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Development of a novel nano-biosorbent for the removal of fluoride from water



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ABSTRACT

The study was designed to investigate the use of two sorbents namely (i) Fe₃O₄ nanoparticles immobilized in sodium alginate matrix (FNPSA) and (ii) Fe₃O₄ nanoparticles and saponified orange peel residue immobilized in sodium alginate matrix (FNPSOPR) as sorbents for fluoride removal from contaminated water. The synthesized nanoparticles were analyzed and characterized by dynamic light scattering, X-ray diffraction, vibrating sample magnetometry, and scanning electron microscopy with energy dispersive X-ray spectroscopy and Fourier transform-infrared spectrometry. The sorbent matrices were prepared in the form of beads and surface functionalized to enable enhanced sorption of fluoride ions. Batch sorption studies were carried out and the sorption isotherm and reaction kinetics were analyzed. Both the sorbents followed Langmuir model of isotherm and fitted well with Pseudo first order reaction. The maximum sorption capacity exhibited by FNPSA and FNPSOPR was 58.24 mg·g⁻¹ and 80.33 mg·g⁻¹ respectively. Five sorption–desorption cycles exhibited 100%, 97.56%, 94.53%, 83.21%, and 76.53% of regeneration of FNPSOPR. Accordingly, it is demonstrated that FNPSOPR could be used as a promising sorbent for easy and efficient removal of fluoride from contaminated water with good reusability. The current work suggests a simple and effective method to remove fluoride from contaminated water.

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1. Introduction

Fluoride is a fairly common element in nature and a highly reactive member of the halogen family. It accounts for about 0.3 g·kg⁻¹ of the earth's crust and exists in the form of fluorides in a number of minerals, such as fluorspar, cryolite, and fluorapatite. There are several investigations mentioning the pathological effects of water fluoridation and other portable water contaminants, but a slew of new scientific findings has sparked even more curiosity on fluoride research than ever before. With the increase in industrialization and commercial activities, water bodies increasingly contaminated with fluoride has become a matter of gravid issue [1].

Fluoride contamination in the portable water has been recognized as a serious problem throughout the world [2]. WHO allows a maximum concentration of 1.5 mg·L⁻¹ as the permissible limit for fluoride in drinking [3]. When ingested in minor quantities, fluoride is said to prevent dental caries in children [4]. Beyond the permissible concentration fluoride is known to cause various diseases like fluorosis (dental and skeletal), brittleness of bones, osteoporosis, arthritis, brain damage, Alzheimer's syndrome, thyroid disorder, and cancer. [5,6]. Hence, it becomes necessary to remove the redundant fluoride from the contaminated water in order to improve the quality of life. Several methods to remove fluoride from drinking and ground water have been in practice,

namely, coagulation and precipitation, ion exchange, reverse osmosis, electrodialysis, nanofiltration and adsorption [7]. Conventional techniques have several demerits which include high operational costs, metal poisoning, wastage of raw water, high pH dependence and require periodic regeneration and skilled labor. The easy and simple working conditions, low cost and flexibility allow adsorption technique to be widely used in fluoride removal [8].

As the conventional methods pose some drawbacks, an alternative strategy to improve the efficiency of fluoride removal is required. The use of magnetic iron oxide nanoparticles (MIONS) has been extensively studied by several investigators for various applications, especially for the removal of contaminants in ground water and waste water [9,10]. They have also been exploited in the detection of fluoride ions from water samples [11]. The other forms of iron oxide and hydroxide nanoparticles used in fluoride removal are nano goethite (α-FeOOH) [12] nano iron oxide hydroxide [13], polypyrrole/Fe₃O₄ magnetic nanocomposite [14], mixed nano iron oxide powder containing goethite (α-FeOOH), hematite (α-Fe₂O₃), and ferrihydrite (Fe₅H₈·4H₂O) [15].

Biosorption, an emerging technique for the removal of contaminants, is being exploited in drinking and waste water treatment. Chitin, chitosan, lanthanum incorporated chitosan, chitosan coated silica, carboxylated, chelated chitosan biosorbent beads etc. have been used in biosorption for the effective removal of fluoride. Metal loaded saponified orange juice residue has been reported to adsorb fluoride from the aqueous phase [16]. Although calcium alginate is a cheap and easily available biosorbent, its use in fluoride removal is limited because of the anionic nature. However surface modifications on calcium alginate may

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allow effective removal of fluoride ions from water. Hence, this study aims at a new strategy to remove fluoride using two biosorbent models: Fe_3O_4 nanoparticles immobilized in calcium alginate matrix and a combination of Saponified orange peel residue and Fe_3O_4 nanoparticles immobilized in the calcium alginate matrix. In order to enhance the adsorption capacity of the biosorbent matrices, the surface was modified by cross linking with glutaraldehyde followed by carboxylation with chloroacetic acid after which Fe^{3+} ions were loaded. Further, the adsorption capacities, isotherm and kinetic modeling of the aforementioned sorbent matrices, upon fluoride adsorption from aqueous phase were also checked.

2. Materials and Methods

2.1. Sorbent preparation

2.1.1. Preparation of Fe_3O_4 nanoparticles

Iron oxide (Fe_3O_4) nanoparticles were synthesized by the modified co-precipitation method adopted by Thapa *et al.* For this purpose, $0.7 \text{ mol} \cdot \text{L}^{-1}$ ammonia solution was added drop wise to 1% FeCl_3 solution, at 80°C , until the development of a black precipitate. The precipitate obtained was then washed thoroughly with Millipore water, until neutral pH and freeze dried for further use [17].

2.1.2. Preparation of Fe_3O_4 nanoparticles immobilized biosorbent (FNPSA)

0.5 g of ultra-sonicated Fe_3O_4 nanoparticle was dispersed in 1.5% sodium alginate solution to obtain a magnetic alginate solution mixture. This solution mixture was stirred well until a uniform black suspension was obtained. Magnetic calcium alginate beads were prepared by adding the black suspension drop wise into 2% CaCl_2 solution using a syringe with 0.45 mm gauge and were allowed to stabilize for 24 h. The nano-biosorbent thus obtained was washed well with Millipore water to remove the excess CaCl_2 solution and further surface functionalized [18].

