



## Studies on sorption of some geomaterials for fluoride removal from aqueous solutions

M.G. Sujana\*, H.K. Pradhan, S. Anand

*Institute of Minerals and Materials Technology, Bhubaneswar 751013, Orissa, India*

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### ABSTRACT

In the present study the defluoridation capacities of some of the naturally occurring materials like low and high iron containing lateritic ores, overburden from chromite mines of Orissa Mining Corporation (OMC) and Tata Steel have been estimated. The various experimental parameters studied for fluoride sorption from aqueous solutions were: time, pH, initial fluoride concentration, sorbent dose and temperature. The three geomaterials, namely chromite overburden from Orissa Mining Corporation, both low and high iron containing lateritic ores sorbed fluoride effectively. The sorption kinetics for these samples was found to follow first order rate expression and the experimental equilibrium sorption data fitted reasonably well to both Langmuir and Freundlich models. The negative values of  $\Delta G^\circ$  suggest the sorption of fluoride onto three samples to be spontaneous and the exothermic nature of sorption is confirmed by the  $-\Delta H^\circ$  values. The negative  $\Delta S^\circ$  values for these sorbents point towards decreased randomness at the solid/solution interface. The sorption studies were also carried out at natural pH conditions for fluoride removal from ground water samples and the fluoride level could be reduced from 10.25 to  $<1.0 \text{ mg L}^{-1}$  by multistage adsorption process using OMC and NH samples.

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### 1. Introduction

High fluoride levels in drinking water has become one of the most critical health hazards of this century as it induces intense impact on human health including skeletal and dental fluorosis [1]. The occurrence of fluoride in ground and surface water in different concentrations has been reported from almost all parts of the world [2]. In India, although water resources are high but there is an acute shortage of safe drinking water due to acceptable water quality. The incidence of high fluoride content in ground water ( $>1.5 \text{ mg L}^{-1}$ ) is not uncommon in both shallow and deeper water bearing zones [3–5]. Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Fluoride can be enriched in natural waters by geological processes. Besides, there can also be formidable contributions from industries. High fluoride containing wastewaters are generated by thermal power plants, rubber, fertilizer and semiconductor manufacturing, glass and ceramic production and electroplating industries. According to the WHO (1994) [6–7] guidelines and recommendations in the areas with a warm climate, the optimal fluoride concentration in drinking water should remain below  $1 \text{ mg L}^{-1}$ , while in cooler

climates it could go up to  $1.2 \text{ mg L}^{-1}$ . The differentiation derives from the fact that people perspire more in hot weather and consequently drink more water [8]. The problem is more acute in rural and small urban communities particularly in the third world countries [9]. Severe chronic and cumulative over exposure can cause the incurable crippling of skeletal fluorosis. The dental and skeletal fluorosis is irreversible and no treatment exists. The only remedy is prevention by keeping fluoride intake within the safe limits.

Defluoridation is normally accomplished by sorption and precipitation processes [10–13]. The most commonly used sorbent for fluoride removal from drinking water is activated alumina. To find out cost effective alternatives for removing fluoride from waters, different geomaterials have been tested in recent years, which includes zeolites, heat-treated soils, fly ash, bauxite, volcanic ash and limestone [14–17]. In the present study, fluoride removal studies have been carried out by sorption onto naturally occurring, low cost materials like low and high iron containing nickel laterites (NL and NH), overburden from chromite mines of Orissa Mining Corporation (OMC) and Tata Steel (TS) from Orissa, India. All these materials have iron as the major component while nickel, cobalt, manganese, calcium, magnesium, aluminium, chromium and silica as the other components. Though considerable research efforts have been made to for nickel and cobalt extraction [18–21] but till now these materials have not been commercially exploited due to low nickel content. The presence of high metal oxides especially

\* Corresponding author. Tel.: +91 674 2581639; fax: +91 674 2581637.  
E-mail address: [mgsujana@gmail.com](mailto:mgsujana@gmail.com) (M.G. Sujana).

iron in these materials may make them suitable for fluoride remediation. The proximity of availability of these materials in Orissa, India and presence of fluoride contaminated ground water in different locations of this state make the present study very useful. In this context, the above said materials were taken for fluoride removal studies from water and their applicability in fluoride containing ground water treatment systems.

## 2. Materials and methods

The samples were crushed, ground and sieved to obtain <100  $\mu\text{m}$  size (100% –150 B.S.S. mesh) and stored in airtight containers for further studies. The chemical analysis of the samples was carried out by following the recommended analytical procedures [22]. Sampling for analysis was done following quarter and cone method. One gram of each sample (in duplicate) was subjected to tri-acid digestion for wet chemical analysis. Iron was analysed volumetrically by taking a known aliquot and first reducing it with stannous chloride followed by addition of saturated mercurous chloride, 10%  $\text{H}_2\text{SO}_4$  and phosphoric acid. The contents were titrated against standard potassium dichromate in presence of BDAS (barium diphenyl ammine sulphonate) as an indicator. The concentrations of other metal ions were determined by Atomic Absorption Spectrophotometer (PerkinElmer 2380) after proper dilutions. The mineral phase compositions were determined by X-ray diffraction (XRD), measurements were done over a range of 10–70° using Phillips Powder Diffractometer Model PW3710 with  $\text{Co K}\alpha$  radiation at a scan speed of 1.2°  $\text{min}^{-1}$ . The surface area was measured by BET nitrogen sorption technique (Quantasorb 1750 instrument).

