

Sorption Kinetics, Isotherm and Thermodynamic Modeling of Defluoridation of Ground Water Using Natural Adsorbents

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ABSTRACT

The aim of study is to investigate the removal ability of some natural adsorbents for fluoride ion from aqueous solution. The batch dynamic adsorption method was carried out at neutral pH as the functions of contact time, adsorbent dose, adsorbate concentration, temperature and effect of co-anions, which are commonly present in water. The sorption kinetics and equilibrium adsorption isotherms of fluoride on natural adsorbing materials had been investigated at aforementioned optimized. Equilibrium adsorption isotherms, viz., Freundlich and Langmuir isotherms were investigated. Lagergren and Morris-Weber kinetic equations were employed to find the rate constants. The negative enthalpy $\Delta H = -46.54 \text{ KJ}\cdot\text{mol}^{-1}$ and Gibbs free energy calculated was $\Delta G_{288-333} = (-2.07785, 3.08966, 4.1064, 4.90716 \text{ and } 5.38036 \text{ KJ}\cdot\text{mol}^{-1})$ respectively, envisage exothermic and spontaneous nature of sorption.

Keywords: Isotherm; Kinetics and Thermodynamic Modeling; Ground Water; Natural Adsorbent; Defluoridation

1. Introduction

Weathering and dissolution of minerals, emitted from volcanoes and marine aerosols are the natural sources of releasing fluorides into the environment [1-3]. Many anthropogenic activities such as combustion and process waters and waste from various industrial processes, including steel manufacture, primary aluminum, copper and nickel production, phosphate ore processing, phosphate fertilizer production and use, glass, brick and ceramic manufacturing and glue and adhesive production are also the reason of fluoride contamination [2,4-5].

Increased fluoride levels in drinking water have become a critical health issue in many countries due to prevailing skeletal and dental fluorosis [6-8]. Though fluoride is an essential constituent for both humans and animals, it can be detrimental to human health depending on its level in drinking water [9]. Beneficial level of fluoride to health is $<1.5 \text{ mg/L}$ as recommended by WHO [10-12]. In Pakistan, the problem is common in Thar Desert, the ground water is highly contaminated and

people are facing many diseases caused by high fluoride concentration [8,13].

Several studies have been conducted to reduce the concentration of F^- ion in drinking water for the benefits of common man. 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 [14-15], zirconium impregnated coconut shell carbon [16-17], cashew nut shell carbon [18], ground nut shell carbon [19] and clays [20-21] have been used as adsorbents for fluoride removal from drinking water. Recently, amorphous alumina supported on carbon nanotubes [22], natural zeolites [23] chemically activated carbon [24] aligned carbon nanotubes [25], ion exchange polymeric fiber [26], double hydrous oxide of Al and Fe ($\text{Fe}_2\text{O}_3\text{Al}_2\text{O}_3\cdot\text{XH}_2\text{O}$) [27] bone charcoal [28] and activated alumina [29] have been assayed for removing fluoride from drinking water as well as industrial wastewater.

This paper concentrates on investigating low cost material for fluoride sorption which can effectively remove fluoride from aqueous solutions at a relatively low level.

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To overcome these problems and enhance the defluorination capacity this study was carried out with the natural adsorbents (coal, brick powder, saw dust) to treat the contaminated water. These adsorbents are cheaper, abundant and easily available in huge amount.

This study leads to the assumption that fluoride deposition occurs by the forces of adsorption over the surface of the adsorbents; also the dynamics and kinetics of the adsorption process are discussed.

2. Experimental

2.1. Apparatus and Materials

781-pH/Ion meter (Ω Metrohm, Herisau, Switzerland) with Ag, Ag/Cl reference electrode 6.0726.100 (Ω Metrohm) and fluoride electrode 6.0502.150 (Ω Metrohm) were used for the quantitative analysis of Fluoride and also for the pH measurement with pH electrode. Gallenkamp thermostated automatic shaker model BKS-305-010, UK was used for the batch experiments at ambient temperature (ca. 25°C).