2.1.3. Preparation of saponified orange peel residue (SOPR)

The saponified orange peel residue (SOPR) was prepared as described by Paudyal *et al.* [16]. Orange peels were bought from a local fruit shop in Vellore, Tamil Nadu. The orange peels were initially rinsed with 2% NaCl to clean the surfaces. 100 g of the peels was crushed along with 8 g of calcium hydroxide in a domestic juice mixer. The contents were transferred to another beaker and after adding adequate amount of water, the suspension was allowed to saponify overnight in an orbital shaker at $120 \text{ r} \cdot \text{min}^{-1}$ [16]. The suspension was filtered and the saponified residue was rinsed until neutral pH with Millipore water, and the cake was dried in an oven at 50°C to obtain dry SOPR, which was then powdered and further processed.

2.1.4. Preparation of Fe_3O_4 nanoparticles immobilized biosorbent (FNPSOPR)

Equal amounts of ultra-sonicated Fe_3O_4 nanoparticles and SOPR were added to 1.5% sodium alginate solution and blended well until a uniform suspension was formed. Stabilized magnetic SOPR beads were formed by adding the suspension drop wise into 2% CaCl_2 using a 0.45 mm gauge syringe and allowing it to polymerize overnight. The nano-biosorbent thus formed was washed the next day and further surface functionalized [18].

2.2. Functionalization/surface modification

The sorbent (sodium alginate) as well as the sorbate (Fluoride ions) are anionic in nature. Hence, to enable alginate to adsorb more fluoride ions, it requires surface modification with more active functional groups. The surface of sodium alginate has been functionalized/modified in 3 following steps: (i) cross linking with glutaraldehyde for 20 h. (ii) carboxylation with chloroacetic acid for 10 h. (iii) loading with FeCl_3 for 24 h. The sorbent was washed well after each step with

Millipore water to remove any excess and unbound components [19]. The functionalized sorbents were further dried completely and then used for fluoride adsorption studies.

2.3. Batch studies

Fluoride stock solution of $1000 \text{ mg} \cdot \text{L}^{-1}$ was prepared and was used to carry out the batch sorption experiments. The sorption studies were carried out in 250 ml Erlenmeyer flasks with a reaction volume of 50 ml. The parameters like contact time, pH, sorbent dosage, initial fluoride concentration and temperature were studied. The flasks containing the synthetic fluoride solution along with a specified amount of sorbent were kept in an orbital shaker at $120 \text{ r} \cdot \text{min}^{-1}$ and fluoride ion concentrations were noted at an interval of every 10 min using fluoride ion selective electrode (EUTECH). Adsorption isotherm and kinetics were also studied.

2.4. Adsorption isotherm

Batch adsorption studies were carried out for the two developed sorbents, FNPSA and FNPSOPR at optimized conditions. Fluoride concentrations ranging from 10 to $70 \text{ mg} \cdot \text{L}^{-1}$ and 10 to $60 \text{ mg} \cdot \text{L}^{-1}$ were used for FNPSA at pH 5.0 and FNPSOPR at pH 7.0 respectively. 50 ml of the synthetic fluoride ion solution was agitated in an orbital shaker at $120 \text{ r} \cdot \text{min}^{-1}$ with the optimized concentration of the sorbents. After the contact time of 40 min, the amount of fluoride adsorbed by the sorbents was determined. The isotherm studies were carried out at 33°C for FNPSA and 30°C for FNPSOPR. Commonly used adsorption isotherm models, Langmuir and Freundlich were applied to study the possible means of interaction between fluoride ions and the developed sorbents.

The interaction of sorbate with the sorbent at equilibrium is well explained by the adsorption isotherms. Batch adsorption studies were carried out for FNPSA and FNPSOPR independently in their respective optimal conditions. The linear form of Langmuir model is expressed by the equation [24]:

$$C_e/q_e = (1/q_0b) + C_e/q_0 \quad (1)$$

where C_e is the residual fluoride concentration at equilibrium, q_e is the fluoride concentration adsorbed on the sorbent at equilibrium, q_0 is the maximum fluoride concentration and b is the Langmuir constant. The sorption capacity of the sorbent can be explained by a plot of C_e/q_e versus C_e theoretically.

The linearized Freundlich isotherm can be represented as [24]:

$$\lg q_e = \lg(K_f) + \lg C_e/n \quad (2)$$

where q_e is the amount of fluoride adsorbed at equilibrium, K_f is the Freundlich constant, C_e is the residual fluoride concentration in solution, and n stands for adsorption intensity. K_f and n values are obtained from plots of $\lg q_e$ versus $\lg C_e$. Higher sorption capacity corresponds to a higher K_f value.

2.5. Adsorption kinetics

Synthetic fluoride solutions of different concentrations 10, 20, 30 and $40 \text{ mg} \cdot \text{L}^{-1}$ were considered to study the adsorption kinetics. A volume of 50 ml of fluoride solution, with an optimized concentration of FNPSA and FNPSOPR at pH 5.0 and 7.0 respectively was agitated at a speed of $120 \text{ r} \cdot \text{min}^{-1}$ in an orbital shaker. At the equilibrium contact time, the concentrations of fluoride adsorbed by the sorbents were determined. Lagergren's pseudo first order and pseudo second order models were applied to the kinetic sorption data to find out the model with the best fit.

Adsorption kinetics of this reaction in particular, describes the rate at which fluoride gets adsorbed to the sorbent surface. The adsorption efficiency is calculated as the amount of fluoride ions adsorbed by a unit of the sorbent. Lagergren's pseudo first order reaction can be written as [25]

$$\lg(q_e - q_t) = \lg q_e - (k_1/2.303)t \quad (3)$$

where q_e and q_t are the amount of fluoride adsorbed at equilibrium and at time t and k_1 is the pseudo first order rate constant. The plot of $\lg(q_e - q_t)$ vs. t gives the linear relationship with which the constant k_1 is determined, if pseudo first order is applicable.

Lagergren's pseudo second order reaction can be represented by the following equation [26]:

$$dq_t/dt = k_2(q_e - q_t)^2 \longrightarrow t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (4)$$

where q_e and q_t are the amount of fluoride adsorbed at equilibrium and at time t and k_2 is the pseudo second order rate constant. The equation can be rearranged as

$$1/(q_e - q_t) = (1/q_e) + k_2 t \quad (5)$$

The plot of $1/(q_e - q_t)$ vs. t gives a linear relationship with which the constant k_2 is determined, if pseudo second order is applicable.

