

Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies

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Received 31 August 2011; Accepted 08 November 2011

Abstract: A new medium, eggshell powder has been developed for fluoride removal from aqueous solution. Fluoride adsorption was studied in a batch system where adsorption was found to be pH dependent with maximum removal efficiency at 6.0. The experimental data was more satisfactorily fitted with Langmuir isotherm model. The kinetics and the factor controlling adsorption process fully accepted by pseudo-second-order model were also discussed. E_a was found to be 45.98 kJmol⁻¹ by using Arrhenius equation, indicating chemisorption nature of fluoride onto eggshell powder. Thermodynamic study showed spontaneous nature and feasibility of the adsorption process with negative enthalpy (ΔH^0) value also supported the exothermic nature. Batch experiments were performed to study the applicability of the adsorbent by using fluoride contaminated water collected from affected areas. These results indicate that eggshell powder can be used as an effective, low-cost adsorbent to remove fluoride from aqueous solution as well as groundwater.

Keywords: Eggshell powder, Fluoride removal, Equilibrium, Kinetics, Thermodynamics.

Introduction

Fluorine, the most electronegative element is distributed ubiquitously as fluorides in nature¹. Water is the major medium of fluoride intake by humans². So the problems associated with the excess fluoride in drinking water are highly endemic and widespread in country like India³. Many available water treatment technologies such as electro-dialysis⁴, Donnan dialysis⁵ and reverse osmosis⁶ which are usually too expensive have been reported by previous researchers. The excessive fluoride intake leads to the loss of calcium from the tooth matrix, aggravating cavity formation throughout life⁷. Severe chronic and cumulative over exposure can cause the incurable crippling of skeletal fluorosis⁸. After recommendations of WHO, a number of countries legislated to set 1.5 mg/L as the maximum contaminant level (MCL) for fluoride in drinking waters². The traditional method of removing high

fluoride contents from water is limiting followed by precipitation of fluorite⁹. Adsorption is an efficient and economically viable technology for the removal of fluoride. Recently, many naturally occurring materials such as activated carbon from plant materials¹⁰, bone-char powder¹¹, calcium alginate beads¹², activated bauxite¹³, fly ash¹⁴, rice husk¹⁵, gibbsite¹⁶, kaolinite¹⁶, brick powder¹⁷, used tea ash powder¹³, clay materials¹⁶, limestone¹⁸ and some commercially available adsorbent such as calcium hydroxide [Ca(OH)₂], calcium chloride [CaCl₂], and calcium sulphate [CaSO₄]¹⁹ have been used for removal of fluoride. Calcium containing materials were used by some researchers to remove fluoride from water^{19,20}. Eggshell is mainly composed of calcium carbonate (94.03%) and it also contains calcite and calcareous soil²¹. Eggshell has a cellulosic structure and contains amino acids; thus, it is expected to be a good biosorbent²² and it was reported that large amounts of eggshells are produced in some countries, as waste products and disposed in landfills annually²³.

In present study eggshell powder has been used as a new low-cost adsorbent for the removal of F⁻ from aqueous solution and groundwater sample. FTIR and SEM studies were carried out for the adsorbent characterization. The effects of various parameters such as pH, adsorbent dose, contact time, initial concentration of fluoride and temperature were studied and discussed in detail in the following sections. The Langmuir, Freundlich, D-R and Tempkin isotherm models were used to describe the adsorption equilibrium data. The kinetics of the adsorption process was examined by fitting the experimental data with three kinetic models, i.e. pseudo-first-order and pseudo-second-order and intraparticle diffusion. The thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 were also calculated from the adsorption measurements in the present study, which are very useful in elucidating the nature of adsorption.

Nomenclature

A_f	Arrhenius constant
C_{ae}	equilibrium dye concentration on the adsorbent (mgL ⁻¹)
C_f	equilibrium dye concentration in solution (mgL ⁻¹)
C_i	Initial dye concentration (mgL ⁻¹)
E_s	mean free energy (kJ mol ⁻¹)
E_a	activation energy (kJ mol ⁻¹)
ΔG^0	Gibbs free energy change (kJ mol ⁻¹)
ΔH^0	enthalpy of reaction (kJ mol ⁻¹)
h	initial adsorption rate (mgg ⁻¹ min ⁻¹)
I	intraparticle diffusion model constant
K_i	distribution coefficient for adsorption

K_f	Freundlich constant (mg g^{-1}) (L g^{-1}) ^{1/n}
b	Langmuir constant (L mg^{-1})
R_L	Dimensionless equilibrium parameter
K_T	Tempkin constant related to equilibrium binding constant (L mg^{-1})
B_1	Tempkin constant related to the heat of adsorption
k	rate constant
K_i	intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-0.5}$)
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$)
W	weight of adsorbent (g)
n	Freundlich adsorption isotherm constant
q_e	equilibrium dye concentration on adsorbent (mg g^{-1})
q_m	maximum adsorption capacity (mg g^{-1})
q_t	amount of dye adsorbed at time t (mg g^{-1})
R	universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
R^2	correlation coefficient
ΔS°	entropy of reaction ($\text{J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
X	volume of the solution (L)
Greek alphabets	
K	D–R isotherm constant ($\text{mmol}^2 \text{ J}^{-2}$)
\mathcal{E}	polanyi potential (J mmol^{-1}) = $RT \ln(1 + 1/C_e)$

Materials and methods

Adsorbent collection and preparation

Eggshells were collected from local market of Burdwan Municipality, Government of West Bengal, India and washed with double distilled water followed by drying in a hot air oven at 110°C for overnight (12hrs). The dried eggshells were grinded and sieved well in fraction of 100, 150, 250, 300, 350 μm mesh size particles that were preserved in different sterilized containers for subsequent use as adsorbent.

Instruments and apparatus

The morphology of eggshell powder was learnt using SEM analyzer (HITACHI, S-530, Scanning Electron Microscope and ELKO Engineering). IR Spectrum of the eggshell powder was recorded on a PERKIN-ELMER, FTIR, Model RX1 Spectrometer. The pH of the solutions at the beginning and the end of the experiments were measured the average values by using Systronic 6.3 digital pH meter. Temperature controlled TARSONS, Spinot digital model MC02, CAT No. 6040, S. No. 173 magnetic stirrer was used during the adsorption experiments. Systronic Vis double beam Spectro- 1203 was used for colorimetric analysis. Analysis of fluoride was carried out by following SPANDS methods²⁴.

Preparation of adsorbate solution

Stock solution of fluoride was prepared by dissolving 0.22g sodium fluoride (MERCK, Germany) in 1L double distilled water. The required concentration of fluoride solution was prepared by serial dilution of 100 mg/L fluoride stock solution.

Zero point charge

The point of zero charge of the adsorbent was determined by the solid addition method²⁵. A 50ml of 0.1M KNO_3 solution transferred into a series of 100 ml conical flask. The initial pH (pH_0) values of the solution was adjusted from 1.0 to 10.0 by adding either 0.05N HNO_3 or 0.1N KOH . Then 1.5 g of eggshell powder was added to each flask which was securely capped immediately. The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h. The pH of the solution affects the surface charge of the adsorbents as well as the degree of the ionization and speciation of different pollutants. Change in the pH affects the adsorptive process through dissociation of functional groups as the active sites on the surface of the adsorbent. This subsequently leads to a shift in the reaction kinetics and the equilibrium characteristics of the adsorption process. Adsorption of the various anionic and cationic species on such adsorbents can be explained on the basis of the competitive adsorption of H^+ and OH^- ions with the adsorbate. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas the surface is active for the adsorption of cations at higher pH due to deposition of OH^- ions²⁵.

