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ORIGINAL CONTRIBUTION

Investigating the Efficacy of Saw Dust in Fluoride Removal Through Adsorption

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Abstract An eco-friendly, innocuous, inexpensive as well as effective treatment of fluoride-contaminated water has been an urgent need to resolve the water-related issues. So for the removal of fluoride, batch adsorption experiments were carried out to study the effect of pH (varied from 2 to 12), adsorbent dose (varied from 0.05 to 0.50 g/L) and initial fluoride concentration (varied from 5 to 20 mg/L) on saw dust adsorbent. The maximum removal of fluoride was found to be 88% at optimum conditions (pH 7, adsorbent dose 0.20 g/L and initial fluoride concentration 5 mg/L). Among the various kinetic models used, pseudo-second-order model best fitted the kinetic data and Langmuir isotherm was also best fitted. The maximum capacity of adsorption was found to be 16.5 mg/g.

Keywords Fluoride · Batch adsorption · Isotherm · Kinetic modelling

Introduction

Life cannot sustain without water, the life supporting system, on this planet. This abundantly available natural resource has been contaminated continuously beyond nature's purification capacity through anthropogenic activities [1]. This has been happening since time immemorial, but during last 2–3 centuries, the environmental health risks multiplied with industrialisation, modern lifestyle, mechanised agriculture with synthesised chemicals and exploitation of ground water which continuously contaminate the land, water bodies with unwanted toxic elements and compounds. Fluoride is one of such ionic elements whose toxicity was recognised in man and livestock in the 1930s [2], and in the same decade, the value of fluoride in the prevention of human dental caries was established [3]. Excess intake of fluoride to the mankind may cause the risk of diseases such as thyroid disorder osteoporosis, brittle bones, alzheimer syndrome, arthritis, cancer, brain damage and infertility in women [4].

Fluoride is widely distributed in the geological regions of the world [5] and released into the groundwater by the slow mixing of fluoride-containing igneous rock such as granite's crystals [6]. Thus, the major source of fluoride is groundwater. Subsequently, countries like Africa, China, the Middle East and Southern Asia as India, Sri Lanka and Bangladesh, particularly in mid-latitude regions, are also been affected with high fluoride concentration in groundwater [7]. Some industries also contribute to fluoride pollution in the groundwater to a great extent besides the natural geological sources [8]. A guideline set by World Health Organization (WHO) for fluoride level in drinking water is 1.5 mg/L [9], and the same concentration (permissible limit) has also been set in Indian standard. In India (19 states and union territories), about 25 million people have already been affected and another 66 million are at high risk. Additionally, another 6 million children under below the age of 14 years are also affected with fluoride-contaminated drinking water. It is also found that some regions of India have a high level (35 mg/L) of fluoride

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concentration observed, and in some parts, its level is below 0.5 mg/L [10].

Various processes such as membrane separation, nanofiltration, precipitation–coagulation, electrolytic coagulation, reverse osmosis, ion exchange and adsorption have been tried so far for the removal of high fluoride content from water. However, most of above methods have high treatment cost (including operational and maintenance) such as in nanofiltration and reverse osmosis. Moreover, some processes have very low removal efficiencies and some adverse effects on water quality. Furthermore, in precipitation–coagulation, huge amount of sludge is generated and complicated procedure is involved in the treatment of contaminated water [3].

Nalgonda technique is used commonly for the treatment of fluoride-contaminated water. This technique is based on precipitation process. The major limitation in this technique is that there is the daily need of addition of chemicals, which produces large amount of sludge. This is also less effective when water contains high total dissolved solids and hardness. In this technique, major portion of ionic fluoride (67–87%) converted into soluble aluminium complex and removed only 18–33% fluoride in the form of precipitate. The residual aluminium concentration ranging from 2.01 to 6.86 mg/L has also been reported in Nalgonda technique [11]. This concentration of aluminium is dangerous to human health, as it is a neurotoxin. The concentration of aluminium in drinking water (about 0.08 mg/L) has also been responsible to cause Alzheimer's disease and has strong carcinogenic properties [12].

Adsorption is considered to be efficient process for defluoridation of water. Various research have been carried on different adsorbents, viz. activated alumina, activated carbon, magnesia, processed bone char powder, spent tea leaves, activated bauxite, coal fly ash, granular calcite, alum, lime, etc. [13]. This is the time of hour to search for an innocuous, inexpensive as well as effective adsorbent for treatment of fluoride-contaminated water in an eco-friendly way. So, acid-treated saw dust is used as an adsorbent for the treatment of fluoride-contaminated water. Batch adsorption processes are conducted in the present study to determine the effects of pH, adsorbent dose and initial fluoride concentration on the removal of fluoride from contaminated water.

