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Removal of Fluoride from Contaminated Drinking Water using Unmodified and Aluminium Hydroxide Impregnated Blue Lime Stone Waste

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Removal of Fluoride from Contaminated Drinking Water using Unmodified and Aluminium Hydroxide Impregnated Blue Lime Stone Waste

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Abstract: The adsorption of fluoride on lime stone (LS) and aluminium hydroxide impregnated lime stone (AlLS) was investigated using a batch adsorption technique. A series of experiments were under taken in an agitated batch adsorber to assess the effect of the system variables such as solution pH, dye concentration and temperature. Removal of fluoride was observed to be the most effective at pH 8. The langmuir and Freundlich isotherm models were applied to the equilibrium data. The results showed that the Freundlich equation fits better than the Langmuir equation. The maximum sorption capacities for the LS and AlLS adsorbents were found to be 43.10 mg/g and AlLS 84.03 mg/g respectively. The FTIR studies indicate that the adsorption of fluoride is physiorption. The adsorption of fluoride onto AlLS proceeds according to a pseudo-first-order model. The results reveal that the LS and AlLS can be economical for the removal of fluoride compared to many other expensive adsorbents.

Keywords: Adsorption isotherm, fluoride, impregnation, kinetic equation, lime stone

INTRODUCTION

Fluoride in minute quantity is an essential component for normal mineralization of bones and formation of dental enamel. The safe limit

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of fluoride in drinking water is 1.0 mg/L (1). However, when the fluoride concentration is above this level it leads to skeletal and dental fluorosis, muscle fiber degeneration, low hemoglobin levels, deformities in red blood cells (RBCs), excessive thirst, headache, skin rashes, neurological manifestations (it affects brain tissue similar to the pathological changes found in humans with Alzheimer's disease), and gasterointestinal problems. It is also responsible for alterations in the functional mechanisms of liver, kidney digestive system and respiratory system. Fluoride pollution in the environment occurs through two different channels which are natural source and anthropogenic activities (2). Fluoride poisoning can be minimized by using alternate water sources, giving nutrition, and defluoridation of water. Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water. Several methods such as adsorption, ion-exchange, reverse osmosis, nanofiltration, electrodialysis, and donnan dialysis (3–8) have been used for the removal of fluoride. Among these methods, adsorption has been found to be superior to other techniques in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances. Activated alumina (9), activated carbon (10), lanthanum impregnated silica gel (11), calcite (12), magnesia (13) etc., are different adsorbent materials reported in the literature for removal of fluoride. These adsorbent materials have limited use due to its high cost. This has led to a search for cheaper substitutes. In recent years many researchers have studied the feasibility of using inexpensive alternative materials like red mud (14), plaster of Paris (15), cement paste (16), brick powder (17), bone charcoal (18) and other waste materials. Lime stone powder emerges as an unwanted byproduct during the cutting of limestone. Limestone is a sedimentary rock and it is composed mainly of calcium carbonate and used directly as a building material.

The study emphasizes on the use of novel adsorbent aluminium hydroxide impregnated limestone for the efficient removal of fluoride from contaminate drinking water. Batch adsorption studies were carried out systematically in terms of process parameters such as agitation time, initial concentration, and pH. Attempts have also been made to understand the adsorption equilibrium and kinetics.

MATERIALS AND METHODS

Preparation of the Adsorbent

The limestone powder was collected from Kota District, Rajasthan, India. It was washed several times to remove earthy matter and finally with distilled water. It was dried in oven at 105°C for 24 h and ground manually to obtain desired particle sizes using British Standard Sieves (BSS) of 240-mesh size.

The limestone was impregnated with aluminium hydroxide by adding 500 ml of 0.01 M NaOH and 500 ml of 0.1 M Al $(NO_3)_3 \cdot 9H_2O$ solution to 15 g of limestone. After 6 h of thorough mixing, the solution was allowed to stand for 24 h at 30°C. Then the aluminium impregnated limestone was washed with distilled water, dried for 24 h at 105°C. The lime stone impregnated with Al $(OH)_3$ was stored in a reagent bottle.

