

Research Article

Study of Fluoride Affinity by Zirconium Impregnated Walnut Shell Carbon in Aqueous Phase: Kinetic and Isotherm Evaluation

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This paper examines the kinetics of fluoride removal from water by the adsorbent zirconium-impregnated walnut-shell carbon (ZIWSC), exploring the mechanisms involved. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH value and a better understanding of the adsorption mechanism. The presence of bicarbonate ions in aqueous solution was found to affect the fluoride removal indicating that these anions compete with the sorption of fluoride on adsorbents. The kinetic profile has been modeled using pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model. The kinetic sorption profiles offered excellent fit with pseudo-second-order model. Adsorption isotherms have been modeled by Langmuir, Freundlich, and Temkin equations, and their constants were determined. The equilibrium adsorption data were fitted reasonably well for Freundlich isotherm model. XRD and SEM patterns of the ZIWSC were recorded to get better insight into the mechanism of adsorption process.

1. Introduction

Fluoride ion exists in natural waters and it is an essential micronutrient in human in preventing dental carries and in facilitating the mineralization of hard tissues. It takes at a recommended range of concentration (1.0–1.5 mg/L). Higher level of fluoride in ground water is a huge problem in all the countries including the USA, the Asian and the African countries [1]. It has become a global issue. In India, although water resources are high, there is an acute scarcity of safe drinking water due to acceptable water quality. According to the World Health Organization (WHO), the maximum acceptable concentration of fluoride in drinking water lies below 1.5 mg/L [2]. The incidence of high fluoride content in ground water (>1.5 mg/L) is common in both shallow and deeper water bearing [3, 4]. Fluoride contamination in ground water arises both from natural causes and anthropogenic activities. Fluoride is a persistent and nondegradable poison that accumulates in soil, plants, wild life, and humans. The presence of fluoride ion in portable

water has adverse effect on human health. Fluoride is affected by positive charged calcium in teeth and bones due to its strong electronegativity, which results in dental, skeletal and nonskeletal form of fluorosis in children as well as adults [5, 6]. The dental and skeletal fluorosis is irreversible and no treatment exists. The only remedy is prevention by keeping fluoride intake within the safe limits.

The excess fluoride (>1.5 mg/L) in drinking water can be removed by various defluoridation techniques. Defluoridation technologies can be divided into following important categories, namely, chemical precipitation [7, 8], membrane processes [9], adsorption and ion exchange [10] and Nalgonda technique [11]. The adsorption process is the most commonly used technique for the fluoride removal from drinking water. The adsorption process is a widely acceptable pollution removal technique because of its ease of operation and cost-effectiveness. Large numbers of adsorbents have been studied for the removal of fluoride from water based on alumina [12], other minerals and metal oxides [13–15], clays [15–17], carbons [18], zeolites [19], agricultural

wastes [20, 21], and so forth. Though the removal of fluoride using zirconium-impregnated cashew nut shell carbon [21], zirconium-impregnated ground nut shell carbon [22] has been reported earlier, the author felt that the use of ZIWSC could definitely give a new dimension in the field of defluoridation; hence defluoridation experiments were carried out using the ZIWSC.

In this study, waste walnut shell was utilized as the raw material for the production of activation carbon, which was impregnated with zirconium oxychloride by chemical methods, and its adsorption capacity for fluoride ions was evaluated. Johns et al. [23] utilized granular activated carbon (GACs) made from walnut hull to successfully remove higher levels of benzene, toluene, methanol, acetonitrile, acetone, and 1,4-dioxane from an aqueous mixture rather than commercial GACs. The effects of contact time, dosage, solution pH, fluoride concentration, and reaction temperature on fluoride were studied in details.

2. Materials and Methods

2.1. Preparation of Activated Carbon. The walnut shell was taken from local natural resources. The materials were cleaned and dried to constant weight at room temperature and then activated as per the procedure [24]. About 100 g of the crushed walnut shell was kept for 3 hours in a low-temperature muffle furnace at 573–673 K. The carbonized material was taken out of the muffle furnace, cooled, powdered, and kept in a beaker and 200 mL of concentrated sulphuric acid was gradually added to it and the contents were stirred continuously to ensure thorough mixing. The activated carbon was then cooled and left overnight and washed free of acid and dried at 383 K for 2 hours, and then sieved using various mesh sizes. Subsequently the activated carbon was further immersed in 2 N NaOH solution and washed free of alkali, providing the desired adsorbent for impregnation.