Adsorption experiment and analysis

Adsorption experiments were carried out for the determination of pH, adsorbent dose variation, equilibrium time and kinetics, selection of an isotherm, effect of temperature and evaluation of thermodynamic parameters. The influence of pH (2.0-10.0), adsorbent dose (0.2-2.4 g /100 ml) and particle size (200-350 μm), contact time (20, 40, 60, 80, 120 and 180 min), initial fluoride concentration (1.5, 3.0, 5.0, 7.0, 10.0 and 20.0 mg/L) and temperature (303, 313, 323 and 333 K) were evaluated during the present study in a 250 ml Erlenmeyer flasks and 100ml of fluoride solution of known concentration was added. The contents

(adsorbent/100ml solution) were kept for constant shaking (at 250 rpm) for 1hr in a temperature controlled magnetic stirrer at $303 \pm 1\text{K}$ and then the solids were separated through filtration. The solutions were collected for analysis and fluoride concentration in the solution was determined by using spectrophotometer. Each experiment was conducted three times and average values are reported. Control experiments, performed without addition of adsorbent, confirmed that the sorption of fluoride on the walls of Erlenmeyer flasks was negligible. The amount of fluoride adsorbed per unit adsorbent (mg fluoride per g adsorbent) was calculated according to a mass balance on the fluoride concentration using Eq. (1):

$$q_e = (C_i - C_f) X / W \quad (1)$$

The percent removal (%) of dyes was calculated using the following equation:

$$\text{Removal (\%)} = (C_i - C_f) \times 100 / C_i \quad (2)$$

Theory

Adsorption isotherm

The adsorption characteristics of eggshell powder were determined using Freundlich²⁶, Langmuir²⁷, Dubinin-Radishkevich²⁸ and Tempkin²⁹ isotherm models.

Freundlich:

$$q_e = K_f (C_f)^{1/n} \quad (3)$$

The Freundlich parameters were obtained by fitting the experimental data to the linearised equation derived from Eq.(3):

$$\log q_e = \log K_f + 1/n \log C_f \quad (4)$$

Langmuir:

$$q_e = (q_m b C_e) / (1 + b C_e) \quad (5)$$

The Langmuir parameters were obtained by fitting the experimental data to the linearized equation derived from Eq. (5):

$$1/q_e = (1/bq_m) 1/C_f + 1/q_m \quad (6)$$

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter R_L was determined by using the following equation³⁰:

$$R_L = 1 / (1 + b C_0) \quad (7)$$

The parameter RL indicates the shape of isotherm. The process is irreversible if RL = 0, favourable if RL < 1, linear if RL = 1 and unfavourable if RL > 1.

Dubinin-Radushkevich (D-R) formulation:

$$q_e = q_m \exp(-K\varepsilon^2) \quad (8)$$

The constant K gives an idea about the mean free energy E_s (kJ mol^{-1}) of adsorption per mole of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be from the equation³¹:

$$E_s = 1 / \sqrt{2K} \quad (9)$$

The typical range of bonding energy for ion-exchange mechanisms is 8 and 16 kJ mol^{-1} , indicating that chemisorption may play a significant role in the sorption process³², while for values of $E_s < 8 \text{ kJ mol}^{-1}$, the adsorption process is of a physical in nature³².

Tempkin:

$$q_e = RT \ln (K_T C_f) / b \quad (10)$$

Equation (10) can be linearized as in eq. (11):

$$q_e = B_1 \ln K_T + B_1 \ln C_f \quad (11)$$

Where $B_1 = RT / b$

Adsorption kinetics

The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to investigate the adsorption kinetics of fluoride and to quantify the extent of uptake in the adsorption process. A simple pseudo first-order kinetic model³³, pseudo second-order model³⁴, intra-particle diffusion model³⁵ are represented by the as given below:

Pseudo first-order:

$$\log (q_e - q_t) = \log (q_e) - (K_1 / 2.303) t \quad (12)$$

Pseudo second-order:

$$t / q_t = 1 / K_2 q_e^2 + t / q_e \quad (13)$$

The initial adsorption rate h ($\text{mg g}^{-1} \text{min}^{-1}$) is defined as³⁴:

$$h = k_2 q_e^2 \quad (14)$$

The intra-particle diffusion:

$$q_t = K_i t^{0.5} + I \quad (15)$$

According to this model, if the plot of q_e versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion, while if the data exhibit multi-linear plots, then two or more steps influence the adsorption process³⁶.

Activation energy and thermodynamic parameters

The activation energy was calculated by using Arrhenius relation³⁷:

$$k = A_f e^{-E_a/RT} \quad (16)$$

Converting Eq. (16) to linear form:

$$\ln k = \ln A_f - E_a / RT \quad (17)$$

In order to study the feasibility of the process, the thermodynamic parameters were obtained from following equations:

$$K_a = C_{ae}/C_f \quad (18)$$

$$G^0 = -RT \ln K_a \quad (19)$$

$$\log K_a = S / 2.303R - (H / 2.303TR) \quad (20)$$

Results and Discussion

Adsorbent characterization

To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{PZC}) of the adsorbent. Adsorption of anion is favored at $pH < pH_{PZC}$ (Figure 1). The physico-chemical properties of the adsorbent are summarized in Table 1.

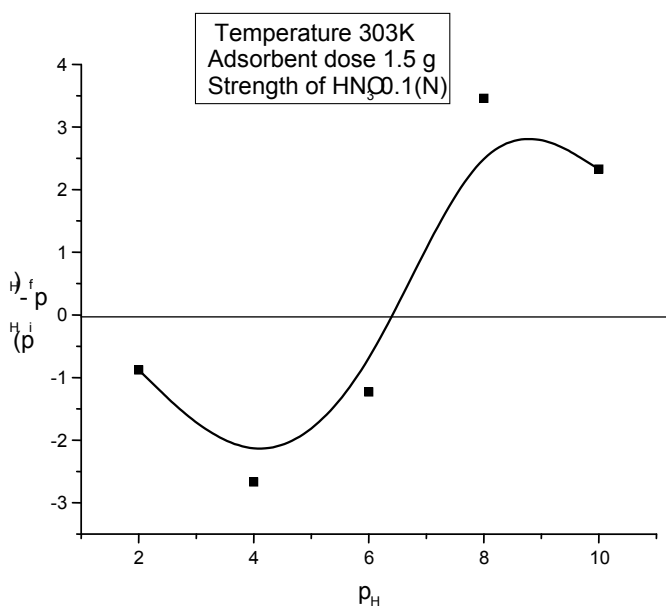


Figure 1. Zero Point charge of eggshell powder.