Physical Characterization

The concentration of fluoride in solution was determined spectrophotometrically on a Shimadzu 1650PC UV-Visible spectrophotometer. The pH of the solution was measured with an Elico (India) pH meter. FT-IR spectra of different samples were recorded using a Perkin FTIR in absorption mode averaging 32 scans and at a resolution of 4 cm^{-}. The X-ray diffraction patterns were obtained by a Phillips X-ray diffractometer using Ni–filtered Cu Kα radiation and scan rate 2°/min. The spectroscopic studies were performed by using a scanning electron microscopy (SEM, model) to detect the impregnation of aluminium hydroxide on lime stone and by energy—dispersive analysis of X-ray (EDAX,) to know the elemental composition of adsorbent (combined with oxygen).

Adsorption Studies

In the batch method, a fixed amount of the adsorbent (0.1 g) was added to 100 ml of fluoride solution of varying concentration taken in 250 ml stoppered conical flasks, which were placed in a thermostated agitation (32°C) assembly. The solution was agitated continuously (200 rpm) at constant temperature for 5 h to achieve equilibration. The concentration of fluoride in the solution after equilibrium adsorption was determined spectrophotometrically at λ_{max} of 584.50 nm. The pH of the adsorbate solution was adjusted using a 0.1 M aqueous solution of either HCl or NaOH.

The adsorbate uptake q_e (mg/g), can be calculated as

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

Where C_o is the initial adsorbate concentration (mg/L), C_e is the equilibrium adsobate concentration in solution (mg/L); V is the volume of the solution, and W is the mass of the adsorbent (g) and q_e is the amount adsorbed.

Kinetic Studies

Samples of modified lime stone were agitated at 200 rpm with a fixed concentration of adsorbate solution (1000 ml) at the desired temperature in a thermostated bath. The adsorbent was introduced to the reaction flask at zero time and 5 ml of the solution phase was withdrawn at various time intervals. These aliquots were centrifuged to remove particulates and were analyzed for the concentration of fluoride.

Methods of Analysis

The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg of anhydrous NaF (Merck, India) in 1 L of distilled water. The sample was analyzed for residual fluoride concentration by SPADNS method, described in the standard Method of Examination of Water and Wastewater (19).

RESULTS AND DISCUSSION

Characterization of the Adsorbent

LS and AlLS were characterized, and the results are summarized in Table 1.

The XRD patterns of limestone before and after treatment with $Al(NO_3)_3$ solution are shown in Fig. 1. It is evident from the XRD study

Table 1. Ph characteristics of LS and AlLS

	Value	
Parameters	LS	AlLS
pH (1%)	8.67	9.27
pHzpc (20)	9.23	10.17
Moisture	0.07 %	1.32%
Ash	78.65%	84.32%
Bulk density	0.92 g cm^{-3}	0.77 g cm^{-3}

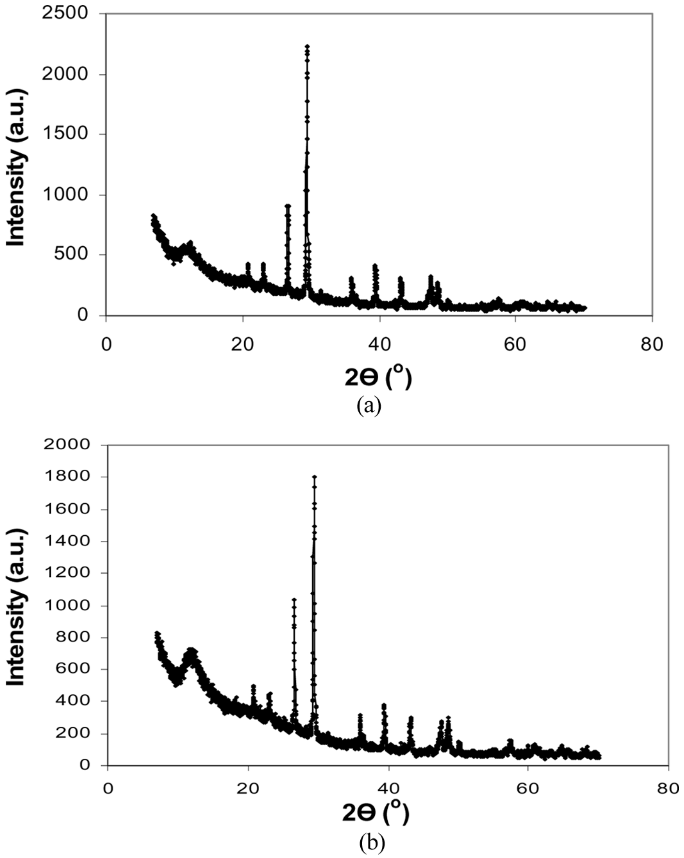
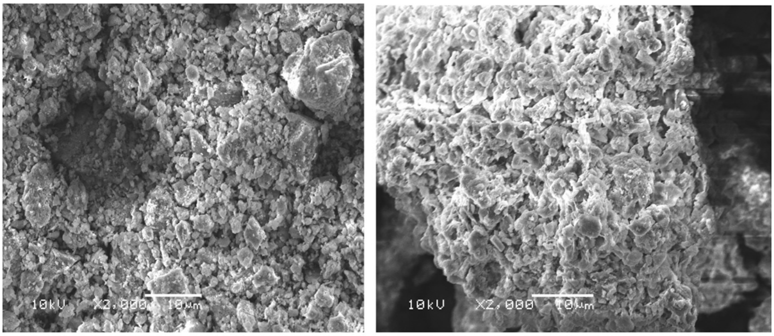