Materials and Methods

Chemicals, Reagents and Preparation of Stock Solution

All the chemicals and reagents used in this study were of analytical grade (AR grade). A stock solution of fluoride having concentration of 100 mg/L was prepared by using 221.01 mg of an-hydrous sodium fluoride (NaF) dissolving in 1 L milli-Q water. Different working concentrations of fluoride solution were prepared from stock solution.

Quality Control

The instruments used in the present study were validated and calibrated by the norms of National Accreditation Board for Testing and Calibration Laboratories (NABL) to eliminate discrepancies in the readings [14]. The experiments were carried out in triplicate for maintaining precision and reproducibility.

Preparation of Adsorbent Material

Saw dust used in the present study was collected from six different saw mills located in Lucknow city, and it was not from a single wood type; rather, it was mixture of different woods. Most common woods were neem (*Azadirachata indica*), mango (*Mangifera indica*) and pipal (*Ficus religiosa*), etc. After homogenous mixing, saw dust was continuously boiled with milli-Q water till clear (without any colour) solution appears. Thereafter, it was dried in a hot air oven (York Scientific Industries, New Delhi, Model: YSI 431) at 50 °C and sieved to get particle size of 0.5 mm to 0.2 mm. The processed saw dust (100 g) was suspended in 500 mL of 1 N HNO_3 in a 1000-mL beaker. The mixture was gently heated on the burner for 20 min after boiling starts. Treated adsorbent was washed again with milli-Q water until the colour was removed and clear water was obtained.

Batch Adsorption Process

Batch adsorption study was carried out in an incubator shaker (Stuart incubator shaker, UK, Model: S1500) to investigate the adsorption of fluoride. The pH of the solution was maintained by adding 0.1 N H_2SO_4/0.1 N NaOH. The sample was agitated in conical flask on incubator shaker at 100 rpm for 120 min (fixed from trial run) having different fluoride concentrations (varying from 2, 4, 5, 8, 10, 15 and 20 mg/L), adsorbent dose (varying from 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.50 g/L) and pH of the solution (varying from 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 to study the removal efficiency and find out saturation) at 25 °C. Afterwards, content of the flask was allowed to settle down and passed through Whatmann filter paper no. 42 and analysed for fluoride concentration using the SPADNS method by serial dilution [15].

The amount of fluoride adsorbed per unit mass (q_t) at time t in mg/g was calculated by:

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (1)$$

where C_o is the liquid-phase initial concentration of fluoride in mg/L, C_t is the liquid-phase remaining concentration of fluoride in mg/L at time t, V is the volume of the solution in L, and W is the mass of dry adsorbent used in g.

The amount of adsorption at equilibrium (q_e) in mg/g was calculated by:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where C_e is the liquid-phase concentration at equilibrium of fluoride in mg/L.

Adsorption Isotherms and Kinetics

Isotherms help in determining the mass of impurities adsorbed per unit mass of adsorbents. Nature of the adsorption can be explained by relating the adsorption capacity to equilibrium concentration of the impurities remaining in the solution using various isotherms such as Langmuir, Freundlich and Temkin and Pyzhev isotherms [16]. However, adsorption isotherms are equilibrium test and thus do not indicate the actual performance of the adsorbent [17, 18]. In present study, isotherms were plotted using the experimental data. Langmuir isotherm [19] described adsorption as a result of formation of an ionic or covalent bond between adsorbent and solute molecules and defined fractional coverage. The linear form of Langmuir isotherm is given in Eq. (3):

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{bq_m}\right)\frac{1}{C_e} \quad (3)$$

Freundlich isotherm [20] assumes that multilayer adsorption occurs over the surfaces. The linear form of Freundlich isotherm is given in Eq. (4):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \times \log C_e \quad (4)$$

In Temkin isotherm [21] is represented by Eq. (5):

$$q_e = B_t \ln K_t + B_t \ln C_e \quad (5)$$

where C_e is the concentration of solute in the solution at equilibrium (mg/L), q_m is the maximum capacity of adsorbent for solute (adsorbate) (mg/g), b is the constant for apparent energy of adsorption (L/mg), K_F is Freundlich constant related to adsorption capacity of adsorbents (mg/g), n is Freundlich exponent constant, K_t is Temkin equilibrium constant corresponding to maximum binding energy (L/mg), and B_t is the variation of adsorption energy (kJ/mol).