All the chemicals used were of analytical reagent grade. Fluoride analysis was carried out by following SPADNS method [23]. A known volume of sample was taken in a 25 mL volumetric flask and 5 mL of SPADNS reagent was added. The volume was made up to 25 mL using distilled water and the absorbance was measured at 570 nm using PerkinElmer Lambda 35 UV/visible spectrophotometer. The pH of the solutions at the beginning and end of the experiments were measured and the average values are reported. All the pH measurements were carried out by an Systronic digital pH meter (Model 361) and the pH of the solutions were adjusted by HCl and NaOH solutions of appropriate strength. The pH was measured by dipping the electrode in the solution. The  $\text{pH}_{\text{pzc}}$  of prepared sample was determined by solid addition method adopted by Balistrieri and Murray [24]. Accordingly, to a series of well-stoppered 125 mL polyethylene bottles containing 40 mL of 0.01 M  $\text{KNO}_3$  electrolyte solution, different volumes of either 0.1 M HCl or 0.1 M NaOH solution were added to obtain wide-ranging pH values from 2 to 8. The total volume of solution in each bottle was made up to 50 mL by addition of distilled water. After 2 h of equilibration the pH values ( $\text{pH}_i$ ) were noted and 0.2 g of sample was added. After 72 h of equilibration at room temperature ( $305 \pm 3 \text{ K}$ ) with intermittent shaking, the pH value of the supernatant liquid in each bottle was noted ( $\text{pH}_f$ ). The difference between  $\text{pH}_i$  and  $\text{pH}_f$  ( $\Delta\text{pH}$ ) were then plotted against  $\text{pH}_i$ . The solution pH at which  $\Delta\text{pH} = 0$  is “the  $\text{pH}_{\text{pzc}}$ ” of the sample. In a similar way  $\text{pH}_{\text{pzc}}$  of all the samples was determined [25].

A 100- $\text{mg L}^{-1}$  fluoride stock solution was prepared by dissolving 0.221 g of sodium fluoride in 1 L of double distilled water at room temperature. The experimental solutions were prepared by appropriate dilutions of the above solution. Batch sorption studies were carried out different conditions, viz. effect of contact time (15–300 min), pH (2.5–10), sorbent dose (2–10  $\text{g L}^{-1}$ ), fluoride concentrations (10–50  $\text{mg L}^{-1}$ ) and temperature (305–335 K). 0.1 g of the sample was taken in a 100 mL polyethylene plastic vial and

**Table 1**  
Chemical analysis of various geomaterials

Element	NH	NL	TS	OMC
%Fe	46.29	28.56	43.75	40.0
%Ni	1.15	0.71	0.79	0.74
%Co	0.07	0.05	0.08	0.09
%Mn	1.06	0.27	0.60	0.15
%Zn	0.01	0.02	0.02	0.05

50 mL of fluoride solution of known concentration was added. The contents (adsorbent/water 2  $\text{g L}^{-1}$ ) were kept for constant shaking in a temperature controlled water bath shaker for required time and then the solids were separated by centrifuging at 3500 rpm on REMI centrifuge. The solutions were collected for analysis and fluoride concentration in the solutions was determined. Each experiment was conducted three times and average values are reported. The sorption capacity  $X$  ( $\text{mg g}^{-1}$ ) of the sorbent was calculated from the following equation:

$$X = \frac{C_i - C_e}{C_A} \quad (1)$$

where  $C_e$  is the residual concentration reached at equilibrium state,  $C_i$  the initial fluoride concentration and  $C_A$  is the sorbent concentration.

