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KINETIC AND EQUILIBRIUM STUDIES ON FLUORIDE REMOVAL BY ZIRCONIUM (IV)-IMPREGNATED GROUNDNUT SHELL CARBON

The carbonized ground nut shell (GNSC) was impregnated with zirconium oxychloride, and tested to determine its capacity and kinetics for fluoride adsorption from aqueous solutions. The analysis of the isotherm equilibrium data using the Langmuir, Freundlich and Redlich–Peterson equations by linear methods showed that the data fitted better with Freundlich model than the other two. Thermodynamic studies revealed that the spontaneous nature of fluoride adsorption with increase of entropy and an endothermic process. The kinetic data obtained for fluoride adsorption on zirconium impregnated ground nut shell carbon (ZIGNSC) obeyed the pseudo-second order equation. X-ray diffraction (XRD) studies confirmed the deposition of fluoride on material and Fourier transform infrared (FTIR) studies also showed the involvement of adsorbate on the adsorbent surface in the adsorption interaction. The ZIGNSC provides a cost effective material to the defluoridation problem in the developing countries by its great potential application in the fluoride removal from water.

Fluoride is an important micro-nutrient for the production and maintenance of healthy bones and teeth. Although a certain amount of fluoride gives good protection against dental decay, excess intake of fluoride ions cause dental fluorosis. When the concentration of fluoride is more than 4 mg/L it causes softening of bones, ossification of tendons and neurological damage in several cases [1]. The problem of excess fluoride in drinking waters is aggravating day by day, as more surveys to assess the ground water quality have been undertaken. Fluoride in water derives mainly from dissolution of natural minerals in the rocks and soils with which water interacts. The distribution and health effects of fluoride have recently been reviewed by Ayoob and Gupta [2]. According to authors, about 200 million peoples from 25 nations are facing the problem of excess fluoride in drinking water among which India and China are the worst affected. In India alone, endemic fluorosis is thought to affect around 1 million people [3] and is a major problem in 17 out of the country's 28 states, especially Rajasthan, Tamilnadu, Madhya Pradesh, Andhra Pradesh, Gujarat and Uttar Pradesh [4]. We have also conducted exhaustive water sampling in Tirunelveli district of Tamilnadu, India to assess the distribution of fluoride in ground water. Fluoride concentrations in large number of samples fall above 1.0 mg/L (WHO prescribed limit for drinking water) and the maximum concentration found was 5.0 mg/L. The most important remedial action is the prevention of further exposure by providing safe drinking water. However in most of the areas source substitution may be impossible due to non-availability of alternate sources and therefore removal of excess fluoride is the only remedy.

Several defluoridation techniques, namely precipitation [5–7], membrane processes [8] electrolytic [9] ion-exchange [10] and adsorption onto various adsorbents have been evaluated both in field and lab. Owing to various drawbacks associated with conventional defluoridation techniques adsorption-based fluoride removal systems are emerging as the feasible option. Large numbers of adsorbents have been studied for the removal of fluoride from water based on alumina [11], other minerals and metal oxides [12–14], clays [14–16], carbons [17], zeolites [18], agricultural wastes [19,20], etc. The present paper deals with preparation of zirconium impregnated groundnut shell carbon (ZIGNSC) and its application for the removal of fluoride from ground water. Though the removal of fluoride using zirconium impregnated cashew nut shell carbon [20] has been reported earlier, the author felt that the use of ZIGNSC could definitely give a new dimension in the field of defluoridation; hence defluoridation experiments were carried out using the ZIGNSC. The effect of various parameters (pH, adsorbent dose, initial fluoride concentration, presence of other anions) on fluoride uptake capacity was investigated. Furthermore the characterization of obtained ZIGNSC before and after fluoride adsorption was done by using XRD analysis and FTIR spectroscopy.

MATERIAL AND METHODS

Preparation of activated carbon

Carbonized ground nut shell (GNSC) was prepared from ground nut shell (*Arachis hypogia*) using the procedure published by Seethapathirao [21]; about 100 g of the crushed ground nut shell was kept for 3 h in a low temperature muffle furnace at 573–673 K. The carbo-