The adsorption/desorption processes of various solid phases are time dependent. Knowledge of the above processes is essential to understand the solute uptake rate, and evidently this rate controls the residence time of adsorbate uptake at solid–solution interface. The dynamic interactions of fluoride adsorption on saw dust were analysed to predict their fate with time using pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetics [22, 23]. The linear form of pseudo-first-order rate expression is given as Eq. (6):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (6)$$

The adsorption kinetics is also described as pseudo-second-order process [24]. The linear form of pseudo-second-order rate expression can be written in the linear form as Eq. (7):

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{1}{q_e} t \quad (7)$$

The finding of diffusion mechanism of intra-particle diffusion model is given in Eq. (8) [25]:

$$q_t = k_{ip} \times t^{1/2} + C_i \quad (8)$$

where q_t is the amount of fluoride adsorbed (mg/g) at time t, q_e is the measured value of equilibrium solute concentration in solid phase (mg/g), C_i is the intercept, determined by the thickness of the boundary layer, t is the time (min), k_1 is the rate constant of the pseudo-second-order kinetics (per min), k_2 is the rate constant of the pseudo-second-order kinetics (g/mg min), and k_{ip} is the intra-particle rate constant (mg/g min$^{1/2}$).

Linear relationships of $\log(q_e–q_t)$ vs. t, (t/q_t) vs. t and q_t vs. $t^{1/2}$ are plotted for pseudo-first-order, pseudo-second-order and intra-particle diffusion models, respectively.

Results and Discussion

Removal efficiency of the fluoride was studied by varying the various factors such as pH (varying from 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12), adsorbent dose (varying from 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.50 g/L) and initial fluoride concentration (varying from 2, 4, 5, 8, 10, 15 and 20 mg/L).

Effect of pH of the Solution

The pH is an important parameter for the removal of fluoride from contaminated water. 1000 mL of fluoride solution having 5 mg/L of fluoride concentration and 0.20 g of saw dust powder (from the trial run) was added to each flask. The solution was agitated on 100 rpm for 120 min (from the trial run) on incubator shaker.

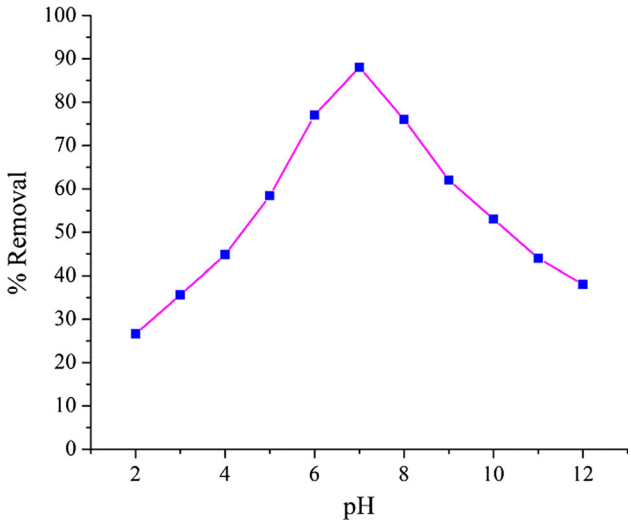

Fig. 1 Removal of fluoride with variation in pH (at adsorbent dose 0.20 g/L, contact time 120 min, fluoride concentration 5 mg/L and agitation speed 100 rpm)

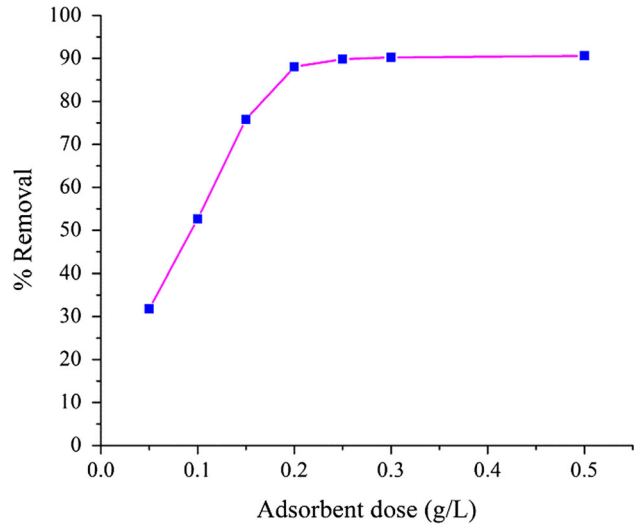

Fig. 2 Removal of fluoride with variation in adsorbent dose (at pH 7, contact time 120 min, fluoride concentration 5 mg/L and agitation speed 100 rpm)