2.6. Characterization of sorbents

The Fe_3O_4 nanoparticles synthesized by the chemical co-precipitation method were characterized by XRD (BRUKER, Germany), DLS (Malvern Instruments Ltd, UK), HR-SEM with EDX (FEI Quanta 200 F, Netherland), VSM (ADE Magnetics) and FT-IR (AVATAR 330). The sorbents FNPSA and FNPSOPR were then subjected to HR-SEM and FT-IR to confirm the adsorption of fluoride onto the sorbent.

2.6.1. X-ray diffraction analysis (XRD)

The nanoparticles in the polycrystalline state were freeze dried and subjected to powder XRD analysis. The analysis was performed at room temperature to confirm the phase purity of the nanoparticles. From the spectra obtained, the lattice structure of the particles was predicted using the Origin 7.0 software.

2.6.2. Dynamic light scattering (DLS)

Dynamic light scattering was carried out to measure the hydrodynamic size of the particles. The Fe_3O_4 nanoparticles were ultrasonicated and diluted with deionized Milli Q water prior to the particle size analysis. The zeta potential of the particles was carried out to measure the stability of the nanoparticles.

2.6.3. High resolution-scanning electron microscopy with energy dispersive X-ray spectroscopy (HR-SEM/EDX)

Fe_3O_4 nanoparticles were subjected to HR-SEM analysis. The samples were gold sputtered to prevent any damage in the vacuum environment and also to increase the electrical conductivity. HR-SEM is used to measure the average size of the Fe_3O_4 nanoparticles and to analyze the surface morphology of the un-interacted and fluoride interacted sorbents. The elemental analysis of the nanoparticles was done using energy dispersive X-ray spectroscopy (EDX).

2.6.4. Vibrating sample magnetometry (VSM)

The magnetic property of the Fe_3O_4 nanoparticles and the sorbents FNPSA and FNPSOPR was measured by the vibrating sample magnetometer. 30 mg of the powdered sorbents were loaded into the instrument and the readings were recorded.

2.6.5. Fourier transform-infrared spectrometry (FT-IR)

The chemical characteristics of the sorbent surface were analyzed using Fourier transform-infrared spectrometer. The un-interacted and fluoride interacted sorbents were crushed with KBr to form a fine mixture which is pressed to form pellets. These pellets were used to record the spectra from 4000 to 400 cm^{-1} .

2.7. Statistical analysis

The batch adsorption experiments were carried out in triplicates and the statistical analysis of the data was done by one way ANOVA with Tukey's multiple comparison test using Graph Pad Prism 5.0 software.

3. Results and Discussion

3.1. Characterization of Fe_3O_4 nanoparticles

The Fe_3O_4 nanoparticles synthesized by chemical co-precipitation, was analyzed using dynamic light scattering and the hydrodynamic size of the particles was found to be $\sim 140\text{ nm}$ [Fig. 1(a)]. The zeta potential value was determined to be -31.9 mV [Fig. 1(b)]. This may be attributed to the tendency of the Fe_3O_4 nanoparticles to aggregate in response to the gravitational force. XRD reveals that the Fe_3O_4 crystals were cubic in shape and Fe_3O_4 phase purity was observed [Fig. 1(c)]. The VSM results reveal that the particles are superparamagnetic in nature with a coercivity of 70.541 Oe [Fig. 1(d)]. Since the particles were oxides, they appeared agglomerated in the SEM images. The average particle size analyzed by SEM analysis reveals that a maximum of particles are in an average range of approximately 21 nm [Fig. 1(e)]. Fe and O peaks in the EDX pattern confirm the formation of iron oxide particles [Fig. 1(f)]. From these results it is inferred that the nanoparticles synthesized were Fe_3O_4 crystals of approximately 21 nm and belonged to the soft magnet category.

3.2. Batch studies

3.2.1. Effect of contact time

The effect of contact time on the fluoride sorption capacity of FNPSA and FNPSOPR was studied to find out the minimal time required for maximum sorption of fluoride. The sorption capacity of FNPSA increased to $22.7\text{ mg}\cdot\text{g}^{-1}$ during the first 10 min and reached a maximum of $35.05\text{ mg}\cdot\text{g}^{-1}$ at 40 min. After 40 min there was no significant increase ($P < 0.05$) in the sorption capacity due to equilibrium sorption. The sorption capacity of FNPSOPR was $46.66\text{ mg}\cdot\text{g}^{-1}$ at 10 min and as time increased from 10 to 40 min it increased from 46.66 to $80.33\text{ mg}\cdot\text{g}^{-1}$. No significant increase ($P < 0.05$) in sorption capacity was observed for FNPSOPR after 40 min. The equilibrium sorption time of 40 min was the optimized contact time for further studies [Fig. 2(a)]. The increase in sorption capacity up to 40 min could be attributed to the availability of free active sites for fluoride ions on the sorbent surface. The saturation observed after 40 min could be related to the non-availability of the active sites on the sorbent surface. FNPSOPR exhibited a higher sorption capacity ($80.33\text{ mg}\cdot\text{g}^{-1}$) compared to FNPSA ($35.05\text{ mg}\cdot\text{g}^{-1}$) at 40 min. Similar studies were reported on the usage of geomaterials like lateritic ores, chromite overburden and Fe (III) loaded carboxylated chitosan beads as effective biosorbents on fluoride removal from aqueous solutions [19,20].