Ion-Chromatography (I.C) (Ω Metrohm, Switzerland) instrument 861 Advance Compact with 833 IC liquid handling unit equipped with self-regenerating suppressor consists of a double gradient peristaltic pump with a conductivity detector was used for validation and correlation of results obtained from 781-pH/Ion meter for the quantification of fluoride. The anion column (4.0 \times 250 mm²) METROSEP A SUPP 4 - 250 (6.1006.430) and Carbonate/bicarbonate buffer mobile phase was used in ion chromatographic study. Whatman no. 42, filter papers were used for all filtration procedures.

All analytical reagent grade chemicals are obtained from the indicated companies and used without any further purification. CDTA (cyclohexylenedinitrilotetraacetate) (Merck, Germany) Anhydrous Sodium fluoride, sodium hydroxide, sodium chloride and acetic acid (ethanoic acid) from (Aldrich Chemical Co.). The adsorbents (coal, brick powder and saw dust) were collected from local area of Hyderabad (Pakistan).

2.2. Preparation of Stock Solutions Specifications

Ultra pure water (conductivity 0.050 $\mu\text{S}\cdot\text{cm}^{-1}$), obtained from a Milli-Q purification system (PURELAB Prima 7 BP, PURELAB Classic UV) was used for the preparation of all samples, standards and blanks. All glassware (pipettes, volumetric flasks, etc.) employed in the preparation of the stock solutions as well as working solutions were all initially cleaned by soaking in acidified (6 M nitric acid) water or in acidified (HNO₃ 1.0 M) solution of potassium permanganate, then thoroughly rinsed with deionized water and then acetone. The glassware was then dried for at least one hour in an oven at 120°C.

The 1000 mg/L of fluoride stock solution was pre-

pared by liquefying appropriate amount of anhydrous NaF in 100 ml volumetric flask and then volume make up to the mark with Ultra pure water.

The adsorbents were first washed with distilled water followed by Milli Q Ultra pure water then dried oven at 105°C for 12 h. After drying adsorbents were passed through sieve to obtain the required particle size for the present study.

No any impregnation or activation process was done before using the above adsorbents as well as these are easily available in rural area decreasing its cost as compare to previous reported materials.

A total ionic strength adjustment buffer (TISAB) buffer solution prepared for potentiometric measurement of fluoride by ion selective electrodes.

2.3. Sorption Procedure

The batch technique was used to examine the %sorption of fluoride onto natural adsorbents at ambient temperature. Sorption of fluoride carried out by taking 10 mL of aqueous solution of fluoride (5.0 mg/L) was added to an Erlenmeyer flask containing 0.2 g of each dried and sieved adsorbent. The mixture was then shaken for a specified time (10 - 100 min) and temperature (25°C) to allow adsorption of fluoride ion. The Erlenmeyer flasks were removed from shaker and allowed to stand for 2 min after attaining the required contact time. Then the mixture was filtered using then remainder was determined by TISAB method using fluoride ion selective electrode.

2.4. Data Analysis

The adsorption behavior of fluoride ion on the adsorbents e.g. coal, brick powder and saw dust surface was investigated using batch equilibrium experiments.

The sorbate concentration of sorbate on sorbent surface was calculated by the difference in the fluoride ion meter response (mg/L) before and after shaking. The distribution ratio R_d and %sorption of fluoride were calculated by using the following equations:

$$\% \text{Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e is the initial and equilibrium concentrations ($\text{mg}\cdot\text{L}^{-1}$) respectively.

All the experiments were performed in triplicate. The linear regression computer program with one independent variable was used for slope and statistical analyses of the data.

3. Result and Discussion

Sorption is a surface phenomenon and is affected significantly by physical and chemical characteristics of sorbent and sorbate. Sorption studies on natural adsorb-

ent was carried out by optimizing various parameters, *i.e.* effect of agitation time, effect of shaking speed, amount of sorbent, pH, concentration of sorbate and temperature.

3.1. Effect of Agitation Time and Speed (rpm)

Effect of shaking time on %sorption of fluoride onto mixture of adsorbents was studied over an agitation time of 10 - 100 min, using 0.2 g of each adsorbent temperature 25°C and 100 rpm shaking speed. The results are shown in **Figure 1**. Percent adsorption increases from 60% to 90% at contact time is increased.