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nized material was taken out of the muffle furnace, cooled, powered and kept in a beaker and 200 ml of concentrated sulphuric acid was gradually added to it, contents were stirred continuously to ensure thorough mixing. GNSC was then cooled and left overnight and washed free of acid and dried at 383 K for 2 h, then sieved using various mesh size. Subsequently, the obtained material was further used as the desired adsorbent for impregnation. Zirconium ion impregnation was carried out by addition of 5% $ZrOCl_2$ solution and GNSC (solution/solid ratio = 2:1) and the mixture was kept for 3 days at room temperature (298 K). The zirconium impregnated carbon was then filtered, rinsed to confirm the supernatant was free of zirconium, dried in an oven at 380K and subsequently used for defluoridation studies. The zirconium concentration in the effluent was determined using ammonia and alizarin red S (ARS) [22]. Zirconium is generally non-toxic as an element or in compound and the oral toxicity is low. Occupation of safety and health administration (OSHA) standard for pulmonary exposure specify a Tolerance value limit (TVL) of 5mg zirconium per m^3. As per the solubility product of zirconyl hydroxide ($K_{sp} = 6.3\times10^{-49}$), the solubility of it, is 26.7×10^{-15} g/L. Hence the amount of zirconium ion concentration in the effluent is well below the safe limit. As solubility factor calculations could be at variance with experimental results, a quantitative analysis was further carried out to determine the concentration of Zr^{4+} in the effluent and in the treated water samples by using spectrophotometric studies at a wavelength of 520 nm, as it is sensitive towards the small change of Zr^{4+} concentration and operate in the dynamic range of 5–35 mg/L at pH 2.5. All the tested samples had the Zr^{4+} concentration less than 5.0 mg/L. The defluoridation capacity of GNSC and ZIGNSC was investigated by pursuing the batch equilibrium and kinetic experiments. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode using the total ionic strength adjustment buffer (TISAB) solution to maintain pH 5–5.5 and to eliminate the interference effect of complexing ions [23]. The pH of the samples was also measured by Orion ion selective equipment. All other water quality parameters were analysed by using standard methods described in reference [24].

Sorption experiments

The defluoridation experiment was performed by batch equilibrium method by mixing 2.0 mg of sorbent with 100 ml of sodium fluoride containing 3 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 200 rpm at room temperature. The defluoridation studies were conducted under different experimental conditions: contact time, pH, initial fluoride concentration and influence of co--ions with fixed dosage. Kinetic studies and isotherm studies were carried out in different initial fluoride concentrations: 2, 4, 6, 8 and 10 mg/L at four different temperatures: 303, 313, 323 and 333 K, on fluoride sorption were studied by using of 2.0 mg of adsorbent and 100 mL of each fluoride solution at neutral pH. The pH at zero point charge (pH_{zpc}) of sorbent was measured using the pH drift method [25]. The pH of the solution was adjusted by using 0.01 mol/L sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 30 °C to remove the dissolved carbon dioxide. 50 mg of the adsorbent was added to 50 ml of each solution. After stabilization, the final pH was recorded. The graph of final pH versus initial pH was used to determine the point of zero charge of both GNSC and ZIGNSC.

Characterization of sorbents

The physiochemical properties of the adsorbent are listed in Table 1. The X-ray diffraction (XRD) pattern of ZIGNSC before and after fluoride adsorption was obtained using a Bruker AXS D8 Advance, Inst. ID: OCPL/ARD/26-002, X-ray diffractometer. Fourier transform infrared (FTIR) spectra of same samples were recorded using Nicolet 6700 FT-IR, Thermo Electronic Corporation, USA. Computations were made using Microcal Origin (Version 6.0) software. The accuracy of fit is discussed using regression correlation coefficient (*r*).

Table 1. The physiochemical properties of the adsorbent

No.	Parameter	Value
1	Surface area, m^2/g	2.12
2	Particle size, μm	> 53
3	Moisture, mass%	76.23
4	Ash content, mass%	22.18

RESULTS AND DISCUSSION

The effect of contact time

The sorption of fluoride ion on GNSC and ZIGNSC has been investigated as a function of contact time in the range of 60–210 min with 3 mg/L as initial fluoride concentration and 2.0 mg of adsorbent at room temperature. Figure 1 illustrates the percentage of fluoride removal by GNSC and ZIGNSC as a function of contact time in the range of 60–210 min at room temperature. The values are increasing linearly up to 180 min and thereafter it remained almost constant indicating the attainment of sorption equilibrium. Therefore 180 min was fixed as minimum contact time for the maximum defluoridation of the sorbent. The zirconium impregnated carbonized ground nut shell recorded a maximum percentage of fluoride removal, 84.00%, when compared with carbonized ground nut shell which showed fluoride removal of 63.67%. For further studies, the defluoridation of zirconium impregnated cashew nut shell carbon was previously reported by the author [20], the percentage of fluoride removal on ZICNSC is 80.33 %. It is compared to ZIGNSC, slightly low percentage of fluoride removal.

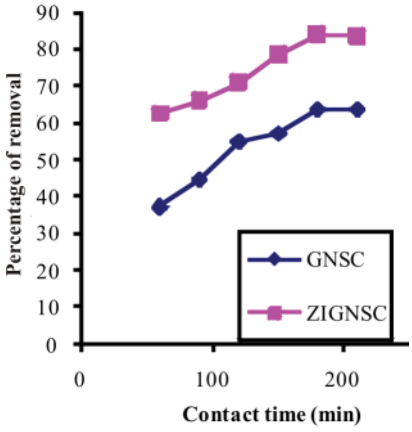

Figure 1. Effect of contact time on fluoride adsorption.