3.2.2. Effect of pH

Sorption of fluoride by the sorbents from the aqueous phase is pH dependant. At pH 5.0, FNPSA had a maximum sorption capacity of $35.07\text{ mg}\cdot\text{g}^{-1}$ and the sorption capacity decreased with increase in pH to 9. The sorption capacity increased from $57.58\text{ mg}\cdot\text{g}^{-1}$ to $80.33\text{ mg}\cdot\text{g}^{-1}$ as the pH increased from 5.0 to 7.0 and then decreased

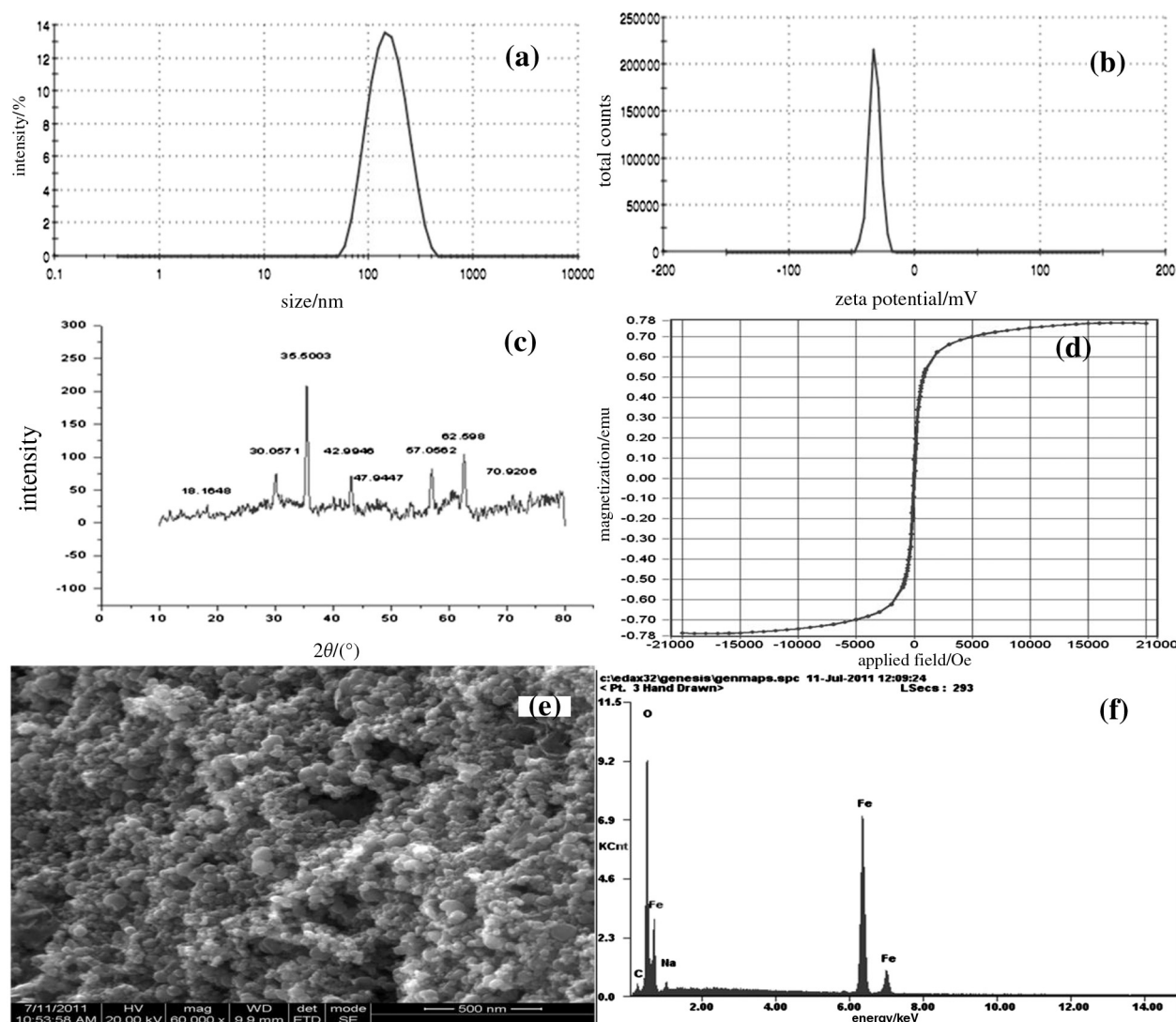


Fig. 1. Characterization of Fe_3O_4 nanoparticles. (a) Particle size measurement by DLS, (b) zeta potential, (c) XRD, (d) vibrating sample magnetometry, (e) scanning electron microscope image, (f) EDAX pattern of the Fe_3O_4 nanoparticles.

as the pH increased any further. FNPSOPR showed a sorption capacity of $80.33 \text{ mg} \cdot \text{g}^{-1}$ at pH 7.0 [Fig. 2(b)]. The influence of pH on the fluoride sorption capacity of FNPSA and FNPSOPR is shown in Fig. 1(b). This phenomena demonstrated by the two sorbents could be mainly because of the competition by excessive hydroxyl ions in alkaline pH for the active binding sites on the sorbent surface. The effect of pH on the fluoride adsorption capacity of chemically modified bentonite clay investigated by Kamble *et al.* is in complete agreement with the results obtained in our study [21].

3.2.3. Effect of sorbent dosage

The effect of sorbent concentration on the fluoride sorption capacity of FNPSA and FNPSOPR was studied by using different sorbent concentrations ranging from 0.25 to $1.5 \text{ g} \cdot \text{L}^{-1}$. The sorption capacity of FNPSA was $45.74 \text{ mg} \cdot \text{g}^{-1}$ at sorbent concentration of $0.25 \text{ g} \cdot \text{L}^{-1}$, and gradually decreased with further increase in sorbent concentration. FNPSOPR exhibited a maximum sorption capacity of $80.33 \text{ mg} \cdot \text{g}^{-1}$ at sorbent concentration of $0.25 \text{ g} \cdot \text{L}^{-1}$. Maximum fluoride sorption occurred when $0.25 \text{ g} \cdot \text{L}^{-1}$ of sorbent was used for both the sorbents and exhibited a decreasing trend in sorption capacity with gradual increase in the sorbent dosage [Fig. 2(c)]. The high sorption capacity at a low sorbent dosage could be ascribed to the excessive availability of active

sorption sites on the sorbent surface. The decrease in the sorption capacity with increase in the sorbent concentration can be attributed to the excess available sorbents for sorption after equilibrium fluoride adsorption. Satish *et al.* observed a similar pattern of adsorption, while studying the kinetics and thermodynamics of water defluoridation using biosorbents [22].