Sorption of fluoride as a function of shaking speed was also studied in the range of 25 - 150 rpm. It was found that %sorption increases with increasing shaking speed and attains a maximum sorption at 100 rpm and then %sorption declines with increasing shaking speed as shown in **Figure 2**. Therefore for further studies 100 rpm shaking speed was employed.

3.2. Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of fluoride was studied by using different grams of adsorbent at 5.0

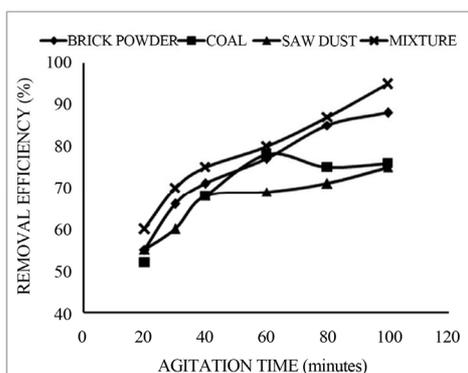


Figure 1. Percentage removal of Fluoride concentration as a contact time for the adsorbent (initial concentration = 5.0 mg/L, adsorbent dose = 1.0 g and pH 7.0).

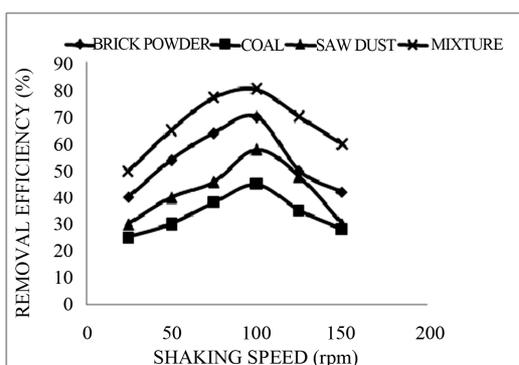


Figure 2. Percentage removal of Fluoride as a function of Shaking speed (initial concentration = 5.0 mg/L, reaction time = 30 min, and pH 7.0, Adsorbent dose 1.0 g).

mg/L fixed fluoride concentration. As shown in **Figure 3**, the fluoride concentration is decreases as the adsorbent dose enhanced. It is manifest that the adsorption process is very fast and most of the fluoride adsorbed within first 10 min and the equilibrium reached within 40 mints. At the high absorbent doses (2.0 g) equilibrium requires shorter time (20 min) and lower absorbent doses (0.1 g) needs longer equilibrium time (40 min). Therefore equilibration time of 30 mints was chosen to conduct further experiments at fixed adsorbent dose.

3.3. Effect of pH

The influence of pH on the fluoride removal efficiency and capacity of the adsorbent were carried out for each adsorbent separately and also in mixture. **Figure 4** shows adsorption capacity of untreated adsorbent at different fluoride concentration within the pH range of 4 - 9 in mixture of all adsorbents. Sorption % is achieved about 80% - 90% at pH 5 - 7 and due to better efficiency at pH 7 further study was carried out in neutral pH.

3.4. Isotherm Studies

The sorption isotherms express the specific relation be-

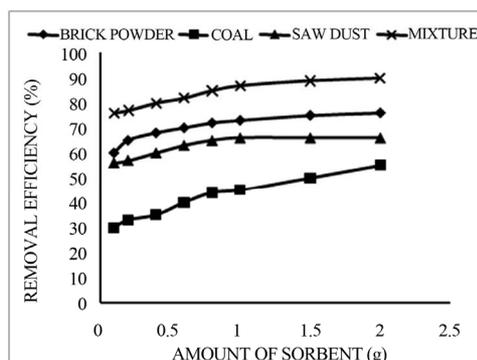


Figure 3. Percentage removal of Fluoride concentration as a function of adsorbent dose (initial concentration = 5.0 mg/L, reaction time = 30 min, and pH 7.0).