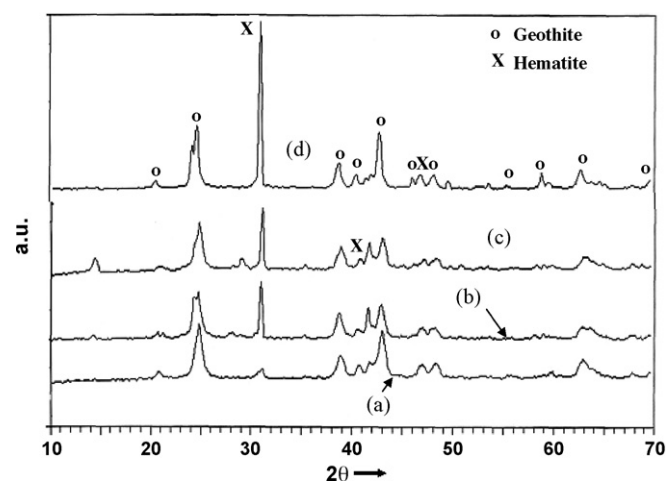
## 3. Results and discussion

### 3.1. Chemical composition and characterization

The chemical composition of various sample are given in Table 1 shows that the major component is iron oxide in all samples. The XRD patterns (Fig. 1) of the samples show presence of goethite and hematite in all the samples. The 100% RI peaks corresponding to hematite are observed for samples OMC, TS and NL whereas for NH 100% RI peak corresponds to goethite. The  $\text{pH}_{\text{pzc}}$  of samples NH, NL, OMC and TS were 6.9, 6.7, 6.7 and 6.5, respectively. The specific surface area of the samples were determined by BET method and were found to be 74, 68, 44 and 51  $\text{m}^2 \text{g}^{-1}$ , respectively.

### 3.2. Effect of contact time

Fig. 2 shows the effect of contact time on the removal of fluoride by different geomaterial samples. It shows that with a fixed amount of sorbent, the fluoride concentration in the solution decreased with time. For all the samples except the OMC, the equilibrium



**Fig. 1.** XRD patterns of various geomaterials (a) NH, (b) OMC, (c) TS and (d) NL.

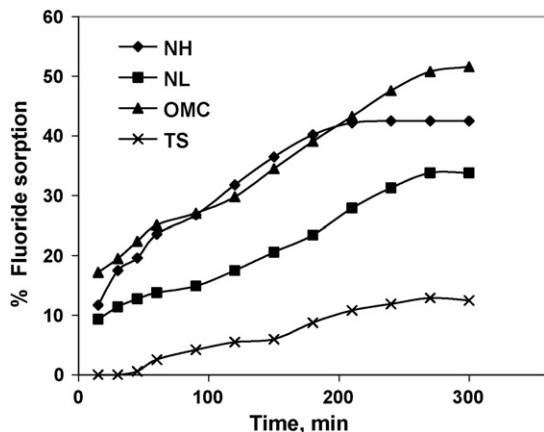


Fig. 2. Effect of contact time on fluoride removal. Conditions: sorbent dose,  $2 \text{ g L}^{-1}$ ; initial fluoride concentration,  $10 \text{ mg L}^{-1}$ ; temperature,  $303 \text{ K}$ ; pH 5.

conditions appeared at 4 h. In case of OMC sample, residual fluoride concentration decreased up to 4.5 h. The order of removal of fluoride from the aqueous solution is:  $\text{OMC} > \text{NH} > \text{NL} > \text{TS}$ . These results indicate that the adsorption is neither dependent on the iron content of the geomaterials nor on the surface area. It is difficult to indicate the exact active adsorption sites in such materials as these constitute a number of oxides such as magnesium, calcium, silica, alumina and chromite along with iron. Further studies were carried out with the three materials that exhibited higher removal capacity, namely, OMC, NH and NL samples.

### 3.3. Sorption kinetics

The time data generated was used to determine the rate constants. The sorption rate constants of fluoride on NH, OMC and NL were determined to understand the adsorption phenomena in terms of the adherence of fluoride on the active sites of the sorbent as well as its intra-particle diffusion within the pores of the sorbent [26]. The sorption rate constants for fluoride were calculated by using the following Lagergren equation [27]:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t \quad (2)$$

where  $q_e$  and  $q$  are the amount of fluoride sorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at any time  $t$  (min), respectively. The sorption rate constant  $k_{ad}$  was determined from the slopes of the linear plots of  $\log(q_e - q)$  vs.  $t$  for three geomaterials (Fig. 3). The values of  $k_{ad}$  for fluoride on OMC and NH were found to be  $3.9$  and  $9.2 \times 10^{-3} \text{ min}^{-1}$ ,

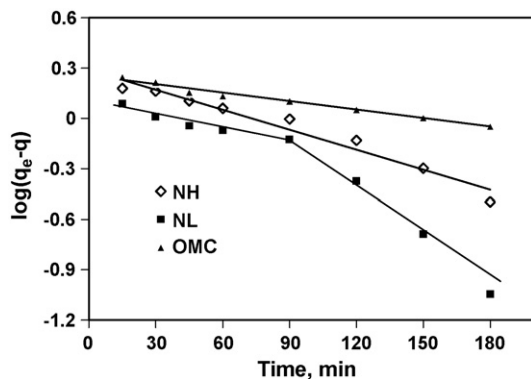


Fig. 3. Lagergren plots for the removal of fluoride on geomaterials (data corresponding to Fig. 2).