3.2.4. Effect of temperature

Batch sorption at various temperatures ranging from 25 to 40°C was carried out to study the effect of temperature on fluoride sorption onto FNPSA and FNPSOPR. FNPSA exhibited a slight decrease in sorption capacity with increase in temperature from 25°C to 30°C . However, a maximum sorption capacity of $58.24 \text{ mg} \cdot \text{g}^{-1}$ was observed at 33°C . Fluoride sorption capacity of FNPSOPR increased from $34.5 \text{ mg} \cdot \text{g}^{-1}$ at 25°C to $80.33 \text{ mg} \cdot \text{g}^{-1}$ at 30°C and then decreased with further increase in temperature. Therefore the optimized temperature for FNPSA and FNPSOPR was found to be 33°C and 30°C respectively as shown in the [Fig. 2(d)]. The decrease in sorption capacity may be attributed to the fact that, temperatures above the optimum level, favors the escaping tendency of the fluoride ions from the interfaces on the sorbent surface [20].

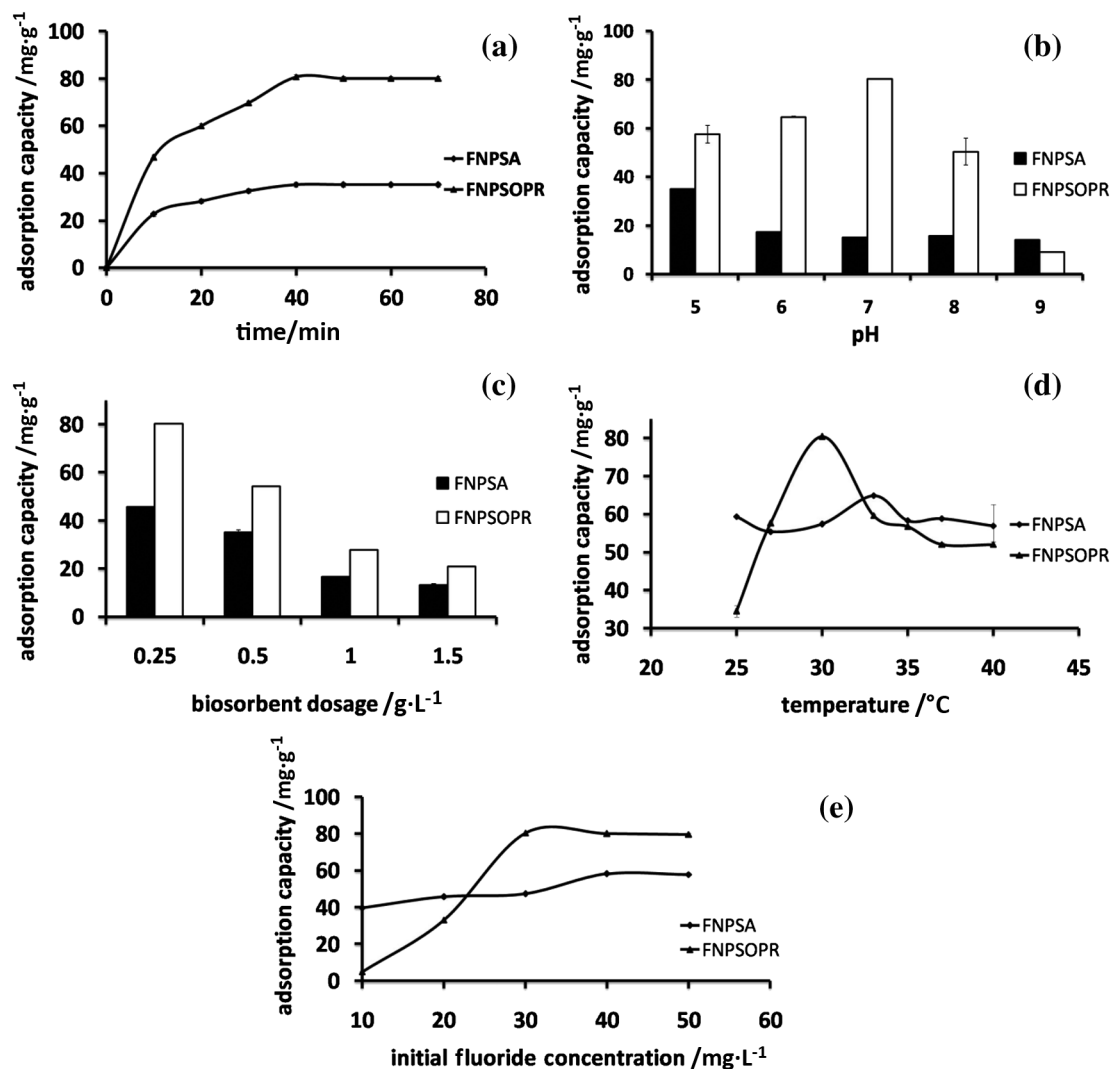


Fig. 2. The plot of sorption capacities at various parameters (a) time, (b) pH, (c) biosorbent dosage, (d) initial fluoride concentration, (e) temperature.

3.2.5. Effect of Initial fluoride concentration

The effect of initial fluoride concentration on the fluoride sorption capacity of FNPSA and FNPSOPR was studied using increasing concentrations of fluoride (10–50 mg·L⁻¹). FNPSA demonstrated an increase in sorption capacity of 39.64 mg·g⁻¹ to 58.24 mg·g⁻¹ with an increase in initial fluoride concentration from 10 to 40 mg·L⁻¹ [Fig. 2(e)]. This sorption attained equilibrium and there was no significant increase in the sorption capacity with the increase in initial fluoride concentration to 50 mg·L⁻¹. FNPSOPR showed an increased sorption capacity of 80.33 mg·g⁻¹ at 30 mg·L⁻¹ and attained equilibrium thereafter. This notable increase in the initial stages of sorption denotes the increased availability of fluoride ions in solution. However, no increase in the fluoride sorption capacity was observed after equilibrium, which is due to the unavailability of sorption sites for the excess fluoride present in solution. Hence, 40 mg·L⁻¹ and 30 mg·L⁻¹ were optimized to be the initial fluoride concentration for effective fluoride removal by FNPSA and FNPSOPR. Lv *et al.* observed similar results in fluoride adsorption while treating water with high fluoride concentration by Mg–Al–CO₃ layered double hydroxides [23].