The IR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of fluoride ions^{38,39}. The IR spectrum of eggshell powder was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectra of eggshell powder before and after fluoride adsorption are shown in Figure 2a and Figure 2b. The IR spectral analysis of eggshell powder shows distinct peak at 712.86, 875.56, 2516.00, 3431.25 cm^{-1} (Figure 2a). The peak observed at 3431.25 and 2516.00 cm^{-1} may be assigned to the presence of alcohol hydroxyl group (-OH) and acidic hydrogen group (-OH) stretching respectively. This result suggests that fluoride interacts with metal oxides and -OH functional group present in eggshell powder. SEM analysis is another useful tool for the analysis of the surface morphology of an adsorbent. The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in Figure 3a. Further, the pores on the surface of the adsorbent are highly heterogeneous as shown in Figure 3b. The heterogeneous pores and cavities provided a larger exposed surface area for the adsorption of fluoride. The sizes of pores are indicative of the expected adsorption of fluoride molecules onto the surface of the adsorbent.

SEM images of eggshell powder before and after F- adsorption are shown in Figure 3a and Figure 3b. It clearly reveals the porous surface textures which endorse the adsorbent with increased surface area and high adsorption capacity. The SEM study also indicates that the treatment of fluoride solution influenced the orientation of the particles of the egg shells. The SEM image of untreated sample of eggshell exhibits non-adhesive appearance and formation of agglomerates, while treated sample shows regular, adhesive appearance causing further adsorption of fluoride³.

Table 1. Physico-chemical characteristics of eggshell powder.

Parameters	Values
pH	6.59
Electrical conductance (mS)	0.1
Specific gravity	0.846
Moisture content (%)	1.174
Bulk density g/cm^3	0.8024
Particle density g/cm^3	1.075
Porosity (%)	25.4
BET Surface area (m^2/g)	21.2
pH _{ZPC}	6.3
Particle size (μm)	150-350

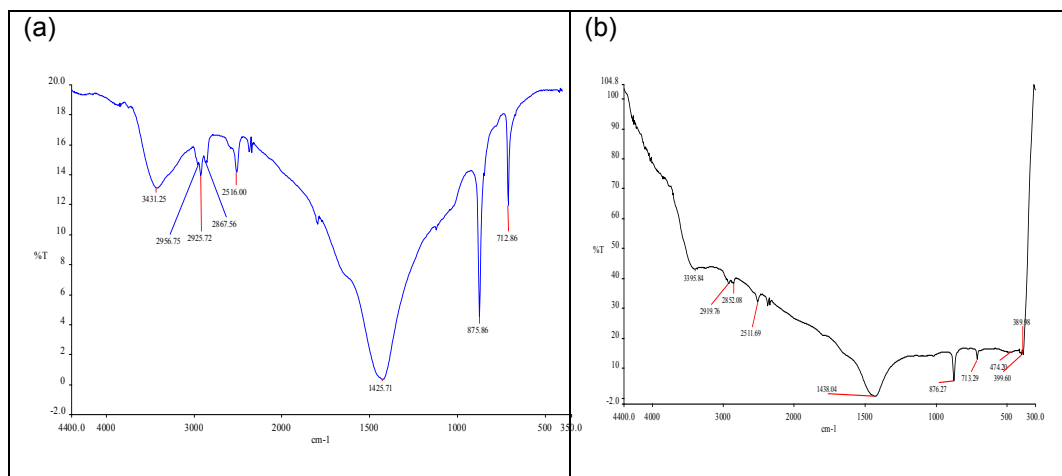


Figure 2. IR Spectrum of eggshell powder (a) before fluoride loaded and (b) after fluoride loaded.

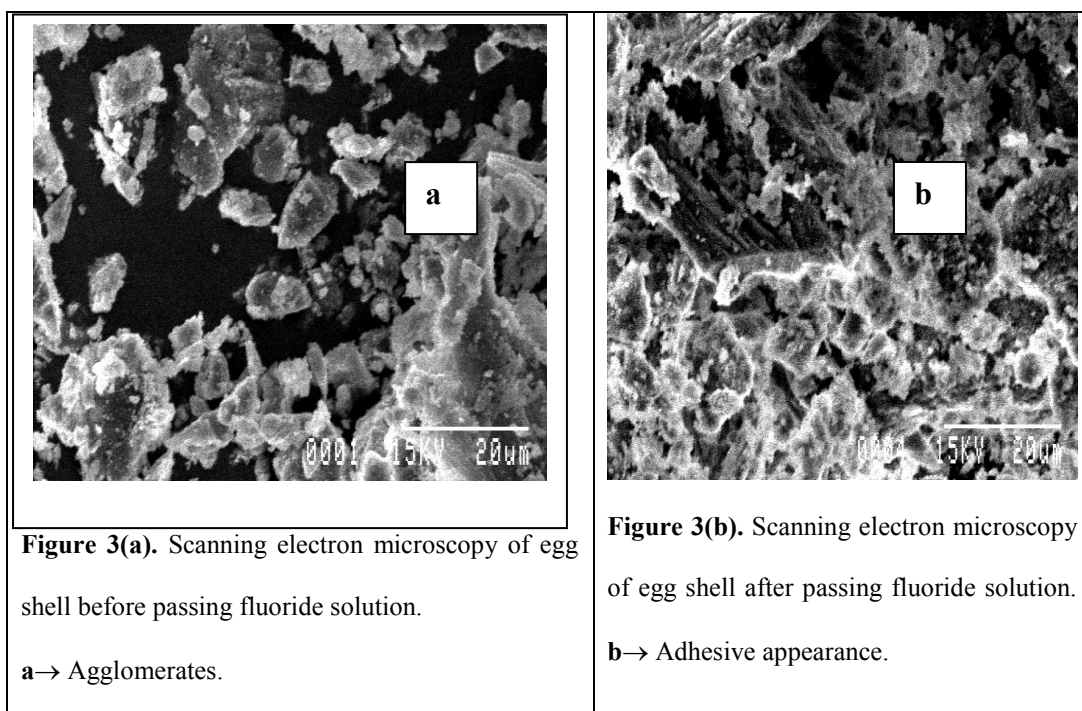


Figure 3(a). Scanning electron microscopy of egg shell before passing fluoride solution.

a→ Agglomerates.

Figure 3(b). Scanning electron microscopy of egg shell after passing fluoride solution.

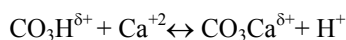
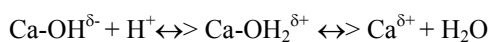
b→ Adhesive appearance.

Effect of operating parameters

Effect of pH

The effect of pH on fluoride removal from aqueous solution by eggshell powder was studied at various pH values (ranging from 2-10). According to Turner et al., (2005) pH of solution affects the surface charge of the adsorbent material. In addition it is directly related with competition ability of $[H^+]$ with adsorbate ions to active sites on the adsorbent surface.

