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Removal of Fluoride from Drinking Water Using Sawdust

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Abstract
In this study, the adsorption behaviour of sawdust has been studied in order to consider its application for fluoride removal. The batch adsorption method was employed: Laboratory investigation of the potential of sawdust to remove fluoride from aqueous solution has been studied. The effects of various experimental parameters, such as pH (3-11), adsorbent dosage (0.5-2.5 g/l),particle size(90µm to 300µm), contact time(30-150 min) and initial concentration(5 to 30mg/l) were investigated . The equilibrium data have been analyzed by the Langmuir, Freundlich and Tempkin isotherm models, the experimental data were better fitted to the Langmuir equation. The adsorption kinetics also investigated by the pseudo-first-order , pseudo-second-order, intraparticle diffusion and Elovich model . The deflouridation process followed pseudo second order model.

Key words: adsorption, deflouridation, isotherms,

I. INTRODUCTION

High fluoride levels in drinking water has become one of the most critical health hazards. Fluoride in nature exists as mineral deposits and, naturally, contaminates our ground water resources. Besides, surface water is also being polluted by fluoride due to various anthropogenic activities. Drinking water containing fluoride may be beneficial or detrimental depending upon its concentration and total amount consumed [1]. Excess intake (>1.5 mgL-1) may cause fluorosis (dental, skeletal and non-skeletal) along with various neurological complication. It is estimated that around 260 million people worldwide (in 30 countries) are drinking water with Fluoride content more than 1.0 mg/L. In India alone, endemic Fluorosis is thought to affect around one million people and is a major problem in 17 of the 25 states, especially Rajasthan, Andhra Pradesh, Tamil Nadu, Gujarat and Uttar Pradesh. In India totally 25 states have been reported as fluoride affected areas but severe problem occurred in the states of Andhra Pradesh[2-5]. The high fluoride levels in drinking-water and its impact on human health in many parts of India have increased the importance of defluoridation studies. Removal of fluoride from the ground water is challenging task among the scientists.

Because of its health risks, defluoridation of drinking water is the best practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available. During the years following the discovery of fluoride as the cause of fluorosis, extensive research has been done on various methods for removal of fluoride from water and wastewater. These methods are based on the principle of adsorption (Raichur and Basu, 2001), ion-exchange (Singh et aI., 1999), precipitation-coagulation (Saha, 1993), membrane separation process (Dieye et ai.,1998), electrodialysis (Hichour et aI., 1999), etc. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations.

Adsorption is one of the significant techniques in which fluoride adsorbed onto a membrane, or a fixed bed packed with resin or other mineral particles. Many natural and low cost materials such as red mud [6,7], zirconium impregnated coconut shell carbon [8], cashew nut shell carbon [9], ground nut shell carbon [10] and clays [11] have been used as adsorbents for fluoride removal from drinking water.

II. MATERIAL AND METHODS

2.1Adsorbent collection and preparation

Sawdust of kail wood is collected from the workshop of Kasturba Polytechnic for Women, pitampura, Delhi and washed with distilled water followed by drying in a hot air oven at 150^0C for 24 hrs. The dried sawdust was grinded and sieved well in fraction of 90, 150, 300µm mesh size particles that were preserved in different air tight containers for subsequent use as adsorbent.

2.2 Preparation of Stock Solution

The fluoride stock solution of 1000 mg/l was prepared by diluting 2.21 g of sodium fluoride salt in one litre of distilled water.

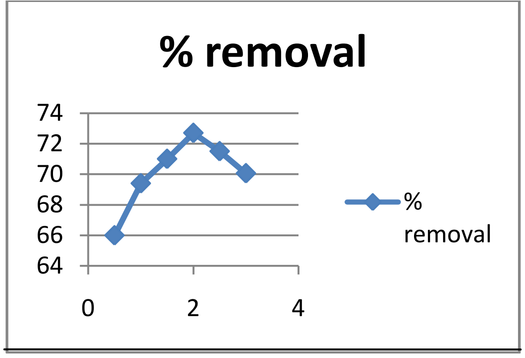
2.3Methodology

Batch sorption studies were conducted to study the effect of controlling parameters like contact time, adsorbent dosage, solution pH, particle size, initial concentration etc. All the experiments were conducted at room temperature (29±20C). Fluoride concentration was estimated by method 23 of IS 3025(electrode method).