Figure 1. XRD pattern of (a) lime stone and (b) modified lime stone.

that the crystal structures of the lime stone do not show any significant changes after modification of limestone. This may be due to the amorphous nature of the $Al(OH)_3$.

Figure 2 (a) and (b) shows the scanning electron microscope picture of unimpregnated and aluminium hydroxide impregnated limestone, respectively. Figure 2b shows aluminium hydroxide particles forms fibrous that agglomerate the limestone. Such behavior is not seen in the unimpregnated limestone.

Energy – dispersive analysis of X-rays was used to analyze the elemental constituents of LS and AlLS (Fig. 3). The spectrum shows the signals corresponding to Al, Ca, and O, which provide direct evidence for alumina on the surface of LS.



(a) (b)

Figure 2. Scanning electron micrograph of (a) lime stone and (b) modified lime stone.

Effect of pH

The adsorption pattern of fluoride on unmodified and modified lime stone in the pH range from 2 to 10 is presented in Fig. 4. The solution pH played a major role in fluoride adsorption. Maximum adsorption of fluoride was found to be 34 mg/g in pH 8. This can be explained by considering the pHzpc of adsorbent. The lower adsorption efficiency of fluoride in acidic medium might be attributed to the formation of weakly ionized hydrofluoric acid, which reduced availability of free fluoride for adsorption. In modified lime stone the adsorption was extremely decreased at pH 2, may be due to aluminium hydroxide dissolution in acidic environment.

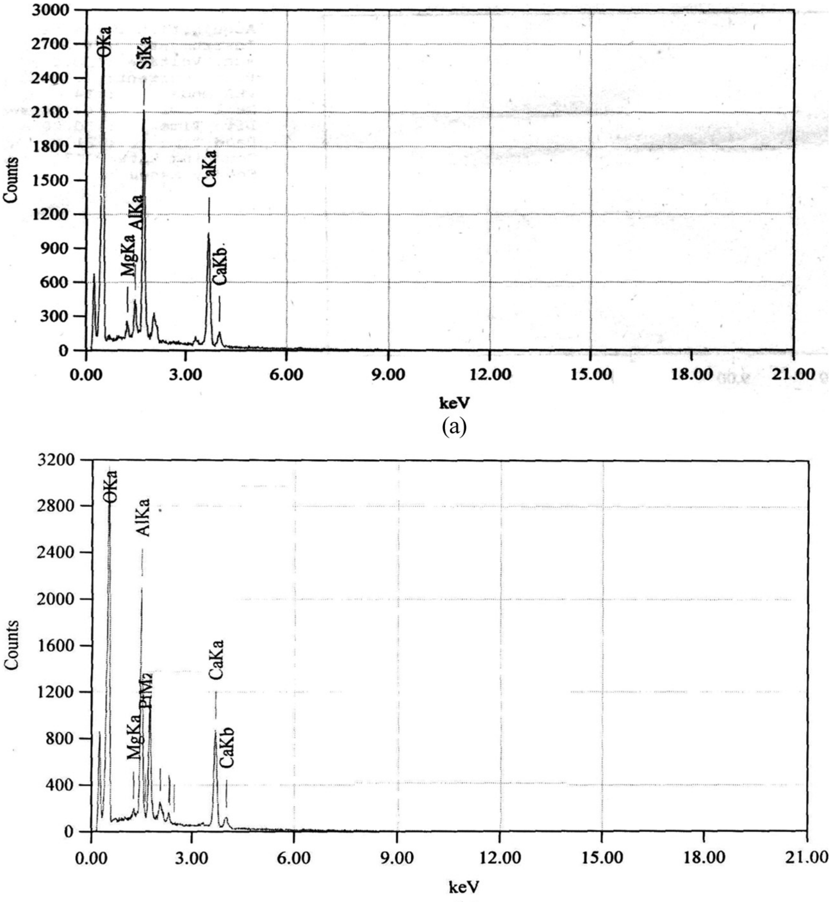
Aluminium hydroxide dissolves in acids to form aluminium salt.