Zirconium ion impregnation was carried out by adding 5% $ZrOCl_2$ solution with activated carbon (solution/solid ratio = 2:1) and the mixture was kept for three days at room temperature (298 K). The impregnated carbon was then filtered, rinsed to confirm the effluent free from zirconium, dried in an oven at 380 K and subsequently used for defluoridation studies. The defluoridation capacity of ZIWSC 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 by use of total ionic strength adjustment buffer (TISAB) solution to maintain pH 5 to 5.5 and to eliminate the interference effect of complexing ions [25]. Fluoride ion concentration and pH of the samples were measured by Orion ion selective electrode equipment. All the other water quality parameters were analysed by using standard methods [26].

2.2. Sorption Experiments. The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 1.5 gm 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 for the optimization of various experimental conditions like contact time, pH, initial fluoride concentration, and influence of coions with fixed dosage. Kinetic studies of sorbent were carried out in a temperature-controlled mechanical shaker. The effect of different initial fluoride concentrations, namely, 2, 4, 6, 8 and 10 mg/L at four different temperatures, namely, 303, 313, 323 and 333 K on sorption rate were studied by keeping the mass of sorbent as 1.5 gm and volume of solution as 100 mL in neutral pH. The pH at zero point charge (pH_{zpc}) of sorbent was measured using the pH drift method [27]. 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 the solution. After stabilization, the final pH was recorded. The graph of final pH versus initial pH was used to determine the zero point charge of the activated carbon.

2.3. Characterisation of Sorbents. The X-ray diffraction (XRD) pattern of the impregnated carbon was obtained using a Bruker AXS D8 Advance, Inst ID: OCPL/ARD/26-002 X-ray diffractometer. Examination of adsorption with Scanning Electron Microscope (SEM) with HITACHI-S-3400N model fitted with an energy dispersive X-ray analyzer (EDAX) allows a qualitative detection and localization of elements in the adsorption. The SEM enables a direct observation of the surface microstructures of the fresh and fluoride-adsorbed adsorbents.

3. Results and Discussion

3.1. Effect of Contact Time and Concentration. In order to determine the equilibration time for maximum adsorption of fluoride and to know the kinetics of adsorption process, the adsorption of fluoride on ZIWSC was studied as a function of contact time. It was noticed that the fluoride removal increased with the time. The adsorbent exhibited an initial gradual uptake of fluoride followed by a slower removal rate that gradually reached an equilibrium condition. Nearly 50% removal of fluoride was achieved, first 60 min of contact time and gradual increasing of removal occurred in the following 180 min. Therefore 180 minutes was fixed as minimum contact time for the maximum defluoridation of the sorbent. The results compared with the other adsorbents to get good removal [21, 22, 28].

3.2. Effect of Adsorbent Dose on the Adsorption Process. The effect of adsorbent dosage on the adsorption of fluoride for the initial concentration of 3.0 mg/L was studied. Adsorbent dosage varied from 0.5 gm to 2.50 gm. It is seen that the

adsorption increased with the increase in the dose of adsorbent. The maximum removal percentage was exhibited at a dosage of 1.5 gm adsorbent per 100 mL. Further addition of the adsorbent did not show a considerable increase in defluoridation, may be attributed to two reasons. The increase in sorbent dose at constant sorbent concentration and volume will lead to unsaturation of sorption sites through the sorption process [29, 30], and secondly may be due to particulate interaction such as aggregation resulting from high-sorbent dose [31].

3.3. Effect of pH on the Adsorption of Fluoride. The pH of the aqueous solution is an important variable, which controls the adsorption at the water-adsorbent interfaces. Therefore, the adsorption of fluoride on the ZIWSC was examined at different pH values ranging from 3 to 12. It can be seen from the investigation that fluoride removal decreases with increasing pH, and the removal of fluoride is maximum 94% (ZIWSC) and 81% (WSC) at pH 3 and is minimum 22% (ZIWSC) and 18% (WSC) at pH 12. This can be explained by the change of surface charge of the adsorbent. It is known that in highly acidic medium, the surface of adsorbent is highly protonated while it is neutralized and tended to have negative charge in alkaline medium. Therefore, high efficiency in acidic medium can be attributed to the gradual increase in attractive forces and low efficiency in alkaline medium can be explained by the repulsion between the negatively charged surface and fluoride. The pH_{zpc} of WSC and ZIWSC are 5.2 and 4.6, respectively. However the percentage of fluoride removal by ZIWSC was higher than WSC in all the pH ranges studied.