III. RESULTS AND DISCUSSIONS

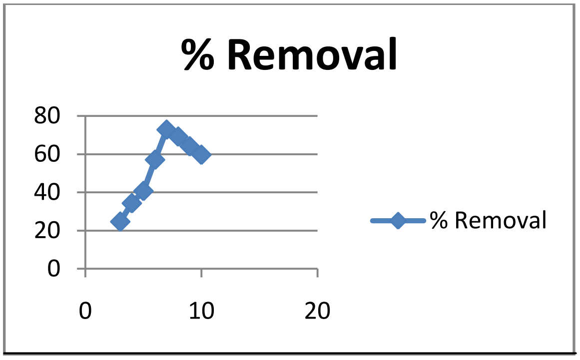
3.1 Effect of adsorbent dose:

Adsorbent dose is an important parameter owing to its effect on efficiency (%) and on the amount of fluoride adsorbed per unit weight of biomass (qe). The influence of adsorbent dose on fluoride removal is checked at a fixed initial fluoride concentration of 10 mg/L, pH 6-7 at temperature 27±3°C. It was noticed that percentage removal of fluoride increased from 66% to 72.7% with a change in adsorbent dose from 0.5 g/L to 3 g/L respectively. From Fig.5.1.1 result shows that the optimum dose of adsorbent was found 2 g/L for fluoride concentration of 10mg/L,which gives 72.7% fluoride ion removal efficiency. An adsorbent dose of 2 g/L was used for further study.



Adsorbent dose in gm/l →

Fig 3.1: Effect of adsorbent dose on fluoride removal



→ pH

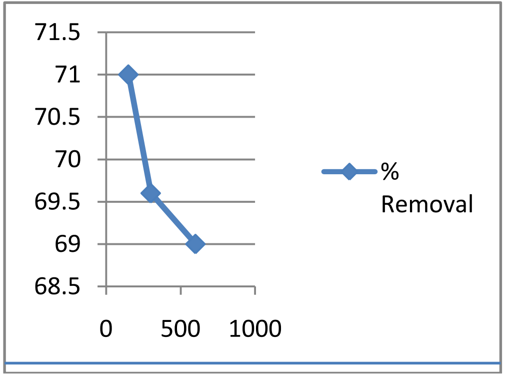
fig3.2: Effect of pH on fluoride removal

3.2 Effect of pH

To find the effect of pH on adsorption by sawdust, study was conducted from pH 3 to10 in acidic and alkaline conditions respectively. The graphical representation is shown in Figure3.2 found that the removal of fluoride was increased up to pH 7 and then decreases. Highest adsorption of fluoride was found to be 70.6% to 75.6 % in the pH range 6.0 and 8.0. It is seen that the sorption of fluoride is good in the pH range 6.0-8.0.This may be due to neutralization of the negative charge at the surface of adsorbent material by greater hydrogen concentration at lower pH values.

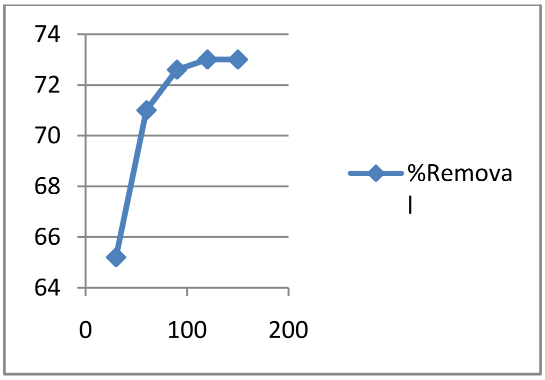
3.3Effect of particle size

Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of fluoride ions, the defluoridation experiments were conducted using *sawdust* with four different particle sizes viz. 90–150, 150–300, and 300-600µm. As the dsorption process is a surface phenomenon, the defluoridation efficiency of the sample with 90µm registered high value, this is mainly true since the surface area and the number of active pores of the adsorbent increase with the decrease in particle size. The percentages of fluoride removal by the sample with different particle sizes are studied. Hence, the material with particle size of 90µm has been chosen for further experiments. Higher percentage of adsorption by *sawdust* with smaller particle size is due to the availability of more specific surface area on the adsorbent surface.