The removal of fluoride by eggshell powder was noted to increase with increase in pH of the fluoride solution appreciably up to pH 6.0 (Figure 4). The mechanism of fluoride removal can be better understood by examining the calcite surface composition⁴¹. Stipp⁴² showed that Ca^{+2} and CO_3^- are only the PDIs (Potential determining ions) in a pure calcite solution and provided a modified electrical double layer model. Stipp's model proposes that along any cleavage point on the calcite surface, the calcium and carbonate ions have unsatisfied partial charges ($>\text{Ca}\delta^+$ and $>\text{CO}_3\delta^-$, where $>$ represents the edge of the bulk calcite surface). This charge imbalance is decreased by the hydrolysis of water, resulting in the formation of $>\text{Ca-OH}\delta^-$ and $>\text{CO}_3\text{-H}\delta^+$ species. The formation of these species is thermodynamically favourable as the added hydrolysis layer lowers the potential with respect to the bulk calcite surface. These species can also react with any other ions in solution. For example, lower pH (increasing H^+ and Ca^{2+}) causes an increase in positive sorption via the reactions⁴¹:



At neutral to higher pH, OH^- and CO_3^{2-} dominate, producing $>\text{CaCO}_3^-$ and $>\text{CO}_3^+$ sorption sites⁴³. Therefore, as well as providing more Ca^{2+} in solution from the dissolution of calcite, decreasing pH effectively increases the number of positive surface sites leading to an increase in the amount of fluoride removed from the system. On the other hand, under highly acidic conditions, the decrease may be attributed to the formation of weakly ionised hydrofluoric acid⁴⁴ or the combined effects of chemical and electrostatic interaction between the calcite surface and the fluoride ions.

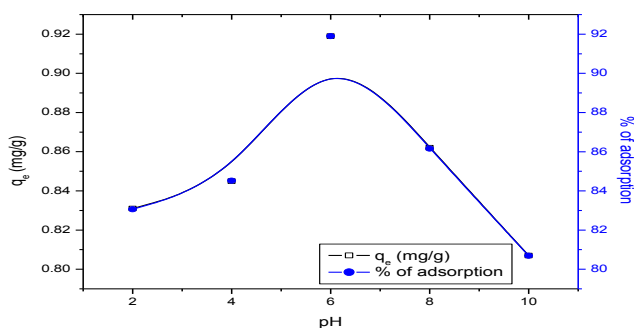
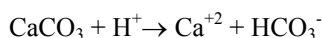


Figure 4. Effect of pH on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, adsorbent dose: 0.5 g/100 ml, agitation speed: 250 rpm, Contact time: 60 minutes, Temperature: 303 K).

Effect of adsorbent dose (g) and particle size (μm)

Adsorbent dose is also an important parameter owing to its effect on efficiency (%) and on the amount of fluoride adsorbed per unit weight of biomass (q_e). Adsorption process mainly depends upon the particle size of the adsorbent, small particle size larger surface area, increases the adsorption capacity. Hence, in this study the sorption capacity of an adsorbent dose and its particle size for a given initial concentration, contact time, agitation speed, temperature and pH at 6.0 were conducted. It was observed that percentage of fluoride removal increased with increasing of adsorbent dose (Figure 5). Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more

active adsorption sites⁴⁵. Figure 5 also shows the decrease of q_e with increase of adsorbent dose might be due to the formation of aggregates between the eggshell powder particles at high adsorbent doses, reducing the effective active site area⁴⁶. Similar observation has been reported for sorption of fluoride onto Ca-pretreated biomass⁴⁶. Here another mechanism is also involved i.e. precipitation, according to Fan et al.,⁴⁷ fluorite is a better substrate for the removal of fluoride than calcite, with F^- adsorbing onto exposed Ca sites parallel to the cleavage plane. It is possible, therefore, that fluorite precipitation increases the number of adsorption sites according to the following reactions:



$$K_{CaCO_3} = [Ca^{+2}][HCO_3^-] / [H^+] \dots\dots\dots (20)$$

Similarly, the fluoride equilibrium is:



$$K_{CaF_2} = [Ca^{+2}][F^-]^2 \dots\dots\dots (21)$$

This indicates that at constant pH, activity of fluoride ion is directly proportional with the concentration of bicarbonate ion. Again, following principle of ionic activity product⁴⁸, CaF_2 precipitates when the concentration of Ca^{+2} and F^- in water exceeds the solubility product of F^- .

Performing the same experiment was carried out varying different particle size from 100 μ m- 350 μ m (Figure 6a) with an initial fluoride concentration (5 mg/L), there is a very little difference (<1.0%) in the amount of fluoride removed, suggesting that the removal mechanism is not limited by surface area at this concentration. Figure 6b shows that for higher initial concentration (20 mg/L) there is a stronger dependence on particle size and surface area than compared to the lower initial concentration of fluoride. This result indicates, at equilibrium, fluoride removal increases with increasing solid-to-solid ratio, which suggest surface adsorption may be occurring and defluoridation mechanism by calcium carbonate cannot be described either by adsorption or precipitation alone⁴⁰.

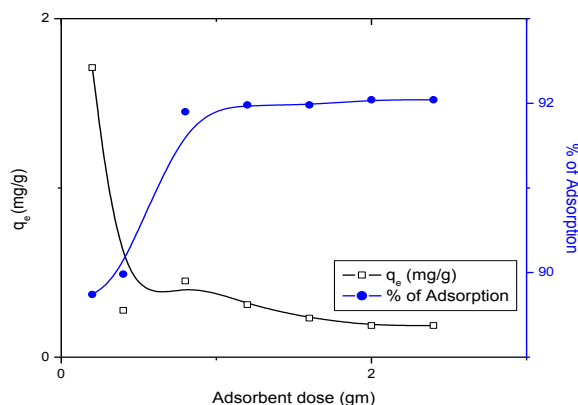


Figure 5. Effect of Adsorbent dose on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, pH: 6.0, agitation speed: 250 rpm, Contact time: 60 minutes, Temperature: 303 K).

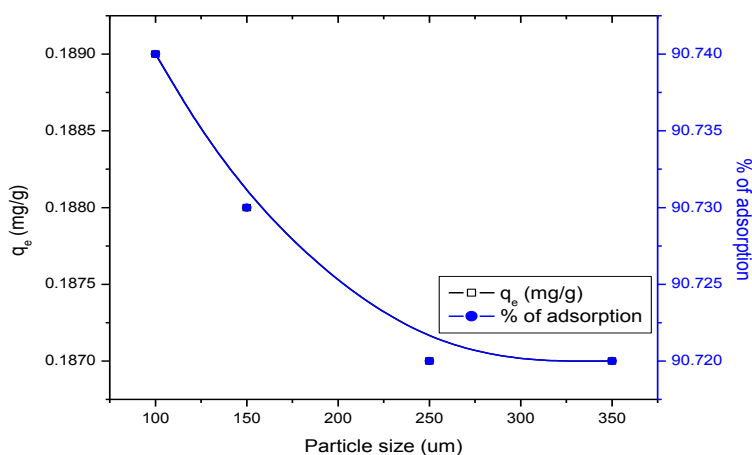


Figure 6a. Effect of particle size on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, pH: 6.0, adsorbent dose: 2.4 g/100ml, agitation speed: 250 rpm, Contact time: 60 minutes, Temperature: 303 K).

