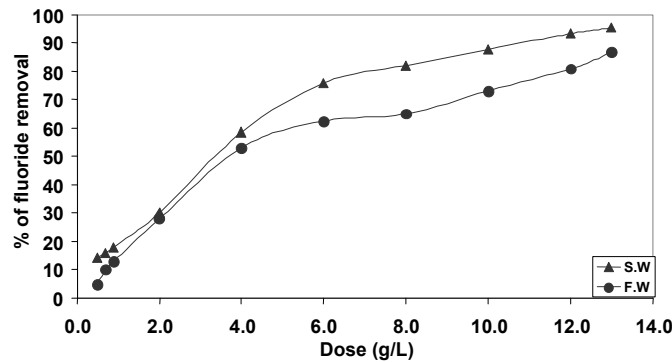


Fig. 13: Comparison of fluoride removal in simulated water (S.W) and field water (F.W) (Initial concentration = 13.2 mg/L, shaking speed = 150 rpm and contact time = 24 h)

**Comparative Studies:** The performance of the adsorbent was studied by treating field water (groundwater) sample collected from fluoride affected areas of Dhar, Madhya Pradesh, Central India. The detailed physicochemical characteristics of the field water before and after treatment of the adsorbent are given in Table (4). It was found that the percentage removal of fluoride in synthetic water was higher than that of the field water as shown in Figure (13). It could be due to both the higher pH of the field water as well as the presence of different types of cations and anions. No heavy metals were released from the adsorbent into the filtrate after the equilibrium studies which was estimated by using by ICP - AES.

## CONCLUSION

The results of the present study indicate that montmorillonite K10 has considerable potential for the removal of fluoride from aqueous solutions. Among the competing ions, sulphate, chloride and nitrate ions have shown little or negligible effect while carbonate and bicarbonate ions have significantly affected the fluoride removal over the range of concentrations studied. The optimum fluoride removal was observed between a pH

range of 4-7. Kinetic examination of the equilibrium data shows that the fluoride removal by this adsorbent follows pseudo-second-order kinetics with a correlation coefficient almost equal to unity (i.e. 0.99). The equilibrium data were fitted to Freundlich, Langmuir and Dubinin-Raduskevich isotherm model. Among them, Freundlich and Dubinin-Raduskevich isotherm model fitted well to this system. Mean adsorption energy value ( $E = 2.82$  KJ/mol) obtained from Dubinin-Raduskevich isotherm model suggests that physisorption plays significant role in the adsorption process. An XRD and EDAX study also suggests that fluoride removal by this adsorbent takes place mostly through surface adsorption or physisorption.

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