Particle size in µm →

Fig 3.3: Effect of particle size on fluoride removal



Contact time →

Fig 3.4: Effect of contact time on fluoride removal

3.4 Effect of contact time

It is very necessary to determine the effect of contact time required to reach equilibrium for designing batch adsorption experiments. The fluoride removal capacity qe (mg/g) on the sawdust was determined by varying contact time (30-150 minutes) for a given initial concentration of 10mg/l and best pH (7.0) at 150 rpm. As illustrated in Figure 3.4, the adsorption of fluoride increased with rise in contact time upto 120 min and further increase in contact time did not enhance the fluoride adsorption process. The adsorption process attained equilibrium after 120 min. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent.

3.5 Effect of initial concentration

The efficiency of fluoride adsorption for different initial F- concentrations ranging from 5 to 30.0 mg/L was investigated by carrying out adsorption experiments at optimum adsorbent dose (2.0 g L-1) with 150 µm particle size, pH 7.0,agitation speed 150 rpm at temperature 30 ^{0}C for a contact time of 120 min. It follows from the result that the amount of fluoride uptake, and qe i.e. uptake per unit weight of sorbent increased with increase in initial fluoride concentrations.

Similar observations have been reported elsewhere (Choi and Chen, 1979, Muthukumaran, 1995). The increase in amounts of fluoride uptake by unit weight of sorbent with increase in initial fluoride concentrations is perhaps due to sorbate concentration gradient, which is the driving force for intraparticle transport which facilitates diffusion of sorbate molecule to the surface sites for ultimate attachment (Karthikeyan, 1982).

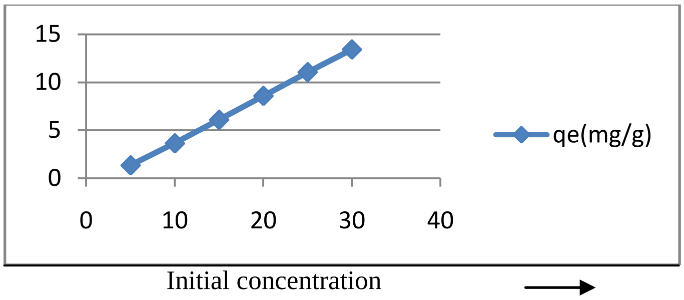


Fig 3.6: Effect of initial concentration on fluoride removal

3.6 Equilibrium of Sorption study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the homogeneity/ heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate fluoride uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce Isothermal equilibrium studies were conducted employing different initial fluoride concentrations of 5, 10, 15, 20, 25, and 30 mg.L-1 of adsorbate.

3.6.1 The Langmuir isotherm

The Langmuir adsorption isotherm equation is represented in Eq. (1):

$$q = a\frac{bCe}{1+bCe} \qquad (1)$$

And the linearized form can be represented as:

$$\frac{1}{q} = \frac{1}{a} + \frac{1}{ab}\left(\frac{1}{Ce}\right) \qquad (2)$$

Where, q is the amount of solute adsorbed per unit weight of material, a is the maximum adsorption capacity, b is the Langmuir constant, and Ce is the equilibrium solute concentration. The plot between 1/qe and 1/Ce is as shown in the figure.