The effect of dosage

The effect of dosage of GNSC and ZIGNSC on fluoride adsorption in the required contact time of 180 min was studied by keeping the concentration of fluoride fixed (3 mg/L) while the doses of each adsorbent varied from 0.50 to 2.50 g. The fluoride adsorption increased exponentially with the increasing the amount of each adsorbent due to increasing the number of active sites. The amount of each adsorbent showing the optimum fluoride removal efficiency was found to be 2.0 g. The maximum percentage of fluoride removal is 64.00% for GNSC and 84.67% is ZIGNSC (Figure not shown). Further addition of the adsorbents did not show a considerable increase of percent of fluoride removal because the overlapping of the active sites at higher concentration of the adsorbent, thus reducing the surface area.

Effect of co-ions

The efficacy of GNSC and ZIGNSC for fluoride removal was also experimentally studied in presence of excess amount of common anions like Cl^-, SO_4^{2-} and HCO_3^-. No significant influence on fluoride removal of the material was observed in presence of Cl^- and SO_4^{2-}. However, in presence of excess HCO_3^- the defluoridation efficiency decreases from 84.0 to 74.6% in presence of about 500 mg/L of bicarbonate. A similar interfering role reported Mariappan *et al.* [27] for defluoridation properties of alumina-gibbsite. This specificity may be due to the competition of bicarbonate with fluoride for the active site at the surface of the adsorbent.

Adsorption isotherms

The sorption isotherm expresses the specific relation between the concentration of sorbate and its degree to accumulation onto sorbent surface at constant temperature. The fluoride sorption capacity of ZIGNSC at four different temperatures (303, 313, 323 and 333 K) was evaluated using three different isotherm models: Langmuir [28], Freundlich [29] and Redlich–Peterson [30].

The linear form of Langmuir isotherm is:

$$c_e / q_e = 1 / Qb + c_e / Q \tag{1}$$

where q_e is the amount of fluoride adsorbed per unit weight of the sorbent at equilibrium (mg/g), c_e is the equilibrium concentration of fluoride in solution (mg/L). The Langmuir isotherm constants, Q and b, were calculated from the slope and intercept of the plot c_e/q_e vs. c_e shown in Figure 2 and these results are listed in Table 2.

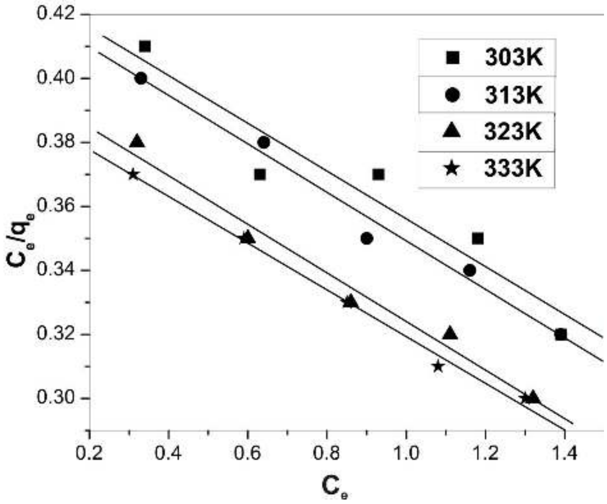

Figure 2. Plot of the Langmuir isotherm for fluoride adsorption on ZIGNSC.

Table 2. Comparative Langmuir constant study of fluoride adsorption onto various adsorbent

No.	Adsorbent	q_e / mg g^{-1}
1	Activated alumina	2.4
2	Fluorspar	1.79
3	Activated quartz	1.16
4	Hydroxy apatite	4.54
5	Calcite	0.39
7	Plaster of pairs	0.366
8	Present work	2.32

The value of Q was found to increase with increasing of temperature which indicated increase of sorption capacity with increase of temperature. These suggested the mechanism of fluoride removal by the sorbent was mainly due to chemisorption. The Langmuir constant Q of ZIGNSC compared with the other commonly used adsorbents were given in Table 3. The higher r values indicated the applicability of Langmuir isotherm.

The linear form of Freundlich isotherm is:

$$\ln q_e = \ln K_F + (1/n)\ln c_e \qquad (2)$$

The values of Freundlich isotherm constants, $1/n$ and K_F, were calculated from the slope and intercept of the plot log q_e *vs*. log c_e (Figure 3) and presented in Table 3. The values of $1/n$ lying between 0 and l and the n values lying in between 1 and 10 indicated that the conditions were favorable for adsorption and the r values indicated the applicability of Freundlich isotherm.