3.4. Effect of Particle Size. The defluoridation experiments were conducted using WSC with five different particle sizes, namely <53, 53–106, 106–212, 212–300, and 300–426 microns. As the adsorption process is a surface phenomenon, the defluoridation efficiency is increased with decreasing of surface of the sample due to larger surface area. Therefore, with a given mass of walnut shell, smaller particle size would increase surface area availability hence the number of sites increased. Hence the material with particle size of <53 microns has been chosen for further experiments. All the forthcoming discussion is based on the experimental result using this sample.

3.5. Assessment of Influence of Interfering Co Ions. Defluoridation studies of ZIWSC were carried out in the presence of common ions like sulphate, chloride, bicarbonate, and nitrate, which are normally present in water, was experimentally verified. The concentration of coexisting ions was varied from 50 mg/L to 500 mg/L with an initial fluoride concentration of 10 mg/L at neutral pH. It was inferred that there was no remarkable influence on the removal of fluoride in presence of Cl^- , SO_4^{2-} , and nitrate. However, the presence of bicarbonate ion resulted in the decrease of percentage from 85.67% to 54.94%. This may be due to the competition of bicarbonate ions with fluoride for sorption sites. Similar trend

was reported while studying montmorillonite as a sorbent for fluoride removal [32].

3.6. Adsorption Isotherms. The isotherm deals with relationship between the equilibrium amount of fluoride on the adsorbent and the solute concentration in solution. The fluoride sorption capacity of ZIWSC was evaluated using three different isotherms, namely Langmuir [33], Freundlich [34], and Temkin [35] isotherms.

The Langmuir isotherm model assumes that adsorption sites are energetically the same with monolayer formation and is generally expressed as

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q}. \quad (1)$$

A plot of C_e/q_e against C_e should yield a straight line with Q and b obtained from the intercept and the slope. The value Q is 3.53 mg/g and Langmuir constant b is 3.11 (L/mg). The results are summarized in Table 1.

The essential characteristics of the Langmuir isotherms can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R , which is defined as [36]

$$R = \frac{1}{(1 + bC_0)}, \quad (2)$$

where C_0 is the initial fluoride concentration and b is the Langmuir isotherm constant. The feasibility criteria of the process can be judged from R values as follows:

Value	Type
$R > 1$	unfavorable,
$R = 0$	irreversible,
$0 < R < 1$	favorable,
$R = 1$	linear.

The R values in Table 2 are also indicating favorable sorption of fluoride on to the adsorbent.

The Freundlich adsorption isotherm equation can be represented as follows:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e. \quad (3)$$

A plot of $\ln q_e$ against $\ln C_e$ should yield a straight line with slope $1/n$ and intercept $\ln K_f$. It is found that the related correlation coefficient r^2 value for the Freundlich models is 0.982.

Another equation used in the analysis of isotherm was the Temkin model is given as

$$q_e = B_1 \ln K_T + B_1 \ln C_e, \quad (4)$$

where $B_1 = RT/b$.

Temkin sorption contains a factor that explicitly takes into the account adsorption species and adsorbent interaction. The heat of adsorption of all the molecules in the layer would

decrease linearly with coverage due to adsorbate/adsorbate interaction [37]. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent and adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energy [38]. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and intercept, respectively. K_T is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, and the constant B_1 is related to the heat of adsorption. A linear relationship between q_e and $\ln C_e$ indicates the applicability of this model to understand the adsorption mechanism. Temkin isotherm for the adsorption of fluoride and the corresponding constant are represented in Table 1. The higher r^2 values Freundlich of over Langmuir and Temkin isotherm indicated the suitability of Freundlich isotherm than the Langmuir and Temkin isotherm.

3.7. Thermodynamic Investigations. The effect of temperature has a major influence in the sorption process and hence the sorption of ZICNSC was monitored at four different temperatures 303, 313, 323, and 333 K under the optimized condition and thermodynamic parameters, namely, standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated [39, 40] and presented in Table 3. 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. Its also indicates the increased disorder in the system with changes in the hydration of adsorbing fluoride ions [41].

3.8. Adsorption Kinetics. The adsorption kinetics was studied with initial fluoride concentration 2, 4, 6, 8, and 10 mg/L. The kinetics analysis of adsorption data is based on reaction kinetics of pseudo-first and pseudo-second-order mechanisms. The uptake of fluoride on zirconium impregnated adsorbent occurred rapidly, and reached equilibrium within 180 min. The kinetics of adsorption was analyzed by using different rate equation. A pseudo-first-order rate expression or the Lagergren rate equation [42] is expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (5)$$

where q_e and q_t are the fluoride on adsorbent (mg g^{-1}) at equilibrium and at time t , respectively, and k_1 (min^{-1}) is first-order rate constant. A plot of $\ln(q_e - q_t)$ against time (t) should yield a straight line and the rate constant k_1 is evaluated from the slope.