3.3. Batch studies at optimized conditions

Batch sorption studies were carried out for FNPSA and FNPSOPR at the optimized conditions as mentioned above. The optimized

Table 1

The optimized parameters for FNPSA and FNPSOPR in batch sorption study

Parameters	FNPSA	FNPSOPR
Time	40 min	40 min
pH	5	7
Sorbent dosage	0.25 g·L ⁻¹	0.25 g·L ⁻¹
Temperature	33 °C	30 °C
Initial fluoride concentration	40 mg·L ⁻¹	30 mg·L ⁻¹
Maximum adsorption capacity	58.24 mg·g ⁻¹	80.33 mg·g ⁻¹
Equilibrium Isotherm model	Langmuir	Langmuir
Rate kinetic model	Pseudo first order	Pseudo first order

parameters for the sorbents FNPSA and FNPSOPR were presented in Table 1. The sorption capacities at various parameters were plotted as shown in the Fig. 2.

3.4. Batch sorption isotherm

Sorption equilibrium data obtained for FNPSA at 30 °C and FNPSOPR at 33 °C was modeled using Langmuir and Freundlich isotherms to understand the possible means of interaction between fluoride ions and the developed sorbents. The isotherm parameters were compared and presented in Table 2. Langmuir model of isotherm was found to be the best fitted model for both the sorbents FNPSA ($r^2 = 0.998$) and FNPSOPR (0.998) respectively. The Langmuir model explains the

Table 2

Represents the Langmuir and Freundlich isotherm model constants and correlation coefficients for fluoride sorption on FNPSA and FNPSOPR at optimized conditions

System	Langmuir			Freundlich		
	$q_e/\text{mg}\cdot\text{g}^{-1}$	$b/\text{L}\cdot\text{mg}^{-1}$	r^2	$K_f/\text{mg}\cdot\text{g}^{-1}$	$n/\text{L}\cdot\text{mg}^{-1}$	r^2
FNPSA	58.823	0.944	0.998	43.451	14.925	0.826
FNPSOPR	83.33	1.001	0.998	55.207	89.28	0.628

monolayer adsorption of fluoride ions based on surface homogeneity. The number of active sorption sites for fluoride sorption was increased by the surface functionalization of the sorbents. Investigation on Fluoride removal by lanthanum alginate bead, by Huo *et al.* is also in complete agreement with the isotherm modeling [32].

3.5. Batch sorption kinetics

Sorption kinetics studies were carried out for the sorbents FNPSA and FNPSOPR. The reaction rate constants for pseudo first order (k_1) and pseudo second order (k_2) are presented in Table 3. The correlation coefficient r^2 value suggests that a pseudo first order for FNPSA and FNPSOPR was a better fit than a second order. The pseudo second order indicates that in the presence of redundant fluoride, the rate of sorption highly depends on the capacity of the sorbent which in turn depends on the available sites for binding or ion-exchange. Therefore, the rate limiting step for sorption is the sorbent capacity. Pseudo first order kinetic modeling plot of $\log(q_e - q_t)$ vs. t is represented as Fig. 3. A similar result was reported by Kamble *et al.* for the defluoridation of drinking water using chemically modified bentonite [21]. The sorption capacities, isotherm and kinetic models of various sorbents previously reported for fluoride removal were compared with the sorbents used in the present study (Table 4). This comparison helps in understanding the efficiency of FNPSA and FNPSOPR over other sorbents available for fluoride removal.

Table 3

Represents the comparison of pseudo first order and pseudo second order rate constants for FNPSA and FNPSOPR at optimized conditions

System	Pseudo first order model			Pseudo second order model		
	k_1/min	$q_e/\text{mg}\cdot\text{g}^{-1}$	r^2	$k_2/\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$q_e/\text{mg}\cdot\text{g}^{-1}$	r^2
FNPSA	0.0759	57.14	0.999	0.0035	62.5	0.952
FNPSOPR	0.0644	76.032	0.995	0.00056	111.11	0.988

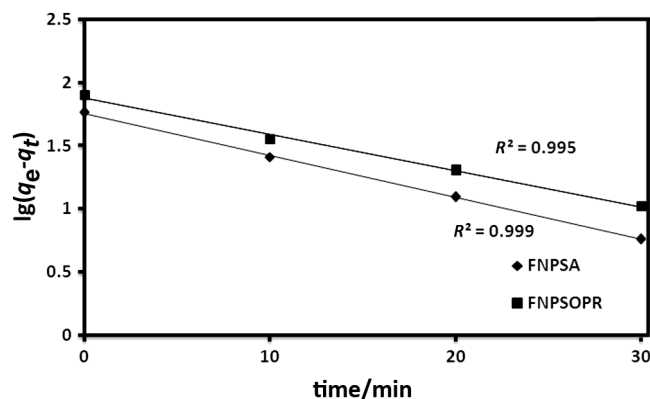


Fig. 3. Pseudo first order kinetic modeling plot of $\lg(q_e - q_t)$ vs. t .

3.6. Characterization of sorbents FNPSA and FNPSOPR

The sorbents FNPSA and FNPSOPR were characterized by VSM, FTIR and SEM analysis.

3.6.1. Vibrating sample magnetometry

Vibrating sample magnetometry (VSM) is used to evaluate the magnetization of magnetic nanoparticles in the presence of an external magnetic field. Based on the curve obtained, the magnetic behavior of the nanoparticles can be identified. The Fe_3O_4 particles prepared in this study were superparamagnetic and belonged to the soft magnet category. The coercivity and magnetization exhibited by the Fe_3O_4 particles and the sorbents are shown in the Table 5. The increase in sorption capacity when comparing FNPSA and FNPSOPR can be attributed to the increase in their respective coercivity. The decrease in magnetization can be attributed to the masking effect of alginate on the Fe_3O_4 nanoparticles. The hysteresis loop of the sorbents FNPSA and FNPSOPR is shown in Fig. 4.

3.6.2. HR-SEM

HR-SEM images of FNPSA and FNPSOPR before and after interaction with fluoride ions are shown in Fig. 5(a–d) respectively. The apparent morphological changes could be identified using SEM images in both FNPSA and FNPSOPR sorbents. The pores and cavities found in the sorbents namely FNPSA and FNPSOPR before interaction with fluoride are found to be smoothened to a certain extent after interaction with fluoride. The change in the morphology can be attributed to the interaction with fluoride ions.