The linear form of Redlich–Petersan isotherm is:

$$\log(K_R c_e / q_e - 1) = \beta \log c_e + \log \alpha_R \qquad (3)$$

Table 3. Langmuir, Freundlich and Redlich isotherm parameters of fluoride sorption on ZICNSC

Isotherm	Parameter	T / K			
		303	313	323	333
Langmuir isotherm	q_m / mg g^{-1}	2.32	2.35	2.50	2.50
	b_L / L g^{-1}	5.77	5.61	5.26	5.37
	r	0.954	0.991	0.989	0.997
	SSE	0.135	0.005	0.006	0.003
Freundlich isotherm	$1/n$	0.454	0.463	0.490	0.502
	n	2.202	2.158	2.037	1.988
	k_F / mg g^{-1} $(L / \text{mg})^{1/n}$	13.91	14.02	14.79	13.84
	r	0.998	0.999	0.999	0.999
	SSE	0.031	0.022	0.016	0.026
Redlich–Peterson isotherm	α_R	3.67	3.55	3.26	3.32
	β	0.189	0.179	0.195	0.180
	K_R / L g^{-1}	13.39	13.19	13.17	13.69
	r	0.955	0.956	0.984	0.971
	SSE	0.033	0.031	0.019	0.025

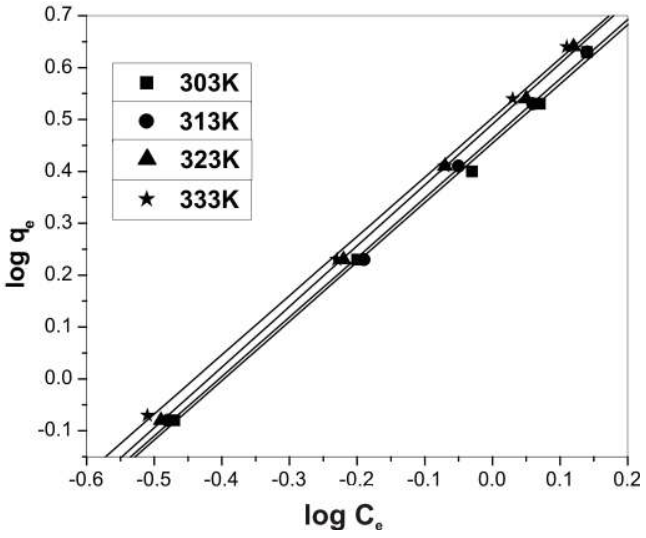

Figure 3. Plot of the Freundlich isotherm for fluoride adsorption on ZIGNSC.

where $K_R = Qb$ (L/g) and Q and b are Langmuir mono layer capacity and energy of adsorption, respectively. α_R is exponent of R–P isotherm.

The values of Redlich–Petersan isotherm constant, α_R and β were calculated from the slope and intercept of the plot $\log(K_R c_e / q_e - 1)$ *vs.* $\log \alpha_R$ (Figure 4) and presented in Table 3. The feasibility of the isotherm was tested by calculating the dimensionless constant separation factor or equilibrium parameter, R_L [31]. The R_L values at different temperatures were calculated and given in Table 4. The R_L values lying between 0 and 1 indicated that the conditions were favorable for adsorption. The higher r values of Freundlich over Langmuir and Redlich–Peterson isotherm indicated that the best fit of experimental data was obtained with Freundlich isotherm than with the Langmuir and Redlich–Peterson isotherm.

Thermodynamic parameters

The thermodynamic parameters for the adsorption process in solution have been calculated using the following standard thermodynamic relations:

$$\Delta G^\circ = -RT \ln K_0 \qquad (4)$$

where ΔG° is the standard free energy change (kJ/mol), T is the temperature (K) and R is universal constant (8.314 J mol^{-1} K^{-1}). The sorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot ln (q_e/c_e) against c_e at different temperatures and extrapolating to zero c_e according to the method suggested Khan and Singh [32].

The sorption distribution coefficient may be expressed in terms of ΔH° and ΔS° as a function of temperature:

$$\ln K_0 = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (5)$$

where ΔH° is the standard enthalpy change (kJ/mol) and ΔS° is standard entropy change (kJ mol^{-1} K^{-1}). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of ln K_0 against $1/T$. Thermodynamic parameters: standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were calculated [33] and presented in Table 5. The negative values of ΔG° indicated the spontaneity of the sorption reaction. The positive values of ΔH° indicated the endothermic nature of the sorption process. The positive value of ΔS° showed the increasing randomness at the solid/liquid interface during sorption of fluoride. It also indicates the increased disorder in the system with changes in the hydration of adsorbing fluoride ions [34].