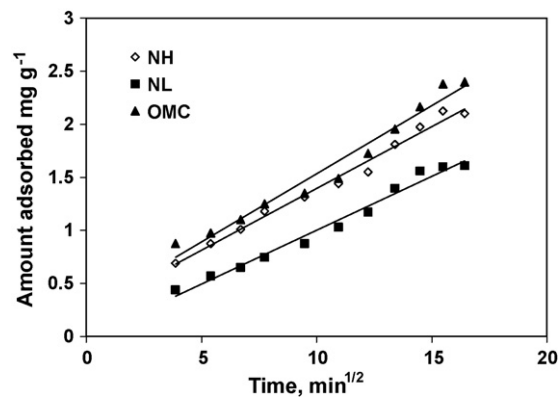


Fig. 4. Intra-particle diffusion of fluoride on surfaces of geomaterials (data corresponding to Fig. 2).

respectively. In case of NL two distinct regions were marked, one up to 90 min and another one from 90 to 180 min with rate constants as  $8.0 \times 10^{-3}$  and  $2.3 \times 10^{-2} \text{ min}^{-1}$ , respectively. This could be probably due to different available surface sites with time resulting in variation of rate constants. However, further studies are required to outline the mechanism.

Besides the sorption at the outer surface of the sorbent, the sorbate molecules may also diffuse into the interior of the porous sorbent [16]. This was studied by plotting the amount of the fluoride sorbed vs. the square root of time (Fig. 4), a straight line representing the control of sorption by intra-particle diffusion. The solute ions diffuse within the pores and capillaries of the metal oxides, as these provide available sites for sorption. The values of intra-particle diffusion rate constants  $K_p$  were calculated from the slopes of the plots from Fig. 4 and are found to be  $13.0$ ,  $12.0$  and  $10.0 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{0.5}$  for OMC, NH and NL samples, respectively.

### 3.4. Effect of pH

Anions can be sorbed on sorbents through specific and/or non-specific sorption. The specific adsorption, involves ligand exchange reactions where the anions displace  $\text{OH}^-$  and/or  $\text{H}_2\text{O}$  from the surface [28]. Where as nonspecific adsorption involves the coulombic forces, and mainly depends on the  $\text{pH}_{\text{pzc}}$  of the sorbent [29]. The effect of solution pH on fluoride removal by different geomaterials was studied by fixing the pH of the working solutions in the range of 2.5–10 and the results are shown in Fig. 5. In all the cases, sorption passes through maxima. The results show for NH and OMC samples, the maxima occurs at pH range of 5–6, whereas for NL sample

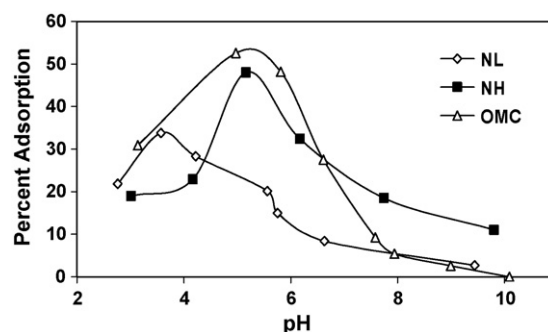


Fig. 5. Effect of solution pH on fluoride removal by geomaterials. Conditions: sorbent dose,  $2 \text{ g L}^{-1}$ ; initial fluoride concentration,  $40 \text{ mg L}^{-1}$ ; temperature,  $303 \text{ K}$ ; contact time, 4 h.

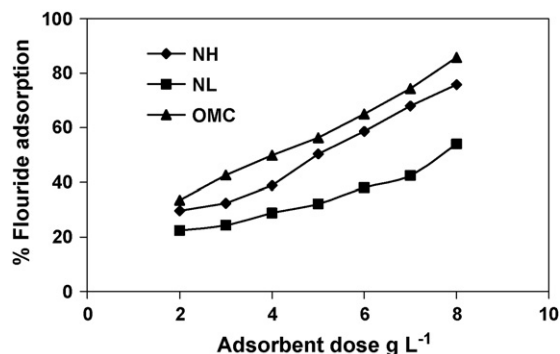


Fig. 6. Effect of sorbent dose of fluoride removal. Conditions: initial fluoride concentration, 40 mg L<sup>-1</sup>; temperature, 303 K; pH 5; contact time, 4 h.

the maxima is in the pH range of 3–5 for fluoride removal. As these geomaterials are combination of hydrous metal oxides like Fe, Al and Si, in humid environment hydroxylated surfaces of these metal oxides develop charge on the surface of aqueous solution. Therefore, the specific sorption of fluoride by these oxide species may be modeled as a two-step ligand exchange reaction:



The over all reaction can be written as



where SOH represents a surface hydroxyl group and SF a surface site occupied by a fluoride ion. The minimum sorption in acidic range for the geomaterials can be attributed to the formation of weak hydrofluoric acid. The decrease of sorption in the alkaline pH (>7) range may be due to the competition of the hydroxyl ions with the fluoride for surface sites on sorbent or electrostatic repulsion of fluoride ion to the negatively charged surface. These geomaterials are attractive sorbents because of their broad pH range of 4–8 for sorption of fluoride.