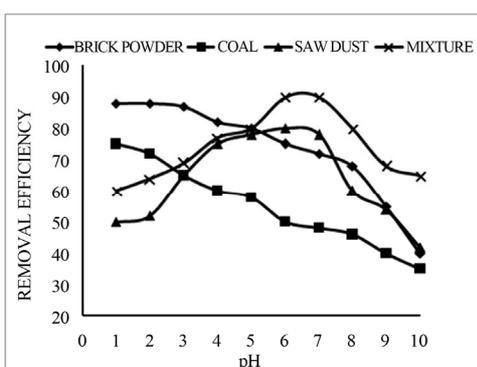


Figure 4. Percentage removal of Fluoride concentration as a function of pH for the adsorbent (initial concentration = 5.0 mg/L, reaction time = 30 min, and adsorbent dose = 2 gm).

tween the concentration of sorbate and its degree of accumulation onto sorbent surface at constant temperature. The Langmuir and Freundlich models are the simplest and most commonly used isotherms to represent the sorption of components from a liquid phase onto a solid phase [30].

The sorption capacities of coal, brick powder and saw dust for fluoride have been evaluated using different isotherms, namely Freundlich, Langmuir. **Table 1** shows the comparison of Freundlich and Langmuir isotherm model.

3.4.1. Freundlich Sorption Isotherm

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on multi-layer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption and given by [31] experimental data well on a phenomenological basis. The linearized form of Freundlich isotherm is tested in the following form:

$$\log C_{\text{ads}} = \log C_m + \frac{1}{n} \log C_e \quad (2) \quad [31]$$

where $1/n$ is a characteristic constant related to sorption intensity, C_{ads} is the sorbed concentration of sorbate onto sorbent ($\text{mol}\cdot\text{g}^{-1}$), C_e represents equilibrium concentration of sorbate in solution, and C_m is the multilayer sorption capacity of sorbent ($\text{mol}\cdot\text{g}^{-1}$). Logarithmic plot of sorbed and equilibrium concentration gives a straight line with coefficient of determination close to unity (0.95 ± 0.032). The values of $1/n$ (0.41 ± 0.01) and C_m ($0.31 \pm 0.001 \text{ mmol}\cdot\text{g}^{-1}$) are derived from the slope and intercept of the straight line, respectively. **Figure 5** shows Freundlich sorption isotherms of fluoride on adsorbents.

3.4.2. Langmuir Isotherm

Figure 6 shows the simplest theoretical model for monolayer sorption, *i.e.* Langmuir isotherm [32] of fluoride onto mixture of sorbents. The Langmuir model was originally developed to represent monolayer sorption on a set of distinct localized sorption sites. It gives uniform

Table 1. Isotherm (Freundlich and Langmuir) characteristic constants for fluoride ion sorption.

Isotherm parameter		Fluoride
Freundlich isotherm	$1/n$	0.41 ± 0.023
	K ($\text{mmol}\cdot\text{g}^{-1}$)	0.2488 ± 0.25
	Correlation factor	0.974 ± 0.05
Langmuir isotherm	Q ($\text{mmol}\cdot\text{g}^{-1}$)	0.6253 ± 0.002
	b ($\text{L}\cdot\text{mol}^{-1}$)	$(6.634 \pm 0.3) \times 10^3$
	Correlation factor	0.992 ± 0.06
	R_L (dimensionless factor)	$0.0278 - 0.9662$

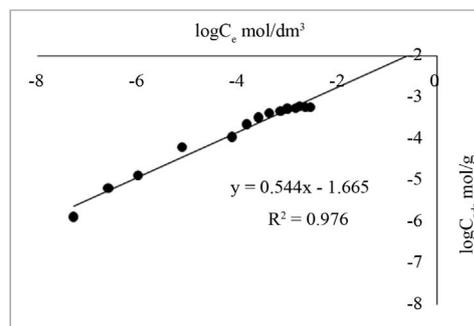


Figure 5. Freundlich sorption isotherms of Fluoride ion onto natural adsorbents.