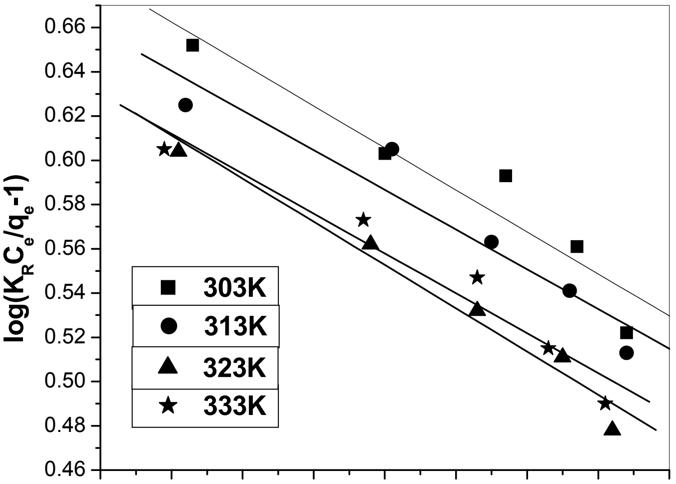

Figure 4. Plot of the Redlich–Peterson isotherm for fluoride adsorption on ZIGNSC.

Table 4. R_L values at different temperatures

No.	Concentration of fluoride, mg/L	T / K			
		303	313	323	303
1	2	0.1773	0.1754	0.1666	0.1639
2	4	0.0972	0.0961	0.0909	0.0893
3	6	0.0670	0.0662	0.0625	0.0613
4	8	0.0511	0.0505	0.0476	0.0467
5	10	0.0413	0.0408	0.0384	0.0377

Table 5. Thermodynamic parameters for adsorption of fluoride onto ZIGNSC

T / K	$\Delta G°$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ / kJ mol^{-1} K^{-1}
303	–0.921	0.717	3.28
313	–0.967		
323	–1.068		
333	–1.125		

Adsorption kinetics

To investigate the mechanism of adsorption, the pseudo-first order, pseudo-second order and intra-particle diffusion were studied. The adsorption kinetics was studied with initial fluoride concentrations of 2, 4, 6, 8 and 10 mg/L and adsorbent dose 2.0 mg at room temperature. The uptake of fluoride on adsorbents occurred rapidely, and reached equilibrium with in 180 min. The kinetics of adsorption was analyzed by using different rate equation; pseudo-first-order rate expression or the Lagergren rate Equation [35] and pseudo-second-order expression [36]. The extend of a particular diffusion to the total process may be estimated by Weber and Morris Equation [37]. The kinetic parameters calculated from the slope and intercept of linear plots (Figures 5–7) are given in Table 6. The kinetic models were evaluated for fitness of the sorption data by the correlation coefficient (r). Higher value of r shows a better fitness of the sorption data. It was identified that the pseudo-second-order was a better fit than pseudo-first-order and intraparticle diffusion model.

The observed higher values of h in pseudo-second order model indicate that the initial fluoride adsorption rate was extremely rapid. Hence it is revealed that the

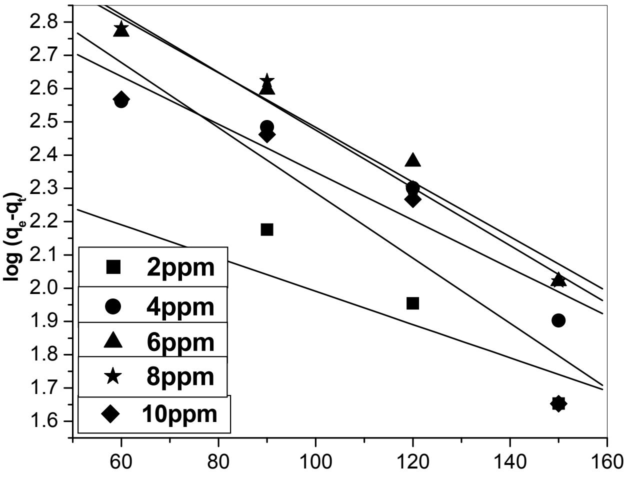

Figure 5. Pseudo first order kinetic fit for fluoride adsorption onto ZIGNSC at room temperature.

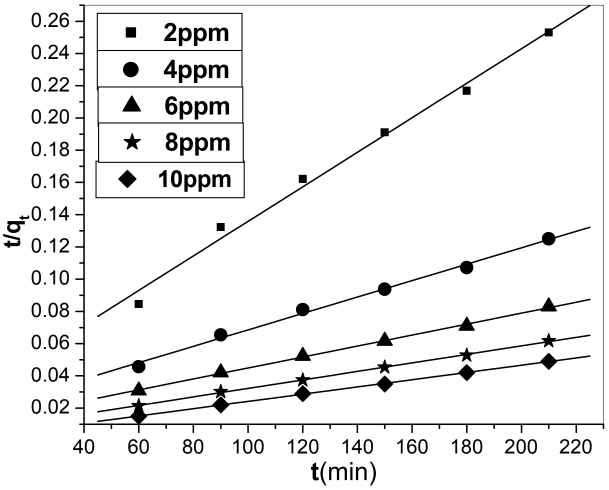

Figure 6. Pseudo second order kinetic fit for fluoride adsorption onto ZIGNSC.