Initially, removal of fluoride was very low at pH 2 (Fig. 1). As pH of the solution increases, the percent of fluoride removal increased and maximum removal of fluoride was observed at pH 7. Further, increasing pH to 8, 9 and above, percent of fluoride removal started decreasing. The maximum removal of fluoride was found to be 88% at pH 7. Therefore, solution of pH 7 was selected as optimum pH for further experiments. Yadav et al. [26] studied the effect of pH on fluoride removal and observed that maximum removal occurs at pH 7.

Effect of Adsorbent Dose

Removal of fluoride on saw dust was also a function of adsorbent dose. In order to optimise adsorbent dose, other parameters such as pH of the solution 7 (from section "Effect of pH of the Solution"), agitation speed 100 rpm (from the trial run), fluoride concentration 5 mg/L (from the trial run) and contact time 120 min (from the trial run) were kept constant. The removal percent of fluoride increased from 32 to 88% when the adsorbent dose was increased from 0.05 to 0.20 g/L (Fig. 2). Further increase in adsorbent dose showed no significant increase in removal of fluoride, and it reached equilibrium at 0.20 g/L. The increase in removal efficiency with an increase in adsorbent dose may be due to the availability of more active sites as well as larger the surface area. So, for further experiments, 0.20 g/L of the adsorbent dose was selected as an optimum dose. Mane et al. [27] have also studied that the fluoride removal efficiency increased with an increase in adsorbent dose.

Effect of Initial Fluoride Concentration

The effect of initial fluoride concentration on the removal of fluoride has also been found to be an important parameter. Fluoride concentration was varied from 2 to 20 mg/L at optimum pH 7 (from section "Effect of pH of the Solution") and saw dust dose 0.20 g/L (from section "Effect of Adsorbent Dose"). When the concentration of fluoride increases, removal percent decreases, i.e. at low concentration of fluoride, more removal was seen and system reached equilibrium value slowly at 5 mg/L. The maximum removal of fluoride was 88% at 5 mg/L (Fig. 3).

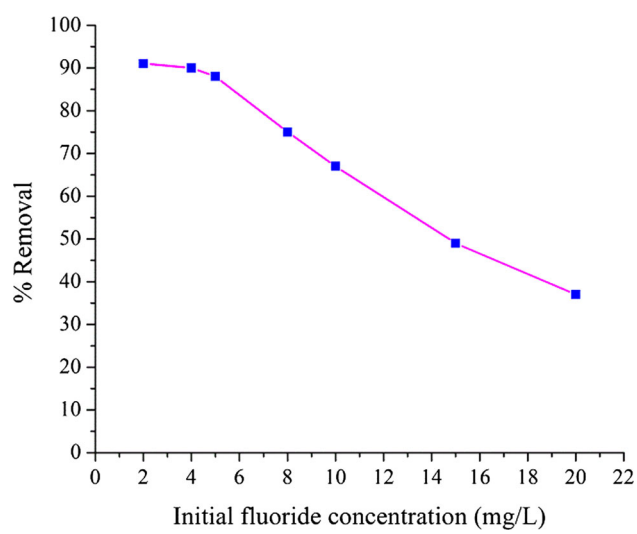

Fig. 3 Removal of fluoride with variation in initial fluoride concentration (at pH 7, adsorbent dose 0.20 g/L, contact time 120 min and agitation speed 100 rpm)

Biswas et al. [28] studied fluoride removal and came up with similar observation. For all the initial fluoride concentrations studied, most of the removal took place in low concentration and the removal was only slightly increased with a decrease in initial fluoride concentration from 5 mg/L to 2 mg/L. Therefore, 5 mg/L was considered for future experiments. This indicates that the initial concentration of fluoride has the least effect on equilibrium time.

Isotherm Analysis

Quantity of fluoride required to form a single monolayer on unit mass of saw dust calculated using Langmuir isotherm. The maximum adsorption capacity of saw dust was found to be 16.50 mg/g. The constant of Langmuir isotherm b was found to be 0.092 L/mg. The comparison of adsorption capacity of this adsorbent with other adsorbents is given in Table 1.