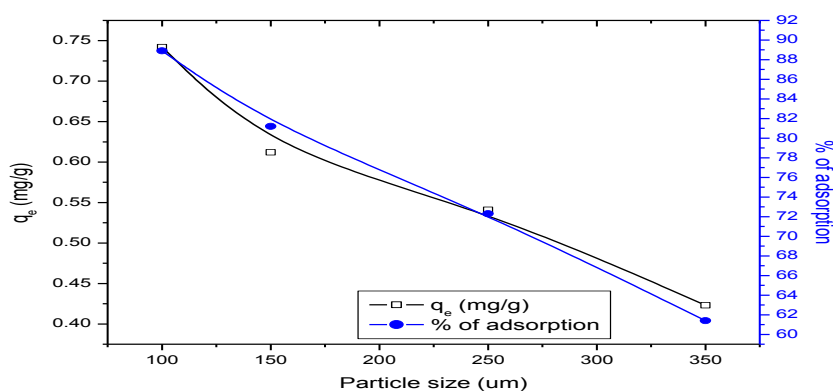


Figure 6b. Effect of particle size on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 20.0 mg/L, pH: 6.0, adsorbent dose: 2.4 g/100ml, agitation speed: 250 rpm, Contact time: 60 minutes, Temperature: 303 K).

Effect of agitation speed

Studies on the effect of agitation speed were conducted by varying speeds from 150 to 350 rpm, at optimum pH of 6.0 with adsorbent dose of 2.4 g/100 ml and contact time of 60 minutes at 313K. The influence of agitation speed on the extent of adsorption is shown in Figure 7. At a given time, fluoride removal increases with the increase in the speed of agitation. The reason for the increase in efficiency is that at higher speeds better contact between the adsorbent and adsorbate is possible⁴⁹. Similar findings for fluoride removal by using activated charcoal have been reported by other investigator⁴⁹.

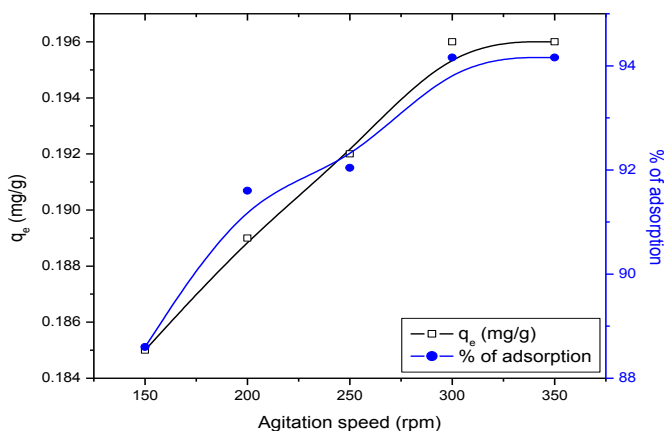


Figure 7. Effect of agitation speed on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, pH: 6.0, adsorbent dose: 2.4 g/100ml and particle size 150 μ m, agitation speed: 250 rpm, Contact time: 60 minutes, Temperature: 303 K).

Effect of Contact time

It is essential to investigate the effect of contact time required to reach equilibrium for designing batch adsorption experiments. The fluoride removal capacity q_e (mg/g) on the eggshell powder (2.4/100 ml) was determined by varying contact time (20-180 minutes) for a given initial concentration and best pH (6.0) at 350 rpm. As illustrated in Figure 8, 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 surface⁵⁰. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. Similar results were reported for adsorption of fluoride from aqueous solution onto tamarind seed, an unconventional biosorbent⁵¹.

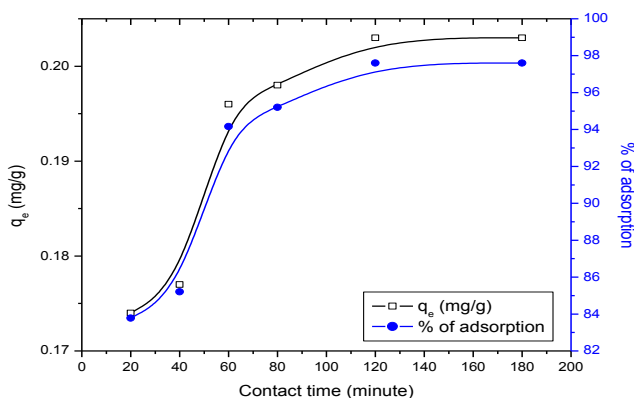


Figure 8. Effect of contact time on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, pH: 6.0, adsorbent dose: 2.4 g/100ml and particle size 150 μ m, agitation speed: 350 rpm, Temperature: 303 K).

Effect of Initial concentration

The efficiency of fluoride adsorption for different initial F^- concentrations ranging from 1.5 to 20.0 mg/L was investigated by carrying out adsorption experiments at the best experimental conditions present in Figure 9. The percentage removal of fluoride decreased with increase in initial fluoride concentration and reached in equilibrium condition at higher concentrations. This is probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, which become saturated at a certain concentration⁵⁰. Due to increasing concentration gradient, acts as increasing driving force to overcome all mass transfer resistances of the fluoride between the aqueous and solid phase, leading to an increasing equilibrium sorption until sorbent saturation is achieved. Similar trend has been reported for fluoride removal by geo-materials⁵² and activated charcoal⁵⁰.

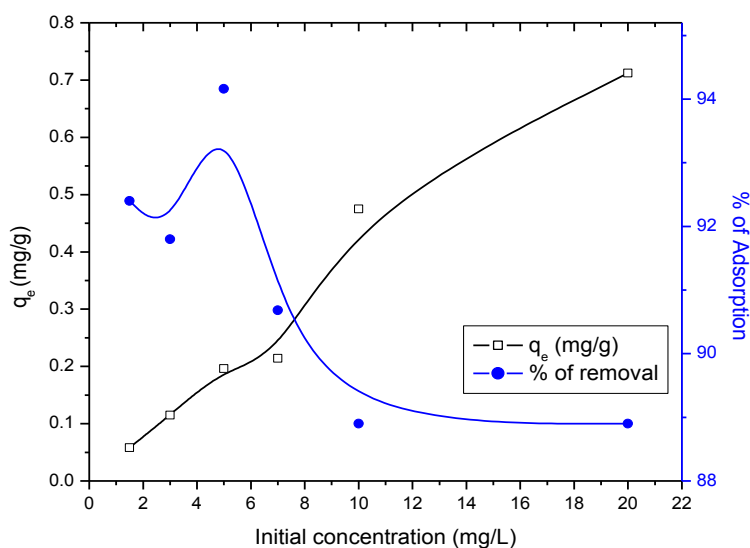


Figure 9. Effect of Initial concentration on the adsorption of fluoride by eggshell powder (experimental conditions: pH: 6.0, adsorbent dose: 2.4 g/100ml and particle size 150 μ m, agitation speed: 350 rpm, contact time: 100 minutes, Temperature: 303 K).

Effect of temperature

It is well established that temperature is an additional factor greatly influence any adsorption process. The effect of solution temperature was investigated at 303, 313, 323 and 333 K. The results summarized in Figure 10, indicating the adsorption rate or precipitation as CaF_2 decreased with increase in temperature. This result indicates low temperature favours the removal of fluoride molecules by adsorption onto eggshell as well as the adsorption process is exothermic in nature. The decreasing of removal may be due to at high temperature the thickness of the boundary layer decreases due to increased tendency of the molecules to escape from the adsorbent surface to the solution phase, which results in a decrease in the adsorption capacity as temperature is increased⁵³. Similar results were previously reported by Sujana and Anand³.