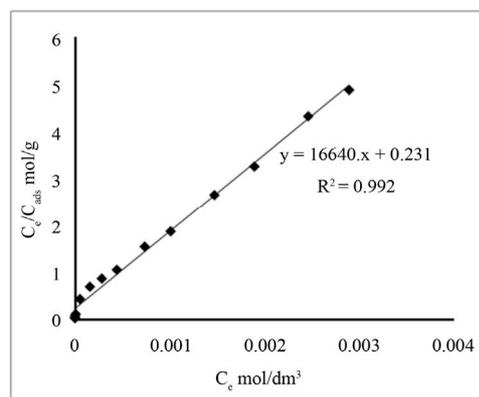


Figure 6. Langmuir sorption isotherms of Fluoride ion onto natural adsorbents.

energies of monolayer sorption onto sorbent surface with no transmigration of sorbate in the plane of the surface. There are no interactions between the sorbed molecules, no steric hindrance between sorbed molecules and incoming ions, and all the sorption sites are alike and uniform on microscopic scale. The sorption data is also applied to the following linearized form of Langmuir isotherm:

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (3) \quad [32]$$

where Q is the monolayer sorption saturation capacity ($\text{mol}\cdot\text{g}^{-1}$), and b represents the enthalpy of sorption ($\text{dm}^3\cdot\text{mol}^{-1}$), independent of temperature. In **Figure 6**, C_e/C_{ads} is plotted against C_e yielding a straight line with R^2 (0.995 ± 0.015) indicating that sorption data fit well into the Langmuir model. The value of Q ($0.0082 \pm 0.00025 \text{ mmol}\cdot\text{g}^{-1}$) was calculated from the slope of the linear plot, whereas the value of b (6.634 ± 1.0) $\times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}$ was derived from the intercept [33]. The essential characteristic of the Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (RL), calculated using the equation:

$$R_L = \frac{1}{1 + bC_i} \quad (4) \quad [33]$$

where b is the Langmuir constant ($\text{dm}^3 \cdot \text{mol}^{-1}$) and C_i is the initial concentration ($\text{mol} \cdot \text{dm}^{-3}$). RL describes the type of the Langmuir isotherm [34]. The values of RL calculated were between (0.02783 - 0.96625), indicating highly favorable sorption of fluoride on the adsorbent surface.

The RL values indicate the type of isotherm [35-36].

RL = 0: irreversible isotherm;

0 < RL < 1: favorable isotherm;

RL = 1: linear isotherm;

RL > 1: unfavorable isotherm.

3.5. Kinetics of Adsorption

Kinetics of adsorption is one of the most attractive characteristics to be responsible for the efficiency of adsorption. To investigate the mechanism of adsorption Lagergren, Morris-Weber pseudo-first order and Ho and McKay pseudo-second order kinetic models have been applied for the experimental data to predict the adsorption kinetics [37-40]. The adsorption kinetics was studied with initial fluoride concentration of 5 mg/L and adsorbent dose 2.0 g at room temperature. The uptake of fluoride on adsorbents occurred rapidly, and reached equilibrium within 40 min. The Lagergren first-order kinetic model equation can be written as follows: Lagergren model

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \quad (5) \quad [37]$$

The Lagergren model was tested by plotting $\ln(q_e - q_t)$ versus t (time), where q_e is the amount of fluoride sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and q_t at time t (min), and k (min^{-1}) is the first-order rate constant. **Figure 7** shows the kinetic study of fluoride on the adsorbents under optimized conditions. Plot of $\ln(q_e - q_t)$ versus agitation time t (mint) exhibit straight line with the coefficient of determination (R^2) having values 0.9961 for fluoride.

The Equation (6) is applied for Morris-Weber model first-order kinetic mode.

$$q_t = R_d \sqrt{t} \quad \text{Morris-Weber model} \quad (6) \quad [38]$$

q_t is the sorbed concentration in $\text{mol} \cdot \text{g}^{-1}$ at time t , which was plotted against \sqrt{t} to test the Morris-Weber equation.

In the intervening time, the same data were evaluated through the Morris-Weber model. Where q_t was plotted against \sqrt{t} that exhibits a straight line with the coefficient of determination (R^2) having values of 0.8762 for fluoride, as shown in **Figure 8**.