$$Al(OH)_3 + 3HCl \longrightarrow (AlCl_3 + 3H2O$$

The decrease of fluoride uptake at $pH > 8$ is possible due to electrostatic repulsion of fluoride ion to the negative charged surface and the competition for active sites by amount of hydroxyl ion.

Adsorption Isotherms

Several models have been published in the literature to described experimental data of adsorption isotherm (Fig. 5). For the sake of convenience, explicit and simple models are preferred and commonly used. The Langmuir and Freundlich models are the most frequently employed models.



(a)

(b)

Figure 3. Energy–dispersive analysis of X-rays (a) lime stone and (b) modified lime stone.

The Langmuir isotherm (21) is represented by the following equation:

$$q_e = \frac{Q_o bc}{1 + bc} \tag{2}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{3}$$

Where, C_e is the concentration of dyes (mg/L) at equilibrium, q_e is the amount of adsorbate adsorbed on per unit mass of adsorbent at

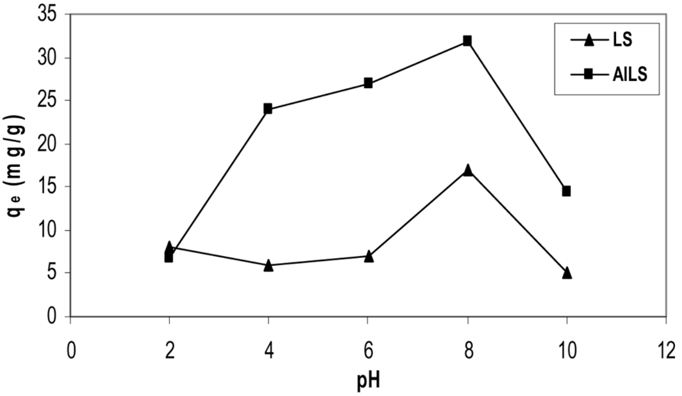


Figure 4. Effect of pH on the adsorption of fluoride on lime stone and modified lime stone. C_0; 50 mg/L, T; 298 K, adsorbent dose; 1 g/L.

equilibrium in (mg/g), Q_o is the maximum adsorption at monolayer coverage in (mg/g), b is the adsorption equilibrium constant related to the energy of adsorption in L/mg, The plots of C_e/q_e vs C_e are linear and presented in Fig. 6.