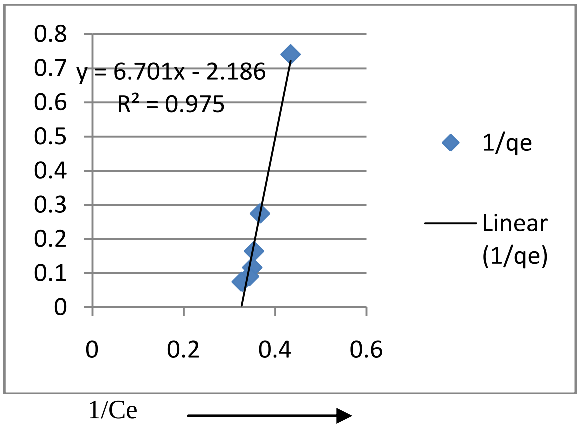


Fig 3.6.1 Langmuir isotherms of fluoride adsorption

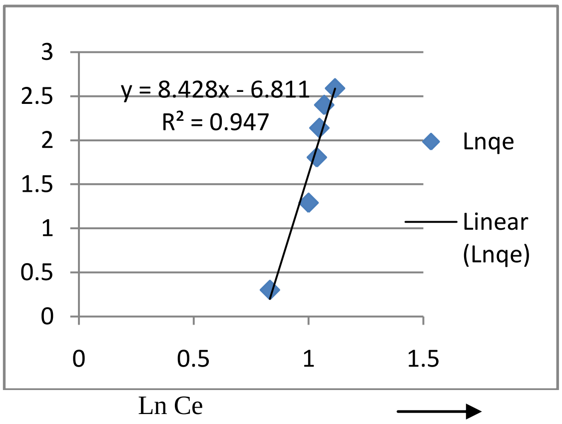


Fig 3.6.2 Freundlich isotherm of fluoride adsorption

3.6.2. The Freundlich isotherm

Freundlich adsorption isotherm is the relationship between the amounts of flouride adsorbed per unit mass of adsorbent, qe, and the concentration of the flouride at equilibrium, Ce.

$$q = KfCe^{1/n} \quad (3)$$

The logarithmic form of the equation becomes

$$logq = log(Kf) + \frac{1}{n}log(Ce) \quad (4)$$

where q = the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g-1)
Ce = the equilibrium solute concentration (mg L-1)
KF = the measurement of the adsorption capacity (mg g-1) based on freundlich isotherm
n = the adsorption equilibrium constant

The ability of Freundlich model to fit the experimental data was examined. Plot between log Ce and logqe was drawn to generate the intercept value of kf and the slope of n as shown in the Figure.

3.6.3 Tempkin isotherm

The Tempkin isotherm (Wasewar et al., 2009) contains a factor that explicitly takes in account adsorbing species- adsorbate interactions
The Tempkin isotherm is represented by the following equation:

$$qe = RT \ln (KT\ Ce) / b \quad (5)$$

Equation (5) can be linearized as in equation (6).

$$qe = B1 \ln KT + B1 \ln Ce \quad (6)$$

Where, B1 = RT / b
Regression of qe versus ln Ce enables the determination of isotherm constants KT and B1

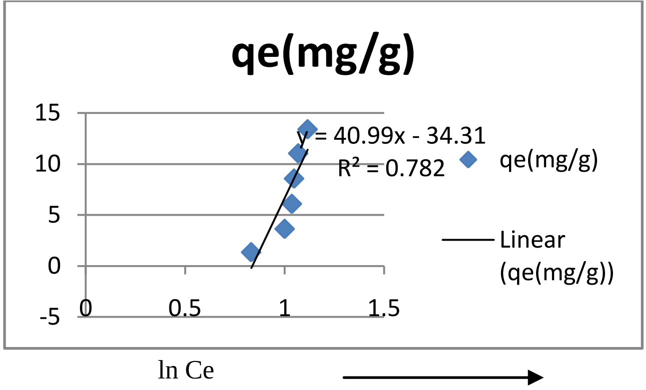


Fig 3.6.2 Tempkin model of fluoride adsorption

The values of sorption capacities and coefficient of correlation (R^2) for various sorbents and equilibrium models are as shown in the Table.

Adsorbent	Langmuir isotherm		
Sawdust	a	b	R^2
	0.457	0.326	0.9754
	Freundlich isotherm		
	Kf	1/n	R^2
	0.0011	8.4284	0.9471
	Tempkin		
	KT	B1	R^2
	0.435	40.995	0.7824

From Table above, The values of coefficient of correlation (R^2) was obtained as 0.9754 giving a best fit for Langmuir equation compared to Freundlich Isotherm. It follows from the data the equilibrium adsorption of flouride follows Langmuir isotherm model, which reflects the formation of a monolayer of sorbate over a homogeneous surface of uniform energy and that the adsorbed layer is unimolecular.