### 3.5. Effect of sorbent dose

The effect of sorbent dosage on fluoride removal at fixed pH and initial fluoride concentration is shown in Fig. 6. It is evident that the percent of fluoride removal increased with the increase of the sorbent concentration which is due to the fact that a greater amount of sorbent implies a greater amount of available binding sites. Therefore, percent sorption increased with increase of sorbent dose. The distribution coefficient ( $K_{DC}$ ) generally used to define the partitioning of an element in a system [30] is expressed by the following equation:

$$K_{DC} = \frac{\text{anion}_{\text{ads}}}{\text{anion}_{\text{diss}}} \frac{1}{C_p} \quad (6)$$

where  $C_p$  is the sorbent concentration in kg L<sup>-1</sup> and  $K_{DC}$  is the distribution coefficient in L kg<sup>-1</sup>. The distribution coefficient  $K_{DC}$  of fluoride for sorbents (NL, NH and OMC) at constant pH increased with increase of sorbent dose (Fig. 7). A distribution coefficient reflects the binding ability of the surface for an element. If the surface is homogeneous, the  $K_{DC}$  values at a given pH should not change with particle concentration but in the present study for all the sorbents,  $K_{DC}$  increases thereby indicating the heterogeneous nature of the surfaces.

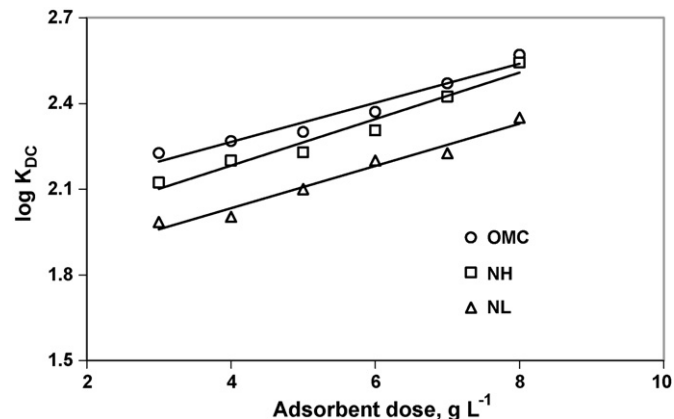


Fig. 7. Plot of distribution coefficient vs. sorbent dose. Conditions: initial fluoride concentration, 40 mg L<sup>-1</sup>; temperature, 303 K; contact time, 4 h.

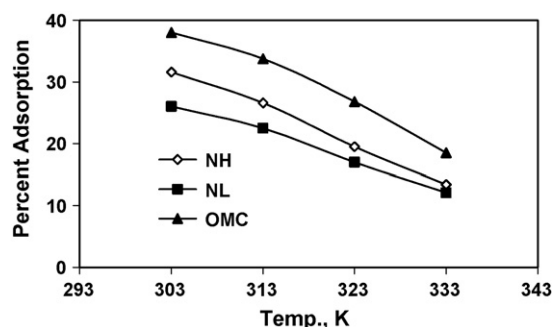


Fig. 8. Effect of temperature on fluoride removal. Conditions: initial fluoride concentration, 40 mg L<sup>-1</sup>; sorbent dose, 2 g L<sup>-1</sup>; pH 5; contact time, 4 h.

### 3.6. Effect of temperature

The effect of temperature on the extent of fluoride sorption was investigated in the solution temperature range from 305 to 335 K for selected agitation time and initial solute concentrations. The data shown in Fig. 8 reveals that rise in solution temperature has an adverse effect on fluoride sorption on NL, NH and OMC. This may be happening because the rise in temperature increases the escaping tendency of the molecules from the interface and thereby diminishes the extent of sorption (decrease in sorption capacity). And it also shows that the interaction between fluoride ion and sorbent is exothermic in nature and confirms the physical sorption of fluoride on NL, NH and OMC surfaces.

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

$$K_c = \frac{C_{Ae}}{C_e} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303TR} \quad (9)$$

Table 2  
Thermodynamic parameters for the fluoride removal on geomaterials

Sample	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> deg <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )
NH	-14.65	-94.4	-27.59
NL	-15.82	-105	-30.13
OMC	-15.9	-101	-28.37
Red soil [16]	-6.09	-46.62	-2.02
Bauxite [17]	-5.76	-29.28	-0.078

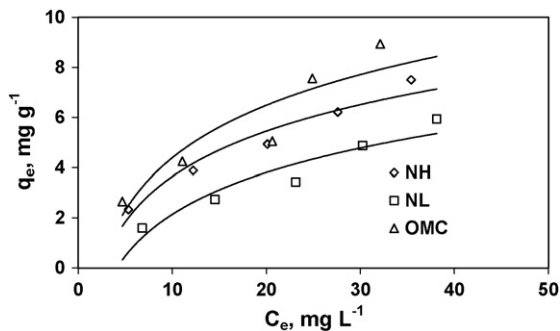


Fig. 9. Sorption isotherms of geomaterials for different initial fluoride concentrations. Conditions: sorbent dose, 2 g L<sup>-1</sup>; pH 5; contact time, 4 h; temperature, 303 K.