For a Langmuir-type adsorption, the isotherm shape can be classified by a term, r a dimensionless constant separation factor

$$r = 1/1 + bC_{ref} \tag{4}$$

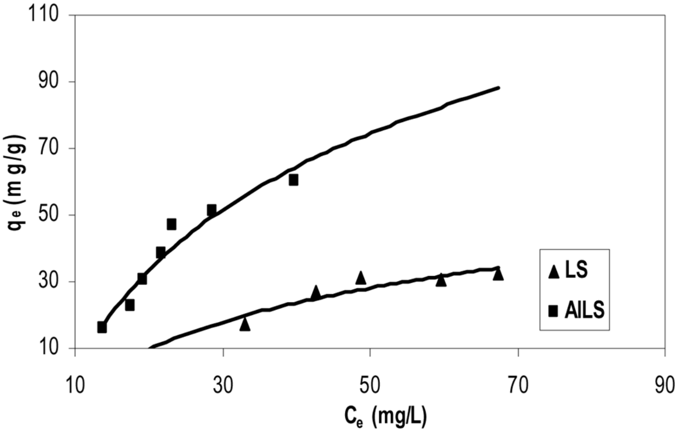


Figure 5. Adsorption isotherms (298 K) of fluoride on lime stone and modified lime stone.

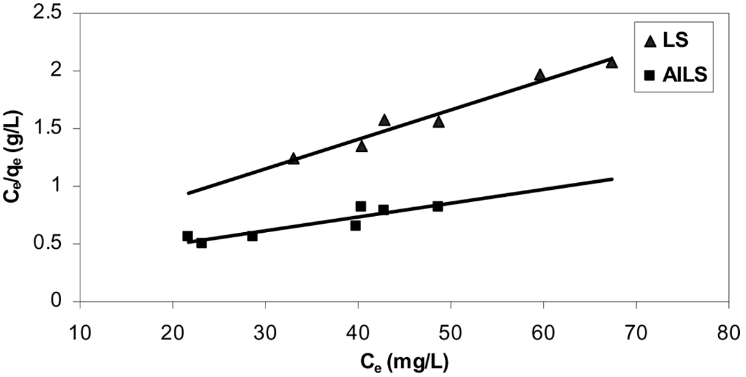


Figure 6. Langmuir plots for the adsorption of fluoride on LS and AlLS Adsorbent dose; 1 g/L, T; 298 K.

Where, C_{ref} is the highest fluid-phase concentration (mgL^{-1}) and b is the Langmuir constant (Lmg^{-1}).

The logarithmic form of the Freundlich model is given by the following equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_f and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively and calculated from the intercept and slope of Fig. 7. The

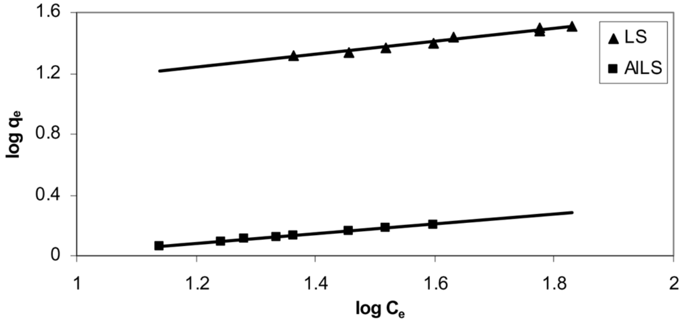


Figure 7. Freundlich plots for the adsorption of fluoride on LS and AlLS Adsorbent dose; 1 g/L, T; 298 K.

Table 2. Langmuir and Freundlich constants for the adsorption of fluoride on lime stone and modified lime stone

	Langmuir constants				Freundlich constants		
Adsorbent	Q_o (mg g^{-1})	b (L mg^{-1})	R^2	r	K_f	n	R^2
Limestone	43.10	0.044	0.9548	0.035	6.41	2.60	0.9849
Modified limestone	84.03	0.047	0.8469	0.056	0.49	3.14	0.9972

correlation coefficient values show that data can be better represented by the Freudlich isotherm model (Table 2). Fluoride is expected to be adsorbed on adsorbent through electrostatic attraction.

A comparison was made, (22–28) in terms of adsorption capacity (Q_o) of the unmodified lime stone and aluminium hydroxide impregnated lime stone with other low-cost adsorbents in Table 3. The present study shows that the lime stone and modified lime stone are effective low-cost adsorbents for the removal of fluoride from aqueous solutions. Lime stone is a waste material and it is used as adsorbent in unmodified and modified form.