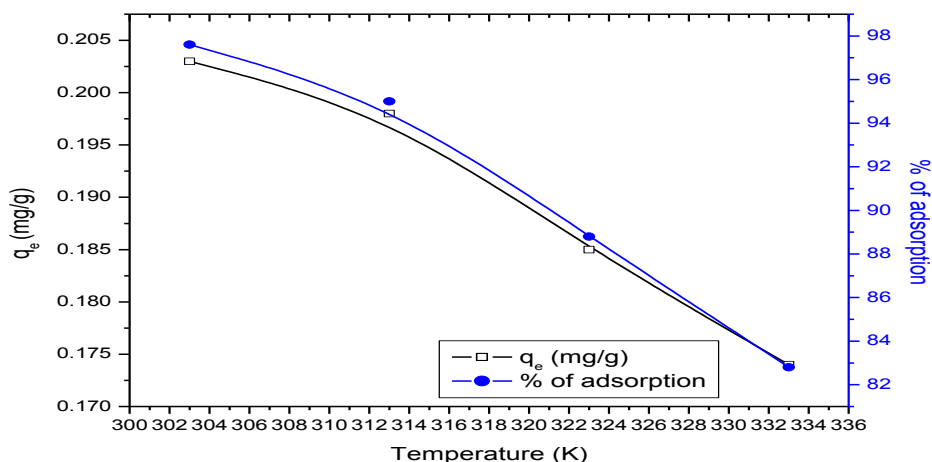


Figure 10. Effect of temperature on the adsorption of fluoride by eggshell powder (experimental conditions: Initial fluoride concentration: 5.0 mg/L, pH: 6.0, adsorbent dose: 2.4 g/100ml and particle size 150 μ m, agitation speed: 350 rpm, Temperature: 303 K).

Adsorption isotherm

In this investigation, the Freundlich, the Langmuir, the Dubinin-Radushkevich and the Tempkin were used to describe the equilibrium data acquired at different temperatures (in the range from 303–333K). The results are shown in Table 2 and the modeled isotherms are plotted in Figure 11. According to Table 2, the Langmuir isotherm model showed excellent fit to the experimental data with high correlation coefficients at all temperatures. The maximum fluoride sorption capacity of eggshell powder was found to be 1.09 mg/g at 303 K. The constant K_L , represents the affinity between the adsorbent and adsorbate. The values of K_L and q_m decreased with increase in temperature (Table 2), the magnitude of the Langmuir constant K_L has small values (0.02–0.04 L/mg), which indicates a low heat of adsorption capacity^{54,55}.

The empirical Freundlich model also showed a fairly good fit to the experimental equilibrium data at all temperatures studied ($R^2 > 0.99$). The values of K_f from the Freundlich model are an indicator of the adsorption capacity of a given adsorbent³². From the Table 2, the sorption capacity (K_f) decreased with increase in temperature which implies the sorption process as exothermic in nature⁵⁴ and lower value for K_f indicates that the rate of adsorbate removal is low⁵⁶. The 'n' should have values lying in the range of 1–10 for classification as favorable adsorption⁵⁷. A smaller value of n (Table 2) indicates a weaker bond between adsorbate and adsorbent^{58,59}.

In order to distinguish between physical and chemical sorption on the heterogeneous surfaces the equilibrium data were tested with D-R isotherm model. The correlation coefficients in D-R model were found to be lower than the Freundlich and

Langmuir isotherm models (Table 2). The constant K gives an idea about the mean free energy (E_s (kJmol⁻¹)) of adsorption per mole of the adsorbate when it is transferred to the surface of the solid from infinity in the solution. In this study the magnitude of E_s were higher than 8 kJmol⁻¹ at all studied temperatures which indicate the adsorption mechanism of fluoride onto eggshell powder was chemisorption.

As seen in Table 2, a decrease in the temperature produced a decrease in the adsorption capacity in Tempkin isotherm models. The fitness of the adsorption data to the Langmuir isotherm implies that the binding energy on the whole surface of the adsorbent was uniform and that sorbate-sorbate interaction was negligible. It also indicates that the adsorbed fluoride did not interact or complete with each other and they were adsorbed by forming a monolayer³². Table 3 summarizes the comparison of the maximum fluoride adsorption capacities of various sorbents including eggshell powder. The comparison shows that eggshell powder has similar adsorption capacity of fluoride as like as other reported adsorbents, reflecting a promising utility for eggshell (waste material as shown in restaurants and hotels) powder utilization in fluoride removal from contaminated water, because in this study removal of F⁻ from groundwater has also been investigated described later.

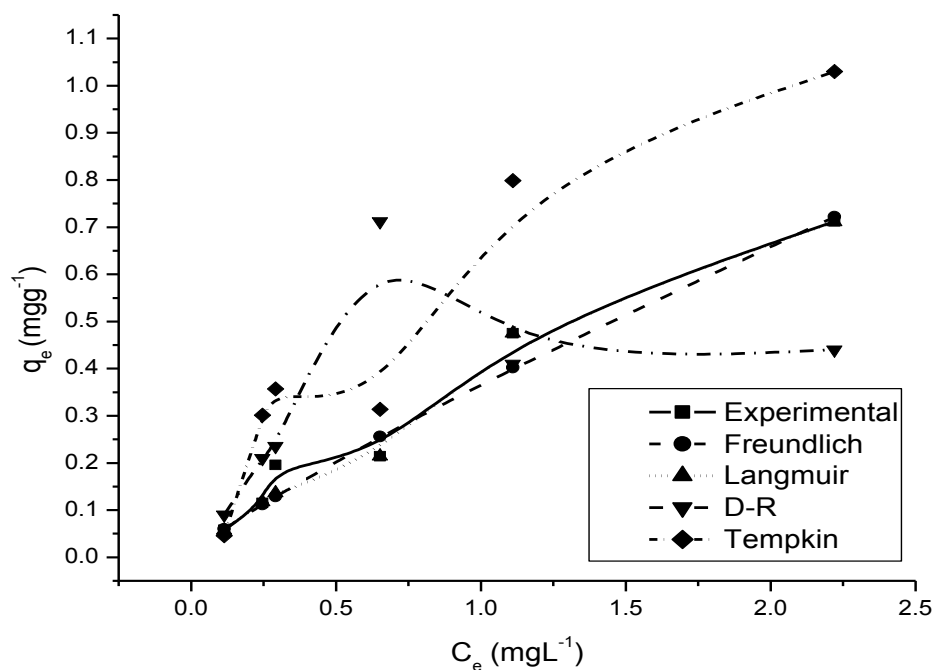


Figure 11. Comparison between the measured and modeled isotherm profiles for the adsorption of fluoride by using eggshell powder on different initial concentration (mg⁻¹L): (experimental condition pH of the solution: 6.0, adsorbent dose: 2.4 g/100 ml, particle size: 150 μ m, agitation speed: 350 rpm, Contact time: 100 minutes, Temperature: 303K).