The linear form of pseudo-second-order expression [43], is expressed as

$$\frac{t}{q_t} = \left(\frac{1}{k_2}\right) \left(\frac{1}{q_e^2}\right) + \frac{t}{q_e}. \quad (6)$$

k_2 can be determined by plotting t/q_t against t of (6) gives the straight line with higher correlation coefficient r^2

values, which is higher than that observed with pseudo-first-order model indicating the applicability of the pseudo-second-order model and the values are shown in Table 4. From the model, the values of q_e increased with increase in initial concentration and it also increased with increasing in Temperature. The values of rate constant (k) have also increased with temperature indicating chemisorptions.

The adsorption process believed to follow a complex phenomenon is accompanied by both the surface and the pore diffusion, but to different extents. The extend of a particular diffusion to the total process may be estimated by a plot following the Weber and Morris equation [44] which is expressed as

$$q_t = K_d \sqrt{t}, \quad (7)$$

where K_d , the date of pore diffusion, is obtained from the slope of the linear portion of the q_t versus \sqrt{t} . The Weber and Morris plot reveals an initial curved portion (indicating of boundary layer effect, that is, surface adherence) followed by the linear portion yields (indicating of intraparticle or pore diffusion). The slope of the linear portion yields the K_d value, while intercept of the plot signifies the extent of the boundary layer effect. The larger the intercept, the greater is the contribution of the surface adherence [45, 46] in the rate limiting steps. It is found that K_d value increases with increased concentration and in lower temperature (Table 4).

3.9. Mechanism of Fluoride Sorption. The fluoride removal by ZIWSC was governed by adsorption mechanism. The surface acquired positive charge at lower pH values and hence the 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. As the pH is increased slowly, the surface acquired negative charges, physisorption dominated and hence percentage removal of fluoride was decreased. The slight enhancement of fluoride removal by ZIWSC over WSC may be due to sorption by Zirconium, adsorption by physical forces and fluoride ion, a Lewis base, coordinates strongly with the Zirconium species adsorbed on WSC, which are Lewis acid sites:



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

3.10. Desorption and Reuse Potential. Any adsorbent is economically viable if the adsorbent can be regenerated and reused in many cycles of operation. For checking the desorption capacity of the sorbent, the material was subjected to an adsorption at an initial fluoride concentration of 3 mg/L. The exhausted ZIWSC was regenerated using HCl and NaOH. NaOH is better regenerated than HCl. The concentrations were ranging from 0% to 10%. At 2.5% NaOH concentration, ZIWSC had desorbed almost 96.2% of fluoride. To test

TABLE 1: Linear isotherm parameters of fluoride adsorption on ZIWSC.

Temp (K)	Langmuir isotherm			Freundlich parameters			Redlich parameters		
	Q (mg/g)	b (L/g)	r^2	K_f (mg/g)	1/n	r^2	K_T (L/mol)	B_1	r^2
303	3.19	2.33	0.963	0.648	0.944	0.982	3.88	8.75	0.965
313	3.01	2.62	0.954	0.590	0.932	0.983	7.12	4.20	0.963
323	3.22	2.74	0.965	0.595	0.953	0.983	4.29	7.19	0.966
333	3.53	3.11	0.919	0.643	0.944	0.980	7.76	6.85	0.964

TABLE 2: R_L values at different temperature.

S. No.	Conc. F^- (mg/L)	303 K	313 K	323 K	333 K
1	2	0.1766	0.1602	0.1543	0.1382
2	4	0.0969	0.0871	0.0836	0.0742
3	6	0.0667	0.0598	0.0573	0.0507
4	8	0.0509	0.0455	0.0436	0.0385
5	10	0.0411	0.0367	0.0352	0.0311

TABLE 3: Thermodynamic Parameters for Adsorption of fluoride onto ZIWSC.

S. No.	Thermodynamic parameters	Temperature (K)	Values
1	ΔG (kJ mol ⁻¹)	303	-0.9282
		313	-1.0545
		323	-1.1043
		333	-1.2394
2	ΔH (kJ mol ⁻¹)		3.3157
3	ΔS (J mol ⁻¹ K ⁻¹)		14.0131

the adsorption potential of regenerated ZIWSC, two more cycles of adsorption-desorption studies were carried out by maintaining the initial conditions the same. In third cycle, the adsorbent capacity has shown 28.00%. However, in the fourth cycle, adsorption capacity was observed as 5%. More tests have to be conducted to determine the exact life cycle of the adsorbent.