FTIR Analysis

The FTIR spectra of the sodium fluoride (a), fluoride adsorbed on modified lime stone (b) and modified lime stone (c) are presented in

Table 3. Comparison of adsorption capacity of lime stone and aluminium hydroxide impregnared lime stone with other low cost adsorbents

	Q_o(mg g^1)	References
Mixed rare earth oxide	12.50	(22)
Aligned carbon nanotubes	4.5	(23)
Lanthanum impregnated cross-linked gelatin	21.28	(24)
Hydrous ferric oxide	16.5	(25)
Titanium rich bauxite	3.8	(26)
Aluminium impregnated carbon	1.07	(27)
La^{+3} exchanged zeolite	59.11	(28)
Lime stone	43.10	This work
Aluminium hydroxide impregnated lime stone	84.03	This work

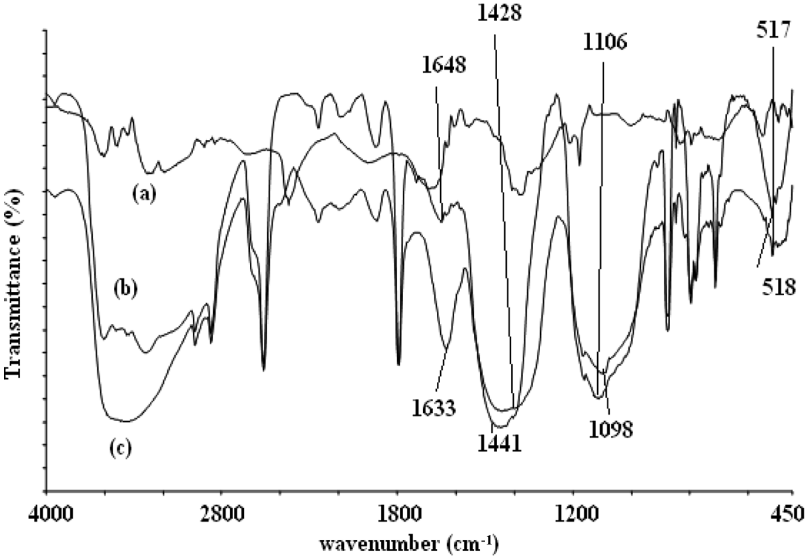


Figure 8. The FTIR spectra of the sodium fluoride (a), fluoride adsorbed on modified lime stone (b) and modified lime stone (c).

Fig. 8. The FTIR spectrum of fluoride adsorbed on modified lime stone (b) is like that lime stone (c) except for a small shift in frequencies like 1633 cm^{-1} shift to 1648 cm^{-1}, 1441 cm^{-1} shift to 1428 cm^{-1}, 1098 cm^{-1} shift to 1106 cm^{-1} and 518 cm^{-1} shifted to 517 cm^{-1} and no extra new band appeared in the spectrum. This indicates that adsorption of fluoride on modified lime stone is physical adsorption.

Kinetics of Adsorption

The rate constants for the adsorption of fluoride on modified lime stone were determined using pseudo-first-order, pseudo-second-order equations and intraparticle diffusion.

The pseudo-first-order rate equation can be written as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{6}$$

Where k_1 is the rate constant for pseudo-first-order adsorption, q_e and q_t are the amounts of adsorption at equilibrium and at time t, respectively and presented in Fig. 9.

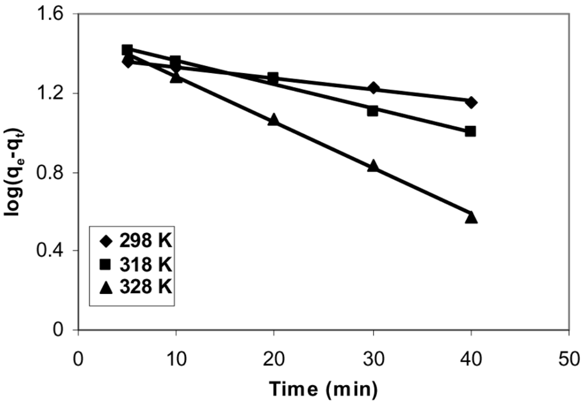


Figure 9. Pseudo-first order plots for removal of fluoride on AlLS.

The corresponding pseudo second order rate equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

Where k_2 is the rate constant for pseudo-second-order adsorption (29). The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t Vs t and presented in Fig. 10.