Multilayer adsorption of ions on saw dust surface was reported by Freundlich isotherm. The value of Freundlich constant K_F shows that saw dust has good tendency to adsorb fluoride ions. K_F was found to be 0.340 L/g. Value of n (1.86) points out a better adsorption mechanism and formation of relatively weak bond between fluoride and saw dust. Low values of Bt (0.534 kJ/mol) in this study also indicate a weak interaction between adsorbent and fluoride. Among Langmuir, Freundlich and Temkin isotherms, it was observed that isotherm data fitted well with Langmuir isotherm, indicating that adsorption of fluoride on saw dust followed monolayer adsorption (Table 2).

Table 1 Comparison of the maximum adsorption capacity of different adsorbents

Material	Removal capacity (mg/g)	Reference
Activated carbon derived from rice straw	15.90	Daifullah et al. [29]
Wheat straw raw	1.93	Yadav et al. [26]
Activated bagasse carbon	1.15	Yadav et al. [26]
Cynodon dactylon-based activated carbon	4.61	Alagumuthu et al. [30]
Iron–zirconium hybrid oxide	8.21	Biswas et al. [28]
Saw dust	16.50	Present study

Adsorption Kinetics

Pseudo-First-Order Kinetic Model

Pseudo-first-order equation or Lagergren's kinetic equation for the adsorption of adsorbate from aqueous solution is generally expressed by Eq. (6). The plots (Fig. 4a) were found linear with good correlation coefficients (> 0.920), and rate constant are reported in Table 3.

Pseudo-Second-Order Kinetic Model

The values of $q_{e,\ cal}$ and k_2 were determined from the slope and intercept of the plot (Fig. 4b) are compiled in Table 3. From Table 3, it can be concluded that $q_{e,\ exp}$ and $q_{e,\ cal}$ values should be as close as possible and follow similar trends in the case of pseudo-second-order kinetic model (increases with the increase in initial fluoride concentration). In the case of a pseudo-first-order kinetic model, over the entire range of initial fluoride concentrations, $q_{e,\ cal}$ values do not follow similar trends. So, it can be concluded that the pseudo-second-order model better represent the adsorption kinetics.

Intra-Particle Diffusion Model

For any adsorption process to follow the model, q_t (fraction of fluoride removal) versus $t^{1/2}$ (square root of contact time) would yield a straight line passing through the origin. It was concluded that fluoride removal from aqueous phase is a complex process as it involves both boundary layer and intra-particle diffusion. The adsorption rates (K_{ip}) at different stages indicated that the adsorption rate was initially faster, and with the progression of time it slowed down. The curve is not linear which in an indication of more than one process affecting the process of adsorption.

Thermodynamic Study

To evaluate practical feasibility and nature of adsorption process, thermodynamics parameters such as change in enthalpy ($\Delta H°$), change in Gibbs free energy ($\Delta G°$) and change in entropy ($\Delta S°$) are used [31, 32], which are determined by Eqs. (9, 10 and 11):

Table 2 Isotherms parameters for adsorption of fluoride on saw dust

Langmuir			Freundlich			Temkin		
q_m (mg/g)	b (L/mg)	R^2	K_F (L/g)	n	R^2	K_t (L/mg)	B_t (kJ/mole)	R^2
16.50	0.092	0.993	0.340	1.86	0.930	0.712	0.534	0.922