Table 2. Adsorption isotherm constants for adsorption of fluoride onto eggshell powder at different temperatures.

Temperature (K)	Langmuir isotherm			Freundlich isotherm			D-R isotherm parameters			Tempkin			
	parameters			parameters									
	q _m	K _L (Lmg ⁻¹)	R ²	K _f (mgg ⁻¹)	(Lmg ⁻¹) ^{1/n}	n	R ²	q _m (mgg ⁻¹)	K	E _s	R ²	B ₁	K _T
303	1.09	0.488	0.998	0.368	1.18	0.997	0.464	2.343 × 10 ⁻³	14.59	0.953	0.331	10.09	0.939
313	1.08	0.412	0.995	0.341	1.11	0.983	0.411	2.412 × 10 ⁻³	13.93	0.907	0.316	7.39	0.868
323	1.06	0.289	0.979	0.334	1.09	0.969	0.378	2.68 × 10 ⁻³	13.64	0.888	0.235	5.59	0.865
333	1.02	0.193	0.954	0.311	1.06	0.951	0.292	2.811 × 10 ⁻³	13.25	0.872	0.211	3.57	0.861

Table 3. Comparison of fluoride adsorption capacity of eggshell powder with other reported low-cost-adsorbents.

Sorbent	q_{max} (mg/g)	Reference
Activated carbon from <i>Dolichos lab lab</i>	0.233	57
Activated carbon from <i>Acacia Arabica</i>	2.06	58
Tamarind seed	6.09	51
Crude fibre content from neem, pipal and Khair	0.04	59
Gibbsite	0.4	16
Kaolinite	0.2	16
Dolomite	0.21-0.29	16
Smectite	0.33	16
Kaolinite	0.07	65
Brick powder	0.55	17
Used Tea powder	0.054	17
Ca-pretreated macrophyte biomass	0.110	46
Eggshell	1.09	Present study

Adsorption kinetics

As mentioned before, three kinetic models i.e. pseudo-first-order, pseudo-second-order and intraparticle diffusion model were applied to investigate the reaction pathways and potential rate limiting steps of the adsorption of fluoride onto eggshell powder.

The pseudo-first-order rate constant, k_1 and the equilibrium adsorption capacity, q_e at different temperatures were determined from the slope and intercept of the plots of $\log(q_e - q_t)$ versus t and are listed in Table 4 along with the correlation coefficient (R^2). From the

kinetic data in Table 4, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e , is observed at all temperatures, indicating a poor fit of the pseudo-first-order equation to the experimental data.

The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t . The plot of t/q_t against t at different temperatures is shown in Figure 12. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$) over the temperature range of 303–333 K. It is also observed from Table 4 that rate constant, k_2 decreased as the temperature increased indicating exothermic nature of adsorption of fluoride onto eggshell powder. Furthermore, the calculated q_e values were found to be quite close to the experimental q_e values at all temperatures studied (303–333 K). So, it was inferred that the adsorption of fluoride onto eggshell followed pseudo-second-order kinetics. This finding suggests that the rate-limiting step of the adsorption system may be chemisorption. The initial adsorption rate, h ($\text{mg g}^{-1} \text{min}^{-1}$), decreased with increase in temperature (Table 4) suggesting that adsorption of fluoride onto eggshell was not favourable at higher temperatures.

The intraparticle diffusion was investigated using the empirical relationship based on the removal of Weber-Morris (Eq.(15)). The results (Table 4) corresponds to the external surface uptake and based on these results it might be concluded that intraparticle diffusion was involved in fluoride adsorption onto eggshell powder, but it was not the sole rate determining step and that some other mechanism also play an important role. Similar trend has already been reported for fluoride adsorption from contaminated ground water by using bauxite³.

Table 4. Kinetics parameters for adsorption of fluoride onto eggshell powder at different temperatures.

Temperature (K)	$q_{\text{exp}}(\text{mg g}^{-1})$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model				Intraparticle diffusion model		
		$q_{\text{cal}}(\text{mg g}^{-1})$	$k_1(\text{min}^{-1})$	R^2	$q_{\text{cal}}(\text{mg g}^{-1})$	k_2	$h(\text{mg g}^{-1} \text{min}^{-1})$	R^2	$K_i(\text{mg g}^{-1} \text{min}^{0.5})$	$I(\text{mg g}^{-1})$	R^2
303	0.203	0.014	0.052	0.723	0.212	4.685	0.211	0.999	0.004	0.169	0.903
313	0.198	0.013	0.014	0.722	0.21	1.047	0.045	0.995	0.003	0.164	0.861
323	0.185	0.012	0.014	0.722	0.19	0.844	0.03	0.994	0.002	0.163	0.863
333	0.174	0.011	0.013	0.721	0.18	0.796	0.026	0.987	0.016	0.155	0.862

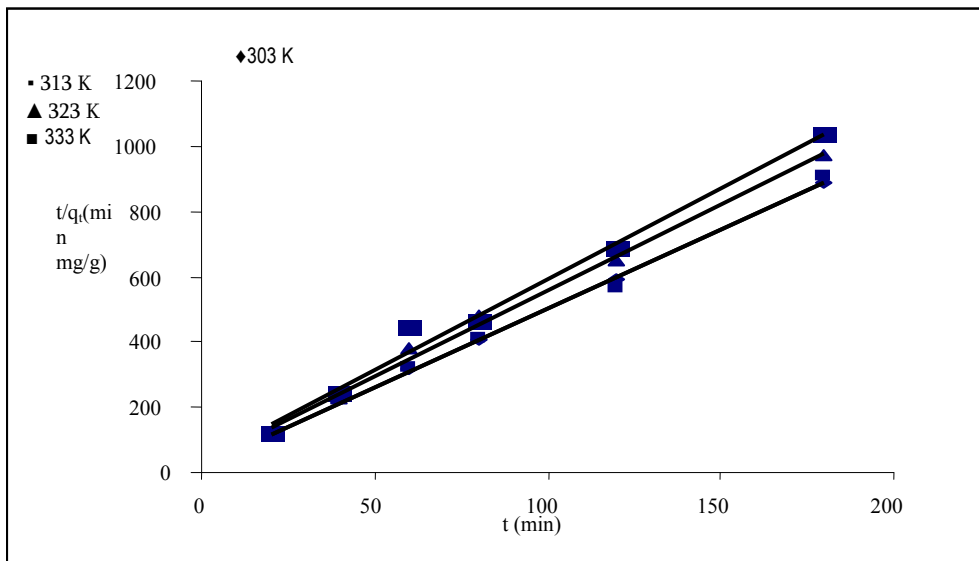


Figure 12. Pseudo-second-order kinetic plots for adsorption of fluoride onto eggshell powder at different temperatures (experimental conditions: Initial dye concentration: 5.0 mg/L, adsorbent dose: 2.4g/100ml, Particle size: 150 μ m agitation speed: 350 rpm, pH: 6.0, Temperature 303K).