It may also be observed that the isotherm fits of sawdust have negative intercepts which indicates that the removal is good at lower concentrations, but not as good, at higher concentrations.

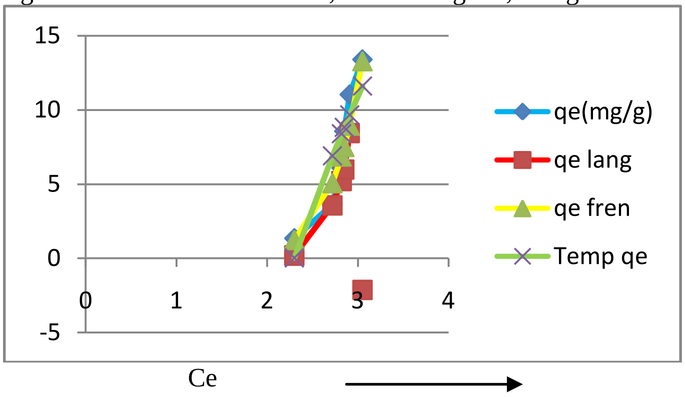


Figure 3.6.4: Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride onto sawdust

3.7 Kinetic model of adsorption

3.7.1 pseudo first order model

In order to determine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first order kinetic model is used to test the experimental data. A simple kinetics of adsorption is given by Lagergren rate equation.[30]

$$\frac{dqt}{dt} = K1(qe - qt)$$

Applying conditions:
qt = 0 at t = 0
qt = qt at t = t

$log(q_e\text{-}q_t) = logq_e - (k_1t/2.303)$

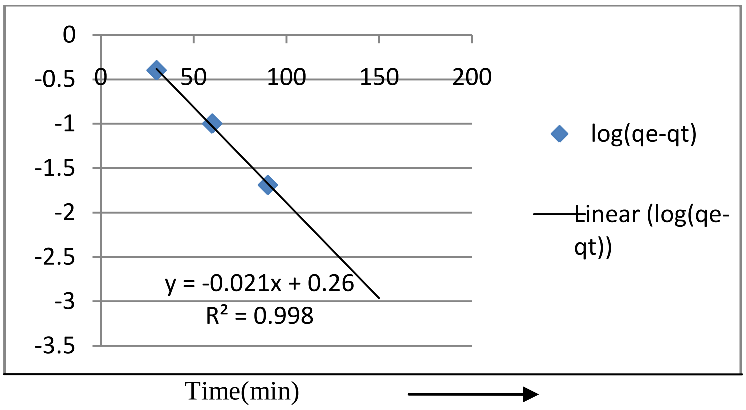


Figure 3.7.1 pseudo first order model

It was observed that the pseudo-first-order model did not fit well. It was found that the calculated qe values do not agree with the experimental qe values .This suggests that the adsorption of flouride does not follow first-order kinetics.

3.7.2 Pseudo-second-order model

The pseudo-second-order kinetics may be expressed in a linear form as[31]

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{1}{qet}$$

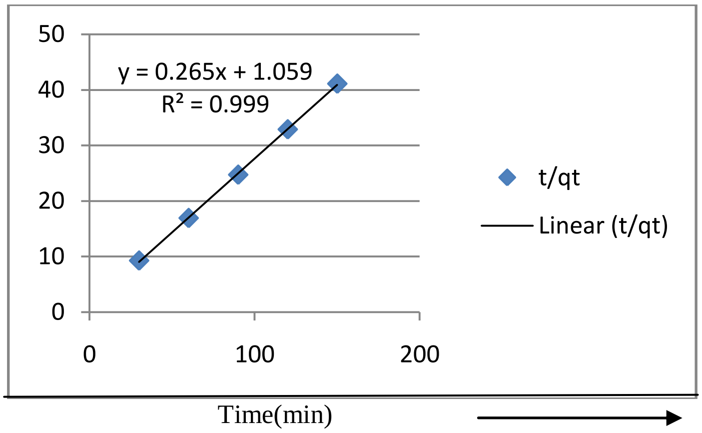


Fig 3.7.2 Pseudo-second-order model

It can be seen from Table that there is an agreement between *q*e experimental and *q*e calculated values for the pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics.