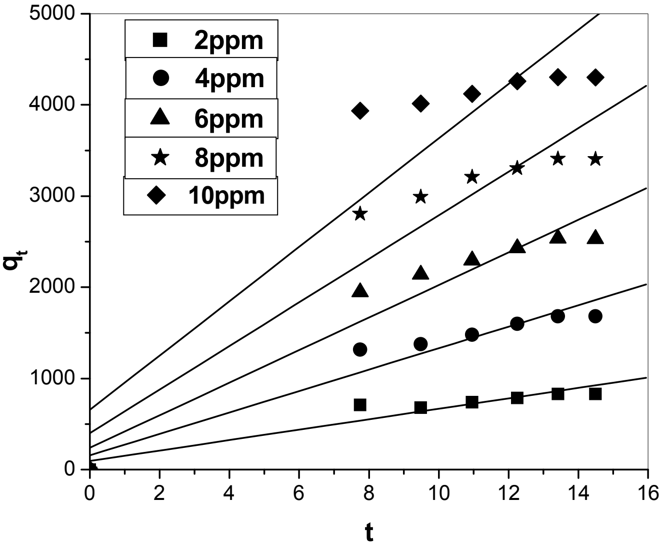

Figure 7. Plot for constant for intraparticle diffusion at different temperature.

Table 6. Kinetic parameters of reaction-based and diffusion-based models with r^2 values of ZIGNSC

Methods	Parameter	Concentration, ppm				
		2	4	6	8	10
Pseudo-first order	k_1 / min^{-1}	0.0115	0.0165	0.0189	0.0199	0.0225
	q_e / mg g^{-1}	0.31	1.17	2.01	2.20	1.84
	r	0.852	0.948	0.985	0.991	0.927
Pseudo-second order	k_2 / g mg^{-1} min^{-1}	3.99	1.47	1.06	1.21	3.04
	h / g mg^{-1} min^{-1}	34.85	56.85	91.65	173.0	602.4
	r	0.995	0.997	0.999	0.999	0.999
Intra-particle diffusion	k_p / min^{-1}	57.21	117.5	178.4	238.9	297.7
	r	0.949	0.967	0.967	0.951	0.920

adsorption of fluoride by ZIGNSC system follows the Freundlich adsorption isotherm and pseudo-second order kinetics.

Effect of pH and mechanism of fluoride sorption

The fluoride sorption by GNSC and ZIGNSC at different pH were also experimentally studied by varying the pH of solution from 3 to 12. At pH 3, the maximum percentage of fluoride removal by GNSC and ZIGNSC was 84.67 and 94.33 % respectively. It is observed that with increasing of pH of solution, the fluoride removal by these sorbents decreased. The same trend was also observed in *Morringa indica* based activated carbon [26]. The determination of the point of zero charge of GNSC and ZIGNSC showed that pH_{ZPC} for GNSC was 5.5 and 4. 6 for ZIGNSC. The maximum percentage of fluoride removal by the samples observed at pH 3, may be due to the availability of more H^+ at the surface of the adsorbent leading to greater adsorption of the fluoride. Hence, fluoride adsorption increases at low pH levels as the surface sites are more positively charged. The positively charged material easily is attracted the negatively charged fluoride ions. Lower percentage of adsorption in alkaline medium can be explained by the fact that the surface acquires negative charge in alkaline pH and hence there is repulsion between the negatively charged surface and fluoride ions. The fluoride removal by GNSC and ZIGNSC was governed by adsorption mechanism. The surface of each adsorbent acquired positive charge at lower pH values and hence high fluoride sorption at this pH level was mainly due to electrostatic attraction between the positive charged surface and negatively charged fluoride ions and chemisorption dominated. When the pH increased slowly, the surfaces of GNSC and ZIGNSC acquired negative charges and have no affinity for anionic species, physisorption dominated and hence percentage of fluoride removal decreased. The slight enhancement of fluoride removal by ZIGNSC over GNSC may be due sorption by zirconium, adsorption by physical forces and fluoride ion, a Lewis base, coordinates strongly with the zirconium species adsorbed on GNSC, which are Lewis acid sites:

$$\mathrm{ZrOCl_2 \cdot 8H_2O + H_2O \rightarrow ZrOOHCl + Cl^-} \tag{6}$$

$$\mathrm{ZrOOHCl(Adsorped\ on\ GNSC) + 2F^- \rightleftarrows} \\ \mathrm{\rightleftarrows ZrOF_2 + OH^- + Cl^-} \tag{7}$$

The chemisorption mechanism of fluoride uptake, involves an exchange of the chloride and the hydroxide of the ZrO(OH)Cl species adsorbed on GNSC by fluorides, leading to the formation of $ZrOF_2$ [38].