3.11. Field Study. In order to gain the practical utility of the studied carbonaceous adsorbents, batch studies were performed to evaluate their viability for real field application. The samples from fluorosis affected areas of Tirunelveli district, India having higher concentrations of fluoride were collected and adsorption studies were performed (adsorbent: 1.5 g; temperature: 303 K; agitation: 200 rpm; pH: 7). The consolidated experimental results for all the water samples studied with the function of adsorbents are depicted in Table 5. The sorption data phenomena were found to be dependent on the concentration of fluoride in the water sample used. It has been observed that all the water quality parameters show marked improvement.

3.12. Instrumental Studies. For understanding the nature of fluoride sorption X-ray and FTIR studies were performed

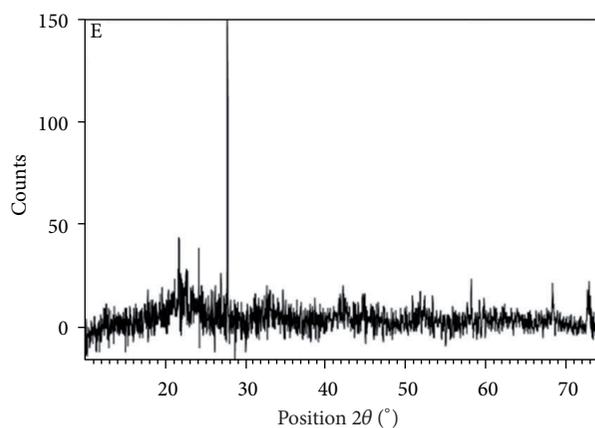


FIGURE 1: X-ray diffraction pattern of ZIWSC.

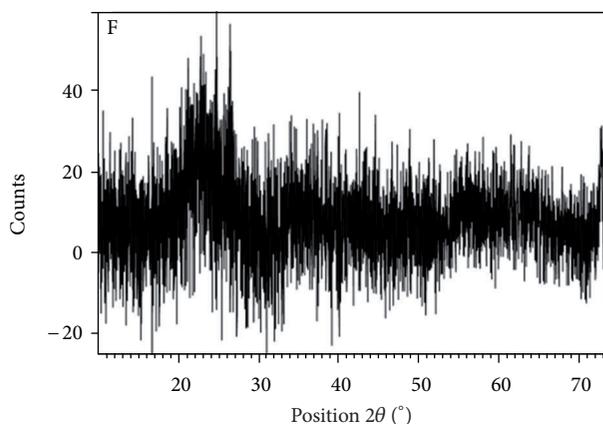


FIGURE 2: X-ray diffraction pattern of fluoride adsorbed on ZIWSC.

using the raw and treated adsorbents. Powder X-ray diffraction was carried out on the raw and fluoride treated ZIWSC samples. The XRD patterns for treated adsorbents showed significant changes. The XRD data of the treated ZIWSC provided evidence of slight modification over the crystal cleavages. The intensity of the peak due to the hkl plane 010 of the monoclinic crystal system of ZIWSC disappeared after the fluoride adsorption on its surface. This is possible due to the lattice dislocation in the crystal system. The X-ray diffraction patterns of raw and fluoride treated material are given in Figures 1 and 2.

The surface condition and the existence of fluoride onto ZIWSC were confirmed by the SEM with EDAX analysis.

TABLE 4: Kinetic parameters of values of ZIWSC.

F^- (mg/L)	Pseudo-First order			Pseudo-Second order			Intraparticle diffusion	
	K_1 (min^{-1})	q_e (mg/g)	r^2	K_2 (g/mg min)	q_e (mg/g)	r^2	K_d (min^{-1})	r^2
2	0.0154	0.905	0.991	0.0188	1.34	0.998	0.79	0.975
4	0.0138	1.159	0.959	0.0094	2.72	0.996	1.60	0.972
6	0.0161	1.481	0.983	0.0066	4.15	0.998	2.47	0.971
8	0.0145	1.421	0.994	0.0073	5.32	0.999	3.30	0.956
10	0.0156	1.366	0.952	0.0104	6.38	0.999	4.11	0.933