The pseudo second-order rate model given by Ho and McKay in Equation (7) was also applied to investigate the data for kinetics of sorption.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Ho and McKay model} \quad (7) \quad [40]$$

Figure 9 shows a plot of $\left(\frac{t}{q_t}\right)$ versus t , which exhibits a straight line with R^2 0.9998 values for fluoride ion.

It is revealed after the kinetic model follow the Ho and McKay model, which elucidates the pseudo second-order kinetics of the sorption of fluoride ion on all adsorbents under study.

3.6. Thermodynamics Studies

The effect of temperature on the sorption of fluoride onto

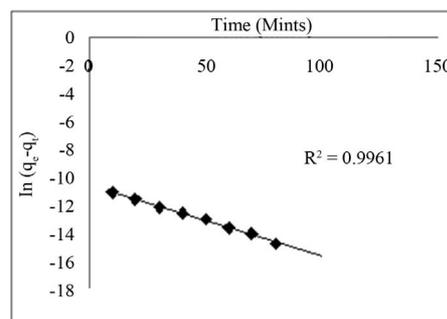


Figure 7. Lagergren model of Fluoride ion onto natural adsorbents.

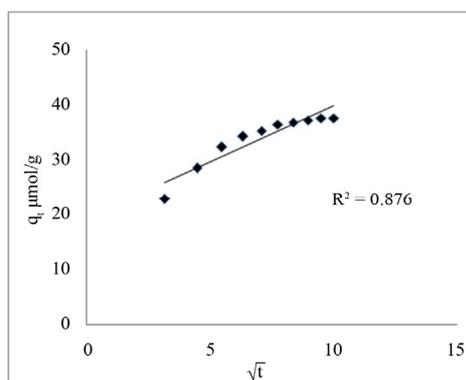


Figure 8. Morris-Weber model of Fluoride ion onto natural adsorbents.

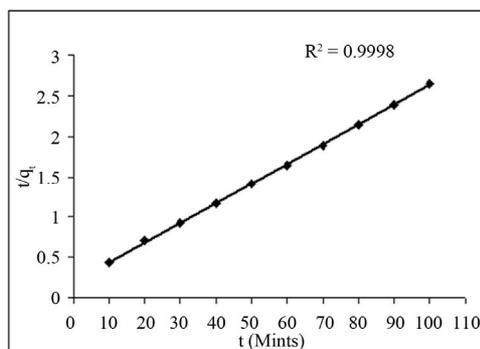


Figure 9. Ho and McKay model of fluoride onto natural adsorbents.

natural adsorbents was studied in the range of 288 - 333 K at optimum conditions. The plot of $\ln K_c$ versus $1/K$ gives a straight line with coefficient of determination R^2 , 0.98 as shown in **Figure 10**.

The thermodynamic parameters, such as enthalpy ΔH , entropy ΔS , and Gibbs free energy ΔG were calculated using following equations:

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

$$\Delta G = -RT \ln K_c \quad (9)$$

where ΔH , ΔS , ΔG , and T are the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively. R is the gas constant and K_c the equilibrium constant. From the slope and intercept of plot, the values of ΔH ($-46.54 \pm 1 \text{ KJ}\cdot\text{mol}^{-1}$) and ΔS ($0.1657 \text{ KJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) have been computed, while Gibbs free energy calculated was $\Delta G_{288-333 \text{ K}}$ (-2.07785 , 3.08966 , 4.1064 , 4.90716 and $5.38036 \text{ KJ}\cdot\text{mol}^{-1}$) using Equation (9). The results are presented in **Table 2**.

It is revealed from the negative values of ΔH and ΔG that the sorption process is exothermic and spontaneous nature of sorption. The decrease in the value of ΔG with the increase of temperature shows that the reaction is more spontaneous at high temperature. The positive

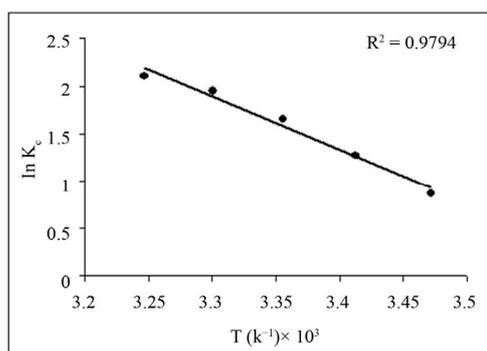


Figure 10. Effect of temperature on sorption of Fluoride ion.