Field trial

The applicability of the ZIGNSC in the field condition was also tested with the sample taken from a nearby fluoride-endemic area. The results are presented in Table 7. The concentration of fluoride in the treated water is well within the tolerance limit and there is no significant change in other water quality parameters after treatment.

Table 7. Field trial results of ZIGNSC

Water quality parameter	Before treatment	After treatment
F^- (mg/L)	3.24	0.89
pH	8.2	7.1
EC (mS/cm^2)	2.32	1.22
Cl^- (mg/L)	559	298
TH (mg/L)	690	280
TA (mg/L)	440	129

Instrumental studies

For understanding the nature of fluoride sorption X-ray diffraction (XRD) and Fourier transform infrared (FTIR) studies were performed on ZIGNSC before and after fluoride adsorption The XRD patterns of adsorbent after fluoride adsorption showed significant changes. The XRD data of the treated ZIGNSC provided evidence of slight modification over the crystal cleavages. The intensity of the peak due to the hkl plane (010), the monoclinic crystal system of ZIGNSC disappeared after the fluoride adsorption on its surface. This is possible due to the lattice dislocation in the crystal system. The XRD patterns of untreated and fluoride treated ZIGNSC are given in Figures 8 and 9. This shows the strong adsorption of fluoride on the surface of the adsorbent. FTIR analysis of the sorbent surface before and after fluoride sorption has provided information regarding the surface groups that might have participated and also about the surface sites at which sorption might have taken place (Figure 10). Adsorption of fluoride has also resulted in several changes like the disappearance of some bands, shifts and decrease in the percentage of transmittance in the IR spectra of the solid surface in the range 4000–300 cm^{-1}. The shift of stretching frequency, corresponding to the presence of OH groups from 3626 to 3451 cm^{-1} is assigned to the involvement of hydroxyl groups in the fluoride adsorption by ZIGNSC.

CONCLUSION

In this study, the possibility of utilization of zirconium impregnated ground nut shell carbon (ZIGNSC) as adsorbent for removal of fluoride from aqueous solution was studied. The equilibrium time for removal of fluoride was determined to be 180 min. The fluoride saturation capacity of zirconium impregnated ground nut shell carbon is 1.26 mg F^{-}/g at room temperature. The best-fitting adsorption isotherm was Freundlich model. In the adsorption kinetic modeling studies, the pseudo second order chemical reaction kinetics provided the best

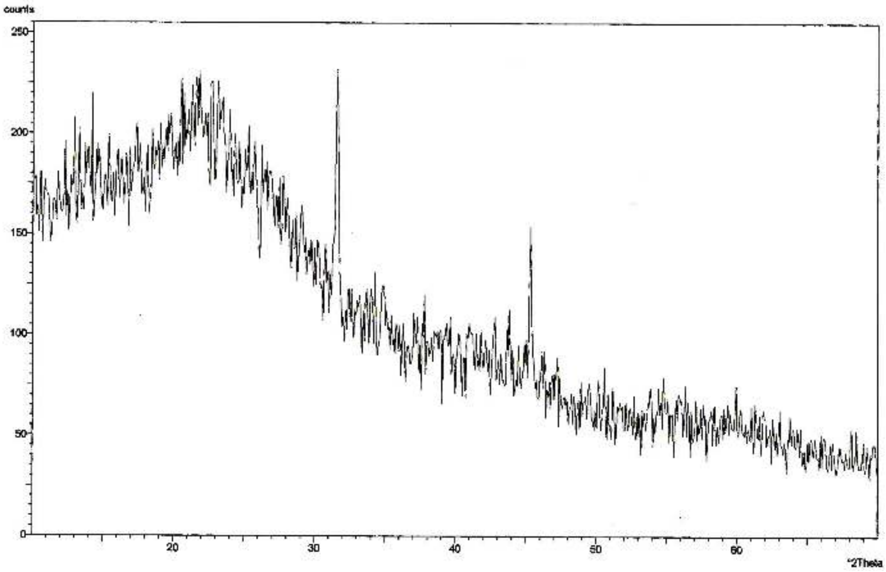

Figure 8. X-ray diffraction pattern of ZIGNSC.