3.7.3 Intraparticle diffusion model

The intraparticle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent (i.e., the process is diffusion-controlled), which is presented by Equation [32] $q_t = K_3 t^{1/2} + c$

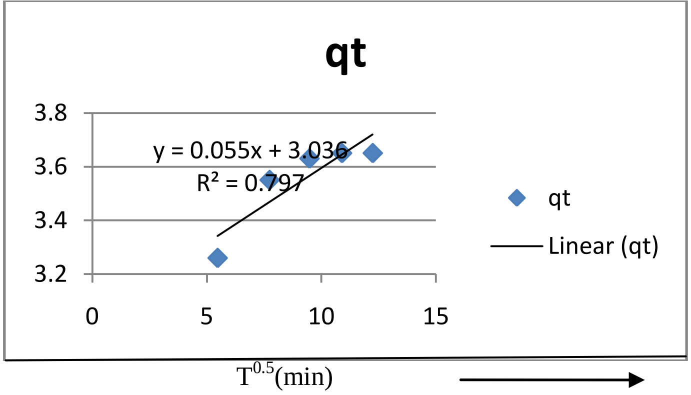


Figure3.7.3: intraparticle diffusion model for sorption of fluoride onto sawdust

3.7.4 Elovich model:

The Elovich model equation is usually expressed as follows.

$$Dqt/dt = \alpha \exp(-\beta qt)$$

$$qt = \beta \ln(\alpha\beta) + \beta \ln t$$

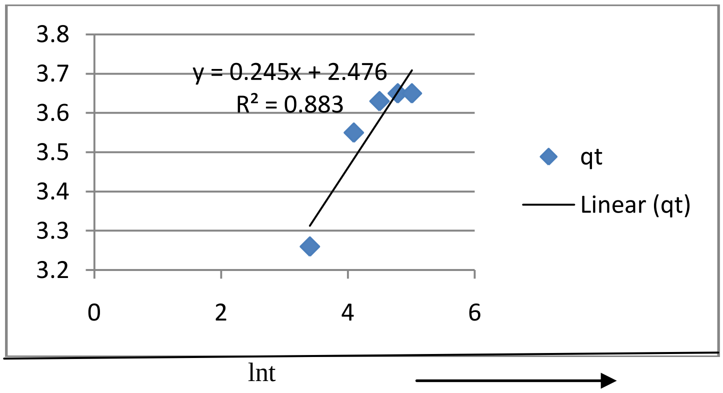


Figure3.7.4 Elovich model for fluoride adsorption

Table3.1 : Comparison of the pseudo-first-order, pseudo-second-order, Intraparticle diffusion model and Elovich model for their adsorption rate constants and calculated and experimental *q*e values obtained

Pseudo-first-order kinetic model			
qe Expt (mg/g)	K1 (l/min)	qe ,calc (mg/g)	R^2
3.65	0.0495	1.26	0.9984
Pseudo-second-order kinetic model			
qe Expt (mg/g)	K2 (l/min)	qe,calc (mg/g)	R^2
3.65	0.066	3.76	0.9997
Intraparticle diffusion model			
qe Expt (mg/g)	K3	qe,calc (mg/g)	R^2
3.65	0.0559	3.64	0.7976
Elvich model			
qe Expt (mg/g)	α	β	R^2
3.65	92.34	0.2458	0.8832

The qe,exp and the qe,cal values from the pseudo-second-order kinetic model are very close to each other. The calculated correlation coefficients are also closer to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetic model , intraparticle diffusion model and Elvich model. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the pseudo-first-order kinetic model and intraparticle diffusion model for the adsorption of flouride onto sawdust.

IV. CONCLUSION

It can be concluded from the results that sawdust have good properties for the sorption of fluoride from aqueous solutions, under optimized conditions, including pH value of 7, contact time of 120 min and adsorbent dosage of sawdust 2 g/L, more than 70% removal efficiency can be acheived. The pseudo-second order model describes the fluoride sorption kinetics at different contact times. The Langmuir model best describes the isotherm's experimental data, which may indicate that the sorption mechanism of fluoride ions on sawdust is chemisorption on a homogeneous material.

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