3.6.3. FTIR

In FNPSA, the presence of $-\text{OH}$ group is identified by the peak at 3421 cm^{-1} . The peak broadening confirms the electrostatic interaction between the fluoride ions and the $-\text{OH}$ groups [27,28]. The peak at 1641 cm^{-1} indicates the presence of carbonyl group and the conjugation of fluoride to the carbonyl group is confirmed by the stretching of the peak [17]. In FNPSOPR, the hydroxyl groups dominate due to their excessive availability. This was confirmed by a peak at 3421 cm^{-1} , which also explains the ligand exchange mechanism with fluoride [19,27]. The FTIR peaks of the sorbents FNPSA and FNPSOPR before and after interaction with fluoride ions is shown in Fig. 6(a, b) respectively.

3.6.4. Possible mechanism of fluoride uptake

In FNPSA, cross linking with glutaraldehyde introduces more $-\text{OH}$ groups on the surface of the sorbent. These hydroxyl groups get converted to $-\text{COOH}$ groups on carboxylation with chloroacetic acid. The carboxyl groups, thus formed are involved in electrostatic interaction with fluoride by H-bond formation [19,29]. The carboxyl group contains oxygen atom that acts as an electron donor to the Lewis acid and the fluoride ions were removed by strong Lewis acid–base interaction and electrostatic interaction [45]. This is schematically represented in the Fig. 7(a). The coercive force exhibited by the nanoparticle and the modified surface of FNPSA favors fluoride sorption. In the case of FNPSOPR, carboxyl groups and the oxygen atom of the pyranose ring of pectic acid from SOPR form a five member chelate ring with the loaded Fe^{3+} ion. This contributes to the excessive availability of hydroxyl ions which aids in ligand exchange with fluoride ions [16]. The chelate ring formed by Fe^{3+} ions as shown in the Fig. 7(b). The main functional group that plays vital role in fluoride adsorption is the $-\text{OH}$ group. Since its availability is more at pH 7 than at pH 5, the optimized pH tends to differ for both the sorbents. The presence of Fe_3O_4 nanoparticles in the FNPSOPR beads and their coercivity in fluoride adsorption should also be taken into account for its higher fluoride sorption capacity.

Table 4

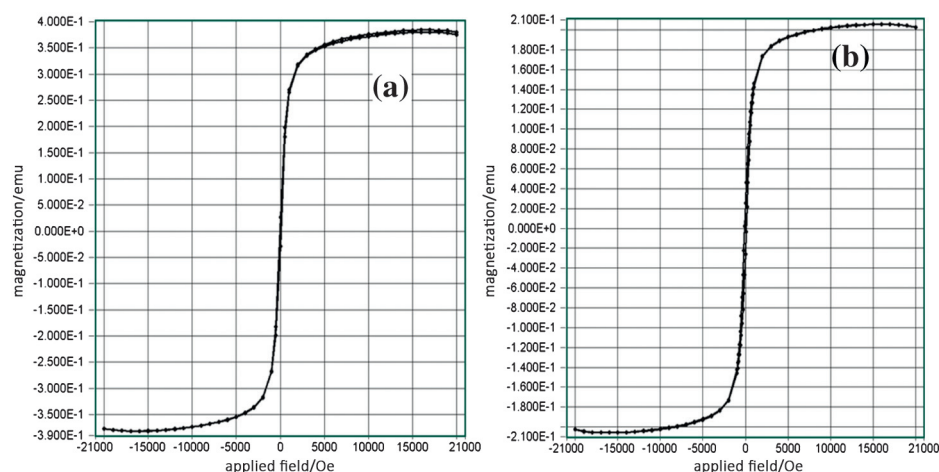
Comparison of the sorption capacity, isotherm and kinetic modeling of various sorbents with the FNPSA and FNPSPR synthesized in this study

Sorbent	Time	pH	Concentration	Temperature	Maximum adsorbent capacity	Isotherm	Kinetic model	Reference
Magnetic chitosan particle	150 min	7.0 ± 0.2	5–140 mg·L ⁻¹	18–20 °C	22.49 mg·g ⁻¹	Two-sites Langmuir isotherm	Pseudo-second-order	[30]
Neodymium-modified chitosan	24 h	7.0	10–100 mg·L ⁻¹	303 K	22.380 mg·g ⁻¹	Langmuir	Pseudo-second-order	[31]
Lanthanum Alginate Bead	24 h	4.0	–	25 °C	197.2 mg·g ⁻¹	Langmuir	–	[32]
Fe(III) loaded carboxylated chitosan beads	40 min	7.0	11–19 mg·L ⁻¹	303 K	4230 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[19]
Multifunctional chitosan beads	30 min	7.0	11–17 mg·L ⁻¹	303 K	1800 mg·kg ⁻¹	Langmuir, Freundlich	Pseudo-second-order	[33]
Al loaded saponified orange juice residue	24 h	6.0	0.52 mmol·dm ⁻³	30 °C	1.03 mol·kg ⁻¹	Langmuir	–	[16]
Glutaraldehyde crosslinked Calcium Alginate	90–120 min	8.0	10–25 mg·L ⁻¹	RT	73.5 mg·g ⁻¹	Langmuir	Pseudo-second-order	[29]
Nano goethite powder	2 h	6.0–8.0	30 mg·L ⁻¹	303 K	59 mg·g ⁻¹	Freundlich	Pseudo-second-order	[12]
Chitosan Coated Silica	180 min	4.0	10–20 mg·L ⁻¹	RT	44.4 mg·g ⁻¹	Langmuir, Freundlich	Pseudo-second-order	[34]
La(III) incorporated carboxylated chitosan beads	60 min	7.0	11–19 mg·L ⁻¹	303 K	4711 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[35]
Magnesia/chitosan composite	30 min	–	10–23 mg·L ⁻¹	303 K	4440 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[36]
Nano-hydroxyapatite/chitin composite	30 min	3.0	10 mg·L ⁻¹	303 K	2840 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[37]
Hydrotalcite/chitosan composite	40 min	3.0	9–15 mg·L ⁻¹	303 K	1255 mg·kg ⁻¹	Langmuir	Pseudo-second-order	[38]
Chitosan supported zirconium(IV) tungstophosphate composite	30 min	3.0	10 mg·L ⁻¹	303 K	2025–2142 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[39]
Aluminum impregnated chitosan	60 min	6.5	10 mg·L ⁻¹	(25 ± 2) °C	1.73 mg·g ⁻¹	Freundlich	Pseudo-first-order	[40]
Chitosan based mesoporous Ti–Al binary metal oxide	24 h	3.0–9.0	–	30 °C	2.22 mg·g ⁻¹	Langmuir	Pseudo-second-order	[41]
Zirconium(IV)-impregnated collagen fiber	24 h	5.0–8.0	1–5 mmol·L ⁻¹	303 K	2.18 mmol·g ⁻¹	Langmuir	Pseudo-first-order	[42]
Alumina/chitosan composite	30 min	7.0	10 mg·L ⁻¹	303 K	3809 mg·kg ⁻¹	Freundlich	Pseudo-second-order	[43]
Chitosan based mesoporous alumina	24 h	–	5.0 mg·L ⁻¹	(30 ± 2) °C	8.264 mg·g ⁻¹	Langmuir	Pseudo-second-order	[44]
FNPSA	40 min	5.0	40 mg·L ⁻¹	33 °C	58.24 mg·g ⁻¹	Langmuir	Pseudo-first-order	Present study
FNPSPR	40 min	7.0	30 mg·L ⁻¹	33 °C	80.33 mg·g ⁻¹	Langmuir	Pseudo-first-order	Present study