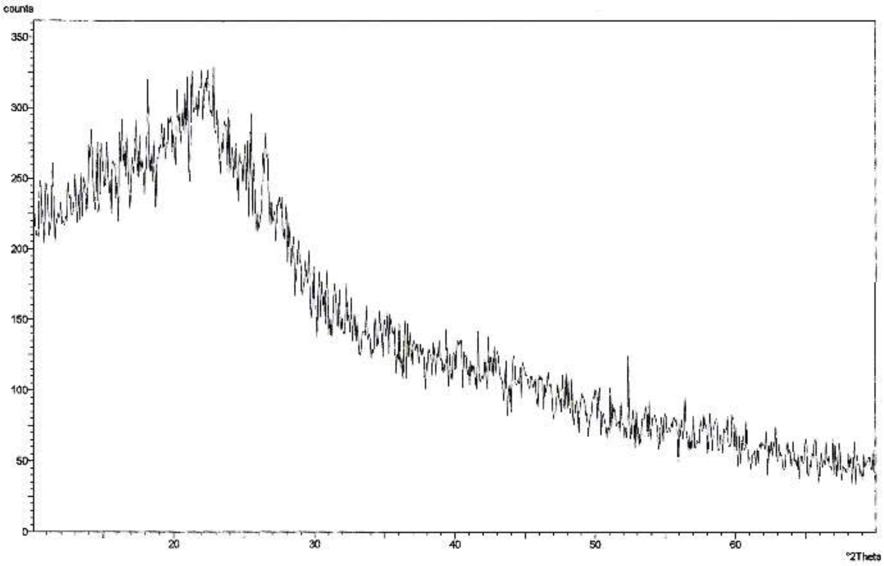

Figure 9. X-ray diffraction pattern of fluoride-treated ZIGNSC.

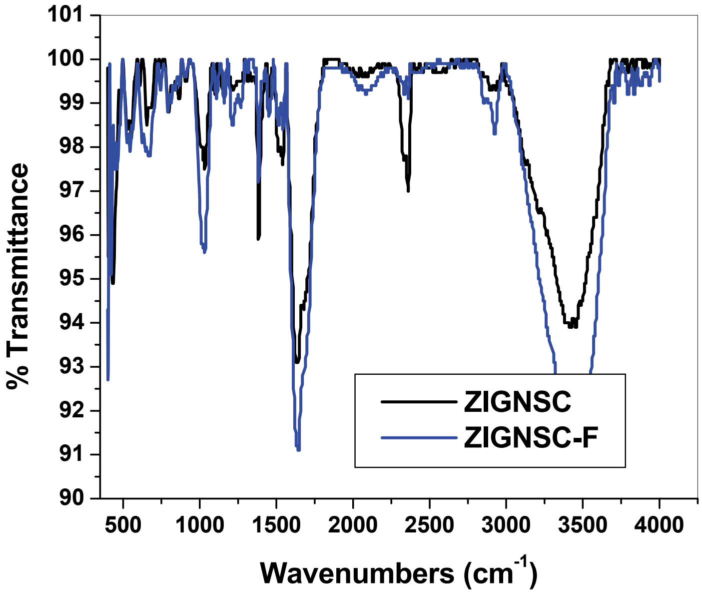

Figure 10. FTIR spectra of ZICNSC and fluoride treated ZICNSC.

correlation of the experimental data for ZIGNSC. This kinetics data would be useful for developing an appropriate technology in designing a treatment plant for fluoride rich water. XRD studies show changes in the crystalline nature of the adsorbent due to the adsorption of fluoride on its surface. The FTIR studies indicate the participation of the surface sites of the sorbent in the adsorbent interaction.

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IZVOD

PROUČAVANJE KINETIKE I RAVNOTEŽE UKLJANJANJA FLUORIDA POMOĆU UGLJENISANOG KIKIRIKIJA IMPREGNISANOG CIRKONIJUMOM(IV)

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(Naučni rad)

Ugljenisani kikiriki je impregnisan sa cirkonijum-oksihloridom, i ispitavana je njegova sposobnost adsorpcije fluorida iz vodenih rastvora. Analiza izotermnih ravnotežnih podataka Langmuir-ovom, Freundlich-o-vom i Redlich–Peterson-ovom jednačinom je pokazala da Freundlich-ova jednačina najbolje opisuje eksperimentalne rezultate. Termodinamičko proučavanje je pokazalo da je adsorpcija fluorida spontan endoteman proces kod koga se entropija povećava. Kinetika adsorpcije fluorida se može opisati reakcijom pseudo-drugog reda. Redgenska strukturna analiza je potvrdila deponovanje fluorida na materijal. Infracrvena spektroskopija (FTIR) takođe je pokazala vezivanje adsorbata za adsorpcionu površinu. Može se zaključiti da je ugljenisani kikiriki impregnisan sa cirkonijum-oksihloridom ekonomski prihvatljiv materijal za rešavanje problema uklanjanja fluorida iz voda u zemljama u razvoju.

Ključne reči: Adsorpcija • *Arachis hypogia* • Defluoridizacija • Cirkonijum

Key words: Adsorption • *Arachis hypogia* • Defluoridation • Zirconium