where  $C_e$  is the equilibrium concentration in solution in mg L<sup>-1</sup> and  $C_{Ae}$  the equilibrium concentration on the sorbent in mg L<sup>-1</sup> and  $K_C$  is the equilibrium constant. The van't Hoff plot of  $\ln K_C$  against  $1/T$  was found to be linear (not shown). The values for the thermodynamic parameters were obtained from the slope and intercept of the plot (Table 2). The negative values of  $\Delta G^\circ$  indicates spontaneous nature of sorption while the negative  $\Delta H^\circ$  values confirm the sorption to be exothermic in nature. Generally, adsorption processes are associated with positive values of  $\Delta S^\circ$ . In contrast, negative values of  $\Delta S^\circ$  for adsorption on some heterogeneous materials are reported [31]. The negative values of  $\Delta S^\circ$  suggest decreased randomness at the solid/solution interface and points towards no significant change occurring in the internal structure of the sorbent through sorption.

### 3.7. Isotherm study

The sorption data usually follow Langmuir or Freundlich isotherms models. The experimental data obtained for different initial fluoride concentration at constant temperature and pH were plotted (Fig. 9) in a linearised form of Langmuir and Freundlich sorption isotherms

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (10)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

where  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>),  $q_e$  the amount sorbed at equilibrium (mg g<sup>-1</sup>),  $Q_0$  the sorption capacity for Langmuir isotherms and 'b' is an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption. The constant 'n' indicates the degree of favorability of adsorption [32] and  $K_F$  is the isotherm constants for

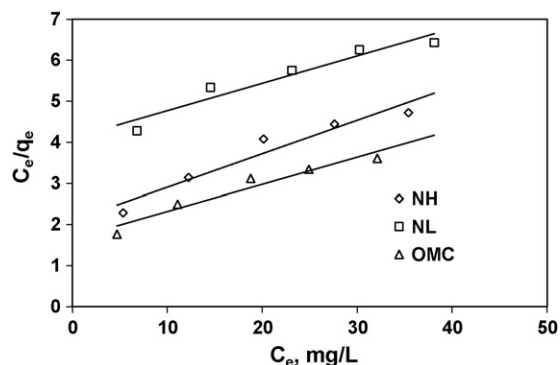


Fig. 10. Langmuir plots for sorption of fluoride (data corresponding to Fig. 9).

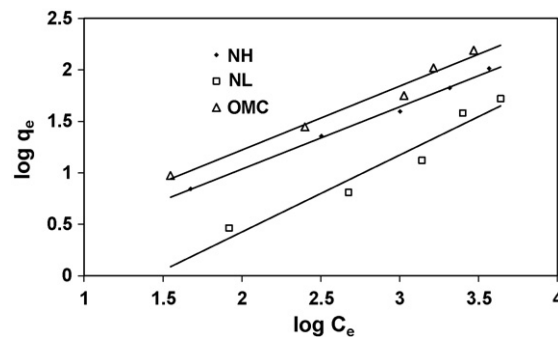


Fig. 11. Freundlich plots for fluoride sorption by geomaterials (data corresponding to Fig. 9).

Table 3

Calculated isotherm parameters for Langmuir and Freundlich models

S. no.	Langmuir isotherm			Freundlich isotherm		
	$r^2$	$Q^\circ$ (mg g <sup>-1</sup> )	b	$r^2$	$K_F$	n
NH	0.925	15.02	0.04	0.996	0.84	1.66
NL	0.967	12.30	0.02	0.959	0.36	1.28
OMC	0.939	15.17	0.04	0.935	0.97	1.66

Freundlich model. The sorption data of fluoride on all the samples followed both Langmuir and Freundlich isotherm models as shown in Figs. 10 and 11 (correlation coefficient > 0.9 for all). The calculated isotherm parameters along with correlation coefficients and are given in Table 3. It was observed that the data fits well to both the models. The magnitude of the Langmuir constant 'b' has small values (0.02–0.04 L mg<sup>-1</sup>), which indicates a low heat of adsorption [33,34]. The 'n' should have values lying in the range of 1–10 for classification as favorable adsorption [35]. A smaller value of 'n' indicates a weaker bond between adsorbate and adsorbent and also it indicates the adsorbent surface to be of heterogeneous [36,37], while a lower value for  $K_F$  indicates that the rate of adsorbate removal is low [38].

### 3.8. Fluoride removal from ground water sample

In Orissa (India), there are many locations where fluoride is present in excess of acceptable limits (>1 mg L<sup>-1</sup>) in ground water. A typical ground water sample was collected from Khurda district for the present study. Chemical analysis is given in Table 4. The data generated on various geomaterials for fluoride removal shows that at a pH of >6% adsorption of fluoride decreased considerably. Due to the presence of other anions such as sulphate and chloride besides fluoride and the high pH of the ground water sample (pH 7.75), it is expected that the amount of adsorbent required would be quite high. Therefore, the adsorption studies were carried out under the following conditions: 14 g L<sup>-1</sup> adsorbent dose (NH or OMC), pH