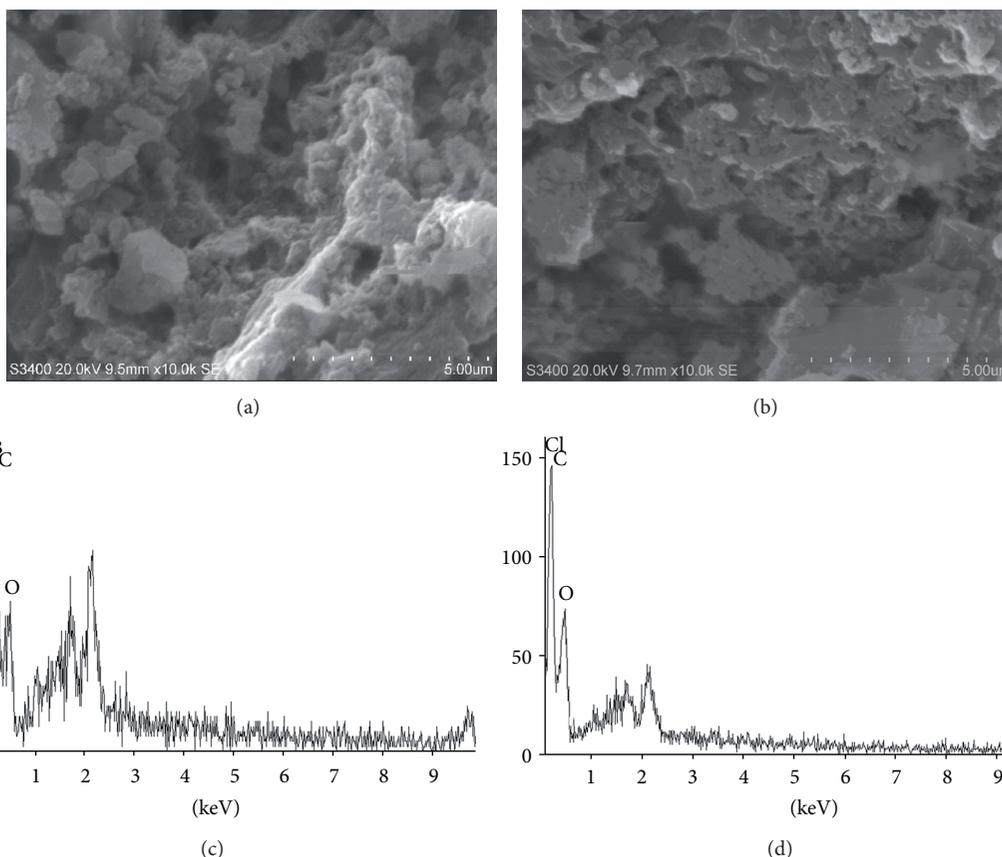


FIGURE 3: SEM images of (a) ZIWSC and (b) fluoride-sorbed ZIWSC, and EDAX spectra of (c) ZIWSC and (d) fluoride-sorbed ZIWSC.

TABLE 5: Field trial results of ZIWSC.

Water quality parameters	Before treatment	After treatment
F^- (mg/L)	3.6	0.53
pH	8.1	7.1
EC (mmho/cm^2)	4.16	1.44
Cl^- (mg/L)	463	222
TH (mg/L)	496	201
TA (mg/L)	467	212

Figures 3(a) and 3(b) show the SEM images before and after fluoride sorption with ZIWSC. The changes in the surface morphology of adsorption before and after fluoride treatment indicate fluoride sorption on ZIWSC. The EDAX

spectrum of ZIWSC confirms the elements present in it and is shown in Figure 3(c). The presence of a fluoride peak in the EDAX spectra of fluoride-sorbed ZIWSC confirms the fluoride sorption onto ZIWSC, which is shown in Figure 3(d).

4. Conclusions

The impregnated walnut shell acts as a reasonably good adsorbent for the removal of fluoride from aqueous solution. The optimum pH for removal was found to be 3.0, at which fluoride removal was 94%. The removal increased with the increase in the adsorbate concentration. An increasing equilibrium adsorption capacity with the rise in temperature indicated that the nature of adsorption process is endothermic, which is further supported by the thermodynamic parameters calculated from the Langmuir isotherm at various

temperatures. The adsorption process was found to follow the Freundlich adsorption isotherm model and Pseudo-second-order. Compared to the various other sorbents reported in the literature, the impregnated walnut shell in this study shows very good promise for practical applicability. However, more studies are needed to optimize the system from the regeneration point of view and to investigate the economic aspects.

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