The possibility of intraparticle diffusion was explored by using an intraparticle diffusion model (30). The corresponding rate equation being

$$q_t = k_{id} t^{1/2} + c \tag{8}$$

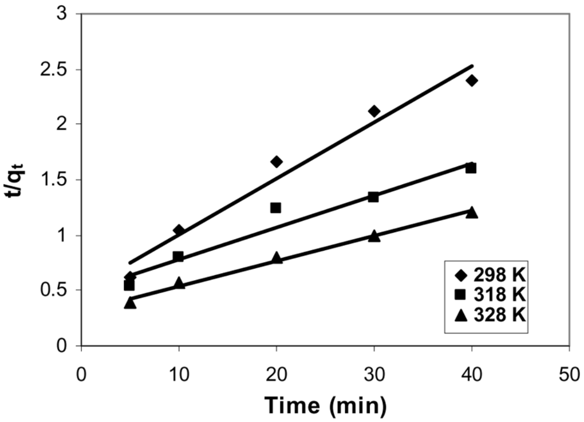


Figure 10. Pseudo-second order plots for removal of fluoride on AlLS.

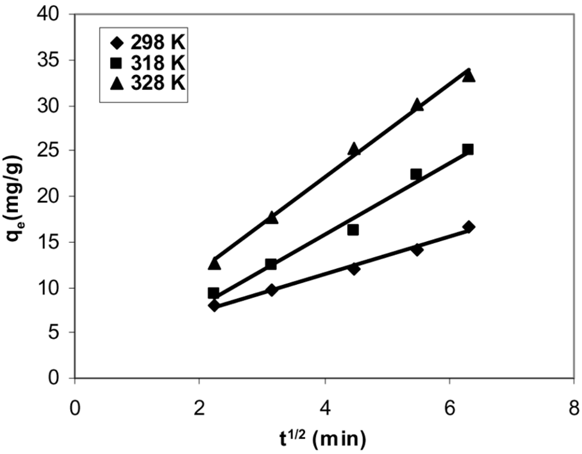


Figure 11. Intraparticle diffusion plots for removal of dyes on AlLS.

Where c is constant and k_{id} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and presented in Fig. 11.

Kinetic parameters for their three kinetics models and correlation coefficients are summarized in Table 4. The values indicate that the adsorption complies with a pseudo-first-order rate equation.

Table 4 shows that the correlation coefficients of first-order kinetics model are greater than those of other rate laws. Also, a comparison is made between the equilibrium adsorption capacity (q_e calc) evaluated from the pseudo-first-order model and achieved from experiments (q_e exp). These indicate that the adsorption complies with a pseudo-first-order rate equation.

Table 4. Kinetics parameters for the effect of temperature on the removal of fluoride

	Pseudo first order				Pseudo second-order			Intraparticle diffusion equation	
T (K)	q_e exp. (mg g^{-1})	$k_1 \times 10^{-3}$ (min^{-1})	q_e, calc (mg g^{-1})	R^2	$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	q_e calc. (mg g^{-1})	R^2	k_2 (mg g^{-1} $min^{-1/2}$)	R^2
298 K	85.1	13.24	84.37	0.9968	5.17	99.6	0.9712	2.07	0.9911
318 K	93.1	27.08	90.32	0.9992	1.66	112.35	0.9869	3.90	0.9852
328 K	96.9	53.23	92.71	0.9976	1.61	128.20	0.9942	0.58	0.9611

CONCLUSION

In this study, a novel adsorbent, aluminium hydroxide impregnated lime stone has been prepared and examined for its potential in removing fluoride from drinking water system. The optimum pH for maximum uptake is found 8. The experimental data generated from bath adsorption experiments fitted well into the Freundlich Isotherm model. The analysis of FT-IR suggests that physisorption is prominent in the removal process. The process is thermodynamically favorable, spontananeous and endothermic in nature. The adsorption follows a pseudo-first-order kinetic model. The present study shows that LSP, unwanted byproduct during the cutting of limestone and inexpensive material, can be an alternative for many other expensive adsorbents used for the removal of fluoride in wastewater treatment.

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