Table 4

Characteristics of water sample

pH	7.75
Conductivity	1061
Calcium (mg L <sup>-1</sup> ) as Ca <sup>2+</sup>	9.61
Magnesium (mg L <sup>-1</sup> ) as Mg <sup>2+</sup>	11.66
Chloride (mg L <sup>-1</sup> ) as Cl <sup>-</sup>	269.42
Sulphate (mg L <sup>-1</sup> ) as SO <sub>4</sub> <sup>2-</sup>	148.89
Phosphates (mg L <sup>-1</sup> ) as PO <sub>4</sub> <sup>3-</sup>	0.0429
Nitrate (mg L <sup>-1</sup> )	0.085
Nitrite (mg L <sup>-1</sup> )	0.012
Total hardness (mg L <sup>-1</sup> ) as CaCO <sub>3</sub>	72
Fluoride (mg L <sup>-1</sup> )	10.25

7.75 and time 4 h, room temperature (303 K). The fluoride content reduced to 7.85 and 8.0 mg L<sup>-1</sup> by OMC and NH samples, respectively. Simulating a counter current removal of fluoride, the filtrate was taken and treated with fresh adsorbent (10 g L<sup>-1</sup>) in two more stages, the fluoride content was reduced to 0.25 and 0.37 mg L<sup>-1</sup> for OMC and NH, respectively. The final solution was analysed for other competing anions and it was observed that chloride was reduced to 212 and 194.7 mg L<sup>-1</sup> while sulphate concentration was reduced to 76.8 and 57.6 mg L<sup>-1</sup>, respectively with OMC and NH samples. These results show a very high uptake of chloride and sulphate along with fluoride ions resulting in high requirement of adsorbent.

#### 4. Conclusions

This study has demonstrated that iron containing lateritic ores (NL and NH) and chromite overburden (OMC of India) can be used as effective adsorbents for fluoride removal from aqueous solutions. The degree of removal was dependent on initial fluoride concentration, pH, sorbent dose and reaction temperature. Maximum adsorption of fluoride on OMC, NH and NL at pH of 5.0, 5.16 and 3.6 were 52.6, 48 and 33.8%, respectively. The time data for three materials followed first order kinetics and was governed by intra-particle diffusion model. The equilibrium data fitted well to both Langmuir and Freundlich isotherms with the increase in temperature from 308 to 338 K, percent adsorption of fluoride on all materials decreased indicating physisorption process. The evaluation of thermodynamic parameters showed that the adsorption process was thermodynamically favorable, spontaneous and exothermic in nature. The negative entropy values for all the samples indicate decreased randomness at the solid solution interface. Fluoride could be successfully removed from ground water samples by multistage adsorption process.