Table 2. Thermodynamic parameters of fluoride sorption on Natural adsorbents.

S. No	Thermodynamic parameters	Temperature	Thermodynamic values
1	$\Delta G^\circ \text{ kJ}\cdot\text{mol}^{-1}$	288	-2.07785
		293	-3.08966
		298	-4.1064
		303	-4.90716
		308	-5.38036
2	$\Delta H^\circ \text{ kJ}\cdot\text{mol}^{-1}$		-46.560304
	$\Delta S^\circ \text{ kJ}\cdot\text{mol}^{-1}$		0.16572212

value of entropy ΔS ($0.1657 \text{ KJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) showed the increasing randomness at the solid/liquid interface and confirms the possibility of favorable adsorption.

3.7. Determination of PZC of Adsorbents

The typical definitions of points of zero charge is generally defined as the pH value where one or more components of the surface charge vanished and charge become zero at a specified temperature, pressure, and aqueous solution composition [41]. The concept of PZC is related to the phenomenon of adsorption. The PZC was determined by following the pH drift method recently reported in the literature [42-43].

The pH of the NaCl of ionic strength 0.01 M was adjusted between 2 and 10 using 0.5 M HCl or 0.5 M NaOH. 0.5 g of adsorbent was added to 20 ml of the pH adjusted solution in a capped tube and equilibrated for 24 h by constant shaking at ambient temperature. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the initial pH = final pH line was taken as the PZC listed in **Table 3** for each adsorbent.

3.8. Application

Under the optimized conditions the efficiency of natural adsorbents (coal, brick powder and saw dust) for the removal of fluoride ions from Groundwater samples collected from villages of Thar Desert Pakistan was tested to check the selectivity and applicability of the all adsorbents. A 100 ml of ground water sample was taken to check directly (at optimum conditions). Another 100 ml aliquot of sample was spiked with 2.0 mg of fluoride ion and then treated with adsorbents as per procedure discussed. The fluoride ion were eluted with $0.2 \text{ mol}\cdot\text{L}^{-1}$ HCl and determined by ion selective electrode and results compared with the results obtained from ion chromatography. The results are given **Table 4**, which shows the suitability of natural adsorbents (coal, brick powder and saw dust) t for preconcentration and removal of fluoride from environmental water samples. The physico-chemical is reported in **Table 5**.

4. Conclusion

The results showed those locally available cheap ad-

Table 3. Point of zero charge of adsorbents.

S. No	Adsorbent	PZC
1	Brick powder	6.1
2	Coal	7.2
3	saw dust	4.9
4	Mixture of adsorbents	6.9

Table 4. Determination of Fluoride in environmental water samples.

Samples	Added amount	Found	%recovery
S1	0.0	5.0	99.85
	2.0	6.99	
S2	0.0	3.06	100
	2.0	5.06	
S3	0.0	0.92	100.33
	2.0	3.0	
S4	0.0	1.65	99.17
	2.0	3.62	
S5	0.0	4.33	100
	2.0	6.33	

Table 5. Physico-chemical parameter of water samples (n = 10).

Parameters	Result range of observed parameter	RSD ^a
Fluoride	0.01 - 5	1.8
TDS (mg/L)	300 - 2500	2.0
Hardness (mg/L)	20 - 500	4.1
Sulfate (mg/L)	20 - 350	3.8
Chloride	30 - 200	2.6
pH	6.5 - 7.8	0.4

^aRelative standard deviation.

sorbents (coal, brick powder and saw dust) are potential adsorption material to remove fluoride from water hence involve no expenditure on transportation and have very low cost for pretreatment of fluoride. A mixture of all adsorbents was applied to remove fluoride from groundwater samples. The neutral pH was found to be highly favorable for utmost adsorption of fluoride; because of neutral pH it became very valuable and applicable for drinking water treatment, especially in poor areas. By making the column of these adsorbents, it will help the poor people to remove fluoride from the drinking water and make it safe.

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