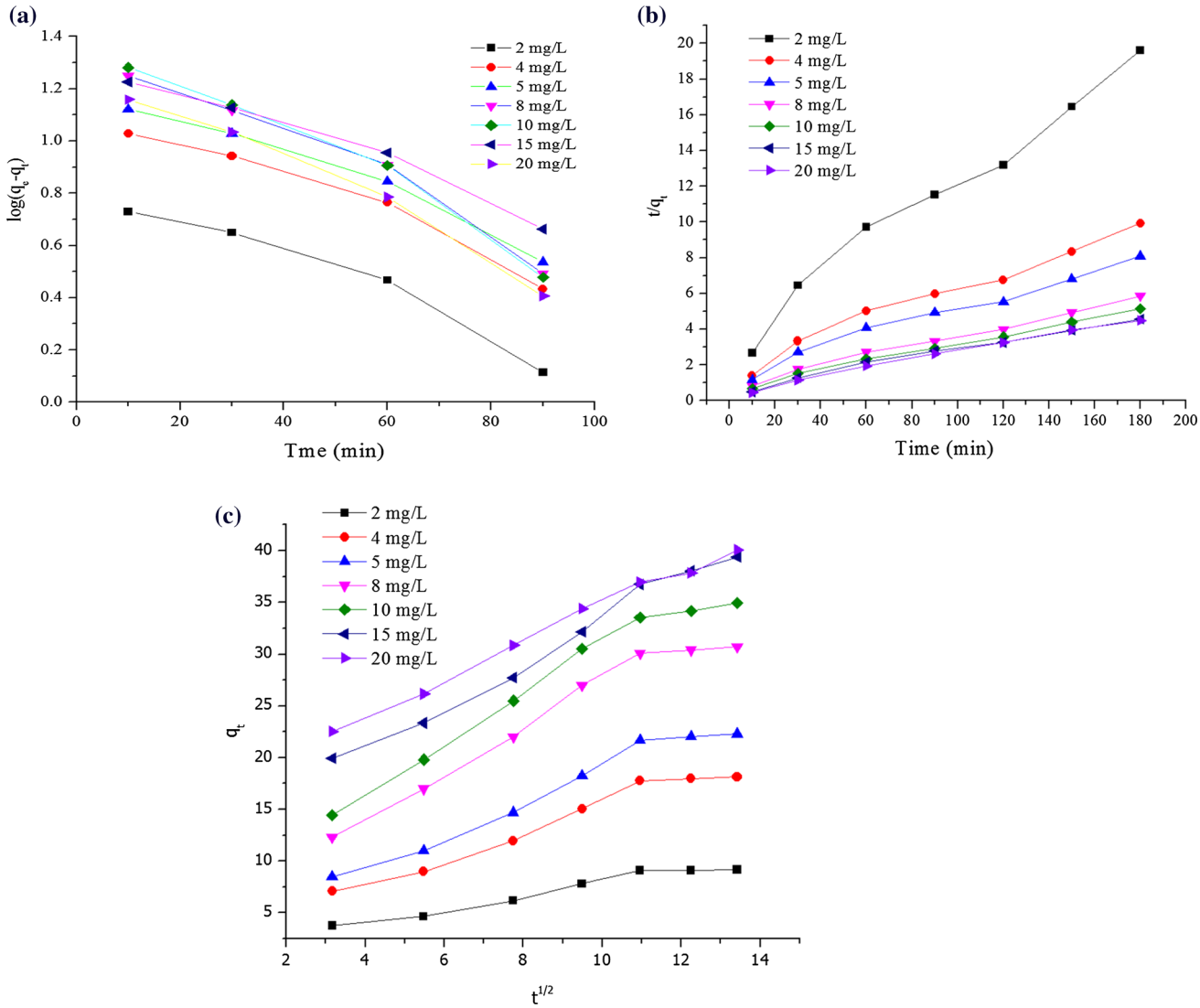

Fig. 4 Kinetic study **a** pseudo-first order, **b** pseudo-second order kinetic model and **c** intra-particle diffusion model

Table 3 Comparison of pseudo-first-order, pseudo-second-order adsorption rate constants and calculated $q_{e,\ cal}$ and experimental $q_{e,\ exp}$ values obtained at different initial fluoride concentrations

Initial fluoride conc. (mg/L)	$q_{e,\ exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1	$q_{e,\ cal}$	R^2	k_2	$q_{e,\ cal}$	R^2
2	9.105	0.01612	0.69315	0.951	0.00273	10.989	0.978
4	17.750	0.01612	1.38629	0.959	0.00123	22.222	0.976
5	21.695	0.01612	1.60944	0.971	0.00101	27.027	0.977
8	30.101	0.02073	2.07944	0.964	0.00099	35.714	0.990
10	33.550	0.02073	2.30259	0.970	0.00095	40.001	0.993
15	36.750	0.01612	2.70805	0.976	0.00087	45.455	0.985
20	36.950	0.02073	2.99573	0.978	0.00131	43.478	0.993