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#### References

- [1] S. Ayoob, A.K. Gupta, Fluoride in drinking water: a review on the status and stress effects, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 433–487.
- [2] RGNDWM, Prevention and control of fluorosis in India Water Quality and Defluoridation Techniques, vol. II, RGNDWM Ministry of Rural Development, New Delhi, 1993.
- [3] K. Kim, G.Y. Jeong, Factors influencing natural occurrence of fluoride rich groundwaters: a case study in the southeastern part of the Korean Peninsula, *Chemosphere* 58 (2005) 1339–1408.
- [4] G. Kartikeyan, A. Shunmugasundaraj, Isoleth mapping and in-situ fluoride dependence on water quality in the Krishnagiri block of Tamil Nadu in South India, *Fluoride* 33 (2000) 121–127.
- [5] S. Das, B.C. Mehta, S.K. Samanta, P.K. Das, S.K. And, Srivastava, Fluoride hazards in ground water of Orissa, India, *Indian J. Environ. Health* 1 (1) (2000) 40–46.
- [6] WHO, "Fluorine and Fluorides" WHO Guidelines for Drinking Water Quality, vol. 2, WHO, Geneva, 1984, p. 249.
- [7] BIS, IS:10500, Indian Standard Code for Drinking Water, BIS, India, 1983.
- [8] Fluoride in water: an overview, information supply by UNICEF India, <http://www.unicef.org/wes/files/fluoride.pdf>.
- [9] A.N. Deshmukh, D.B. Malpe, Fluoride in Environment, Gondwana Geological Society, Nagpur, India, 1996, pp. 1–13.
- [10] M. Young, T. Hashimoto, N. Hosho, H. Myoga, Fluoride removal in a fixed bed packed with granular calcite, *Water Res.* 33 (26) (1999) 3395–3402.
- [11] A.M. Raichur, M.J. Basu, Sorption of fluoride onto mixed rare earth oxides, *Sep. Purif. Technol.* 24 (2001) 121–127.
- [12] Y.H. Li, S. Wang, A. Cao, D. Zhao, X. Zhang, C. Xu, Z. Luan, J. Liang, D. Ruan, D. Wu, B. Wei, Sorption of fluoride from water by amorphous alumina supported on carbon nanotubes, *Chem. Phys. Lett.* 350 (2001) 412–416.
- [13] Y. Wang, E.J. Reardon, Activation and regeneration of a soil sorbent for defluoridation of drinking water, *Appl. Geochem.* 16 (2001) 531–539.
- [14] M.G. Sujana, R.S. Thakur, S.B. Rao, Removal of fluoride from aqueous solution by using alum sludge, *J. Colloid Interface Sci.* 275 (1998) 355–359.
- [15] P.P. Coetzee, L.L. Coetzee, R. Puka, S. Mubenga, Characteristics of selected South African clays for defluoridation of natural waters, *Water SA* 29 (2003) 331–338.
- [16] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Sorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.* 115 (2002) 41–47.
- [17] D. Mohapatra, D. Mishra, S.P. Mishra, G. Roychaudhary, R.P. Das, Use of oxide minerals to abate fluoride from water, *J. Colloid Interface Sci.* 275 (2004) 355–359.
- [18] S.C. Panda, D.N. Dey, P.K. Rao, P.K. Jena, Extraction of nickel and cobalt from lateritic nickel ores of Orissa by pressure leaching with sulphuric acid, *Trans. IIM* 28 (1975) 483–487.
- [19] G.V. Rao, T. Gouricharan, Process for enriching nickel from nickel containing overburden of chromite mines, Indian Pat. filed, NF/48/90, 1990.
- [20] S. Anand, M.K. Ghosh, R.P. Das, Ammonia leaching of reduced nickel laterites, Internal Report, RRL(B), Orissa, India, 1991.
- [21] G.K. Das, S. Anand, S. Acharya, R.P. Das, Characterisation and acid pressure leaching of various nickel-bearing chromite overburden samples, *Hydrometallurgy* 44 (1997) 97–111.
- [22] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, English Language Book Society and Longmans Green Publishers, 2000.
- [23] A.E. Greenberg, L.S. Coesreri, A.D. Eaton (Eds.), Standard Methods For the Examination of Water and Waste Water, John Willey and Sons, New York, 1987, p. 325.
- [24] L.S. Balistrieri, J.W. Murray, The surface chemistry of goethite (alpha FeOOH) in major ion seawater, *J. Am. Sci.* 281 (1981) 788–806.
- [25] M. Mohapatra, S. Anand, Studies on sorption of Cd(II) on Tata Chromite Mine Overburden, *J. Hazard. Mater.* 148 (2007) 553–559.
- [26] R. Leyva-Ramos, J.R. Rangel-Mendez, L.A. Bernal-Jacome, M.S. Berber-Mendoza, Intraparticle diffusion of cadmium and zinc ions during sorption from aqueous solution on activated carbon, *J. Chem. Technol. Biotechnol.* 580 (2005) 924–933.
- [27] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe *Kungliga Svenska Vetenskapsakademiens, Handlingar* 24 (4) (1898) 1–39.
- [28] D.M. Ruthven, Principles of Sorption and Sorption Processes, John Wiley & Sons Publishers, New York, 1984 (Chapter 6).
- [29] P.D. Rude, R.C. Aller, The influence of Mg<sup>2+</sup> on the sorption of fluoride by hydrous oxides in seawater, *Am. J. Sci.* 293 (1993) 1–24.
- [30] L.S. Balistrieri, T.T. Chao, Selenium adsorption by goethite, *Soil Sci. Soc. Am. J.* 51 (5) (1987) 1145–1151.
- [31] M. Sarkar, A. Banerjee, P.P. Pramanick, A.R. Sarkar, Use of laterite for removal of fluoride from contaminated drinking water, *J. Colloid Interface Sci.* 302 (2006) 432–441.
- [32] E.R. Treybal, Mass Transfer Operations, 3rd edition, McGraw Hill International Editions, Chemical Engineering Series, Singapore, 1981.
- [33] M. Doğan, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, *J. Hazard. Mater. B* 109 (2004) 141–148.
- [34] K.K. Pandey, G. Prasad, V.N. Singh, Removal of Cr(VI) from aqueous solution by adsorption on fly ash wollastonite, *J. Chem. Technol. Biotechnol.* 34A (1984) 367–374.
- [35] M. Rao, A.G. Bhole, Chromium removal by adsorption using fly ash and bagasse, *J. Indian Water Works Assoc.* XXXIII (1) (2001) 97–100.
- [36] A.Z. Aroguz, Kinetics and thermodynamics of adsorption of azinphosmethyl from aqueous solution onto pyrolyzed (at 600 °C) ocean peat moss (*Sphagnum* sp.), *J. Hazard. Mater.* B135 (2006) 100–105.
- [37] A. Ramu, N. Kannan, S.A. Srivathsan, Adsorption of carboxylic acid on fly ash and activated carbon, *Indian J. Environ. Health* 34 (1) (1992) 192–199.
- [38] M. Ajmal, A. Mohammad, R. Yousuf, A. Ahmad, Adsorption behaviour of cadmium, zinc, nickel and lead from aqueous solution by mangifera indica seed shell, *Indian J. Environ. Health* 40 (1) (1998) 15–26.