Activation energy and thermodynamic parameters

From the pseudo-second-order rate constant K_2 (Table 4), the activation energy E_a for adsorption of fluoride onto eggshell powder was determined using Arrhenius equation (Eq.(16)). By plotting $\ln K_2$ versus $1/T$ (Figure not shown), E_a was obtained from the slope of the linear plot. The value of E_a for fluoride adsorption on eggshell powder was 45.98 kJ mol⁻¹. The magnitude of activation energy may give an idea about the type of sorption. In the present study, the value of the activation energy confirms that the nature of fluoride adsorption onto eggshell is chemisorption⁵⁰. The Gibbs free energy (ΔG^0) for adsorption of fluoride onto eggshell at all temperatures was obtained from Eq.19 and presented in Table 5. The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ΔG^0 versus T (Figure 13) and are also listed in Table 5. The negative value of ΔG^0 at all temperatures indicates the feasibility of the process and the spontaneous nature of the adsorbate onto adsorbent. Increase in value of ΔG^0 with increase in temperature suggests that higher temperature makes the adsorption unfavourable. The negative value of ΔH^0 implies that the adsorption phenomenon is exothermic and obtained entropy ΔS^0 (-0.162 Jmol⁻¹ K⁻¹) indicates that the process is enthalpy driven⁵⁰.

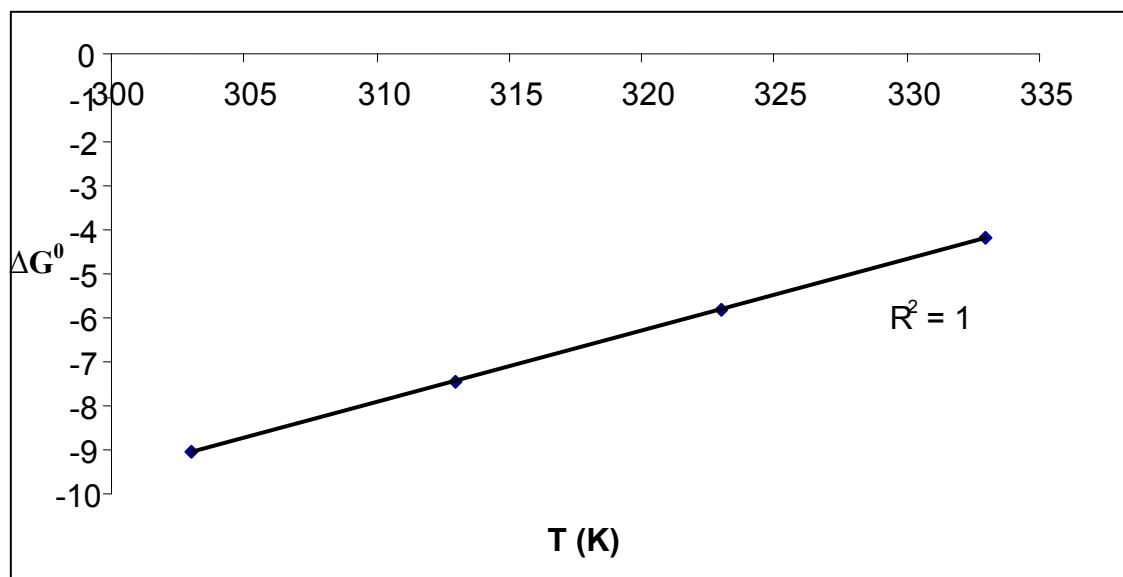


Figure 13. Plot of Gibb's free energy change versus temperature for adsorption of fluoride onto eggshell powder.

Cost analysis and removal of F⁻ from ground water

With a view to making use of this finding in domestic applications eggshell powder is an effective and low-cost adsorbent for removal of fluoride from drinking water as well as groundwater. The overall cost of the adsorbent material is governed by several factors which include its availability (whether it is natural, industrial/agricultural/domestic wastes or by-products or synthesized by-products), the processing required and reuse. Eggshell is available in abundance as a domestic waste product and collected from target site. The most popular commercial adsorbents of the present time for removal of fluoride are activating charcoal, activated alumina etc. Compared to these commercially available adsorbents, the total cost of eggshell powder is extremely low. In this study, use of eggshell powder can fulfill its effectiveness as an adsorbent for removal of F⁻ through batch techniques from contaminated ground water samples collected from different locations (villages), Nasipur and Nowapara of Birbhum district in West Bengal, India. Analysis of these samples was carried out and given in Table 6 with high F⁻ concentrations in ground water obtained from Nasipur and Nowapara in Birbhum district. The batch adsorption studies were carried out as such as normal conditions with concentration variation of eggshell powder dose (2.4 g) for 100 minutes of constant agitation at 350 rpm in temperature controlled magnetic stirrer at 303 K. The results show that the F⁻ levels in the ground water samples collected from study area decreased to <1 mg/L with 2.4 g/100 ml of eggshell powder. Thus the use of eggshell powder is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for contaminated groundwater treatment process in affected areas.

Table 5. Activation energy and thermodynamic parameters for adsorption of fluoride onto eggshell powder.

E_a (kJ mol ⁻¹)	ΔG^0 (kJ mol ⁻¹)				ΔH^0 (kJ mol ⁻¹)	ΔS^0 (Jmol ⁻¹)
	303 K	313 K	323 K	333 K		
45.98	-9.063	-7.7443	-5.823	-4.203	-58.149	-0.162

Table 6. Physico-chemical analysis of groundwater samples collected from study area (Nasipur and Nowapara).

Parameters	Nasipur	Nowapara
pH	7.2	7.7
Conductivity (mS/cm)	2.8	3.0
Fluoride (mg L ⁻¹) as (F ⁻)	7.1	10.0
Total hardness (mg L ⁻¹) as Ca and Mg	944	40
Chloride (mg L ⁻¹) as (Cl ⁻)	545.93	31.48
Sulphate(mg L ⁻¹) as (SO ₄ ⁻²)	186	112.2
Phosphate (mg L ⁻¹) as (PO ₄ ⁻²)	16	0.048
Ammonical nitrogen (mg L ⁻¹)	1.53	0.095
COD (mg L ⁻¹)	16	24
Iron (mg L ⁻¹) as Fe ⁺²	0.404	0.153

Conclusions

The role of eggshell powder as an adsorbent for removal of fluoride from aqueous solution using batch technique has been established. The maximum adsorption occurred at pH 2.0-6.0. Experimental equilibrium data provided best fit with the Langmuir isotherm model, indicating monolayer sorption on a homogenous surface (maximum monolayer sorption capacity was 1.09 mg g⁻¹ at 303 K). According to Dubinin-Radishkevich (D-R) isotherm model, adsorption of fluoride onto eggshell powder was Chemisorption. The adsorption kinetics followed pseudo-second-order kinetic model indicating towards chemisorption. Intra-particle diffusion was not the sole rate controlling factor. The activation energy of the adsorption process (E_a) was found to be 45.98 kJmol⁻¹ by using Arrhenius equation, indicating chemisorption nature of fluoride onto eggshell powder also. Thermodynamic analysis suggests that removal of fluoride from aqueous solution by eggshell powder was a spontaneous and exothermic process. The eggshell powder has also been encouraging results with groundwater sample collected from villages (Nasipur and

Nowapara) in Birbhum district, West Bengal, India. The present findings suggest that such eggshell is an expensive as a waste material available in many parts of the world, it also can provide a simple, effective and low cost method for removing F^- form contaminated water.

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