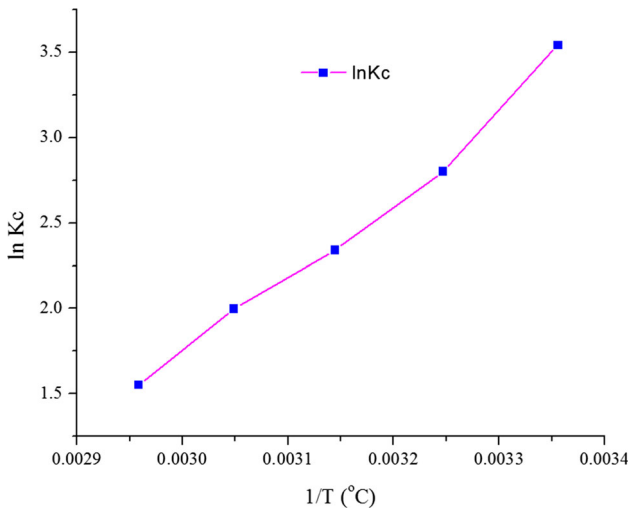

Fig. 5 Plot to obtain thermodynamic parameters

$$K_c = C_0/C_e \tag{9}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

$$\Delta G^\circ = -RT \ln K_c \tag{11}$$

where K_c is the coefficient of distribution, ΔS° is the entropy change (J/mol/K), ΔH° is the enthalpy change (KJ/mol), ΔG° is the change in Gibbs free energy (J/mol), T is the temperature (K), and R is the gas constant (8.314 J/mol/K).

The negative values of Gibbs free energy (ΔG; − 11.3457) indicated that the process is spontaneous and no need of extra energy for the penetration of fluoride ions (Fig. 5). However, negative values of entropy (ΔS; − 184.522) and enthalpy change (ΔH; − 37.2767) showed that the adsorption process is exothermic, releasing heat, where adsorbent and fluoride ions interfaces are arranged in an ordered manner.

Recovery and Reusability Study

Recovery and reusability capacity of the saw dust is important for making it cost-effective and the possibility to recover solute from the solution for further reuse [22]. Reusability capacity of saw dust was achieved by breaking the bond between fluoride ions and reactive sites of saw dust using desorbing agent [33]. Desorption study was carried out in three cycles with 0.20 g of dried fluoride adsorbed on saw dust using 1 N NaOH, ethanol, methanol, acetonitrile and dichloromethane. The variation of desorption capacity of saw dust is represented in Fig. 6. Desorption was found to be in order of NaOH < ethanol < methanol < acetonitrile < dichloromethane. Recovery of fluoride in chloroform is maximum as compared to other desorbing agents

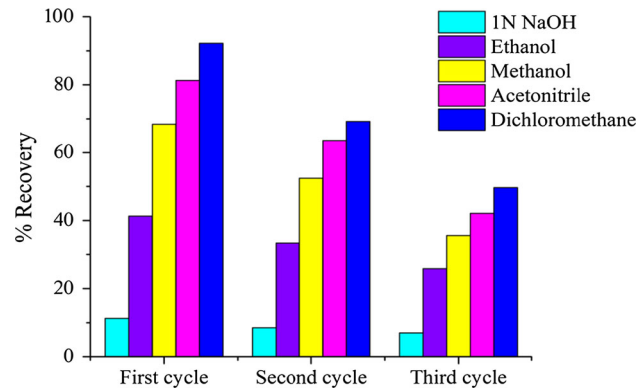

Fig. 6 Recovery and reusability study up to third cycle

simultaneously recovery percent decrease with successive cycles. It can be said that fluoride is ionic in nature and gets dissolved in an organic medium having low dielectric constant due to the delicate physical interaction between saw dust and fluoride ions.

Conclusions

Results concluded that saw dust adsorbent could be productively used for the removal of fluoride over a wide range of concentrations. The percent of fluoride removal was found to be a function of various parameters (such as pH, adsorbent dose, contact time and initial fluoride concentration). The maximum removal of fluoride was 88% at pH 7 and increased with the increase in adsorbent dose, whereas an increase in initial fluoride concentration resulted in decreased fluoride removal. Defluoridation using saw dust exposes that the equilibrium data best fitted to Langmuir isotherm as compared to Freundlich and Temkin isotherms which involve statistical and experimental data estimated from isotherm equation. Fluoride adsorption on saw dust from aqueous solution was found to be better correlated with pseudo-second-order reaction, and adsorption of fluoride was found to be complex. The reusability of saw dust was found in dichloromethane, and after the third cycle, removal capacity was found to be 49%. Used saw dust can be disposed of safely by burning after use. Saw dust is locally available in the area and hence involves no expenditure on transportation and also has a low cost for pre-treatment.

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