Table 5

Comparison of coercivity, saturation and remnant magnetization of the sorbents as analyzed using vibrating sample magnetometer

Parameters	Fe ₃ O ₄ nanoparticles	FNPSA	FNPSPR
Coercivity	70.541 Oe	67.213 Oe	109.669 Oe
Saturation magnetization	7.691 × 10 ⁻¹ emu	3.830 × 10 ⁻¹ emu	2.057 × 10 ⁻¹ emu
Remnant magnetization	9.166 × 10 ⁻² emu	2.824 × 10 ⁻² emu	2.585 × 10 ⁻² emu

**Fig. 4.** Vibrating sample magnetometry of (a) FNPSA and (b) FNPSPR.

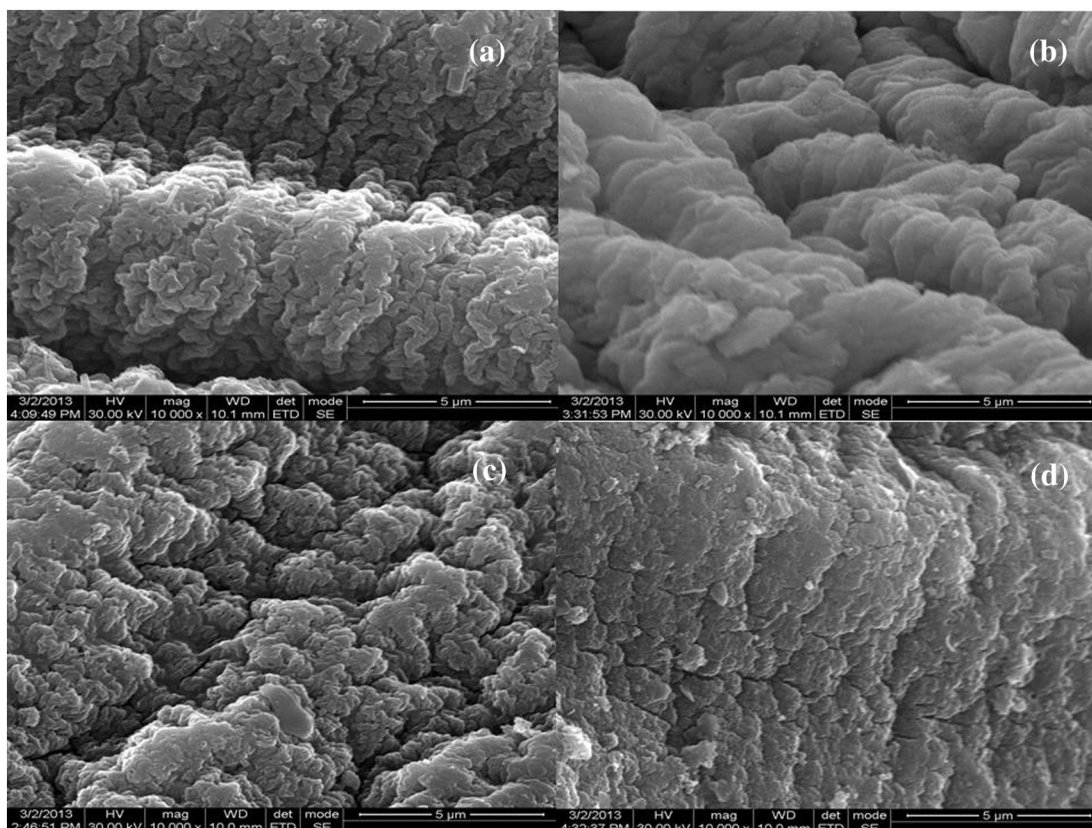


Fig. 5. Scanning electron microscopic image of FNPSA and FNPSOPR before (a and c) and after (b and d) interaction with fluoride.

3.7. Sorbent regeneration study

Regeneration of the sorbent is of vital importance in water treatment process. Since the sorbent FNPSOPR exhibited a higher sorption capacity of $80.33 \text{ mg} \cdot \text{g}^{-1}$, its regeneration capacity is evaluated by alternating adsorption–desorption cycles. The sorbent regeneration study was conducted with 50 ml of $100 \text{ mg} \cdot \text{L}^{-1}$ of synthetic fluoride solution at the beginning of every cycle. The study was carried out with 1% sodium hydroxide as desorbing agent. The sorption capacities of each cycle were 100%, 97.56%, 94.53%, 83.21%, and 76.53%. These results show that FNPSOPR can be effectively reused to remove fluoride ions from drinking water (Fig. 8).

4. Conclusions

The sorbent FNPSA was prepared by immobilizing Fe_3O_4 nanoparticles in the calcium alginate matrix while FNPSOPR was developed by entrapping a mixture of Fe_3O_4 nanoparticles and saponified orange peel residue (SOPR) in the calcium alginate matrix and then both the sorbents were surface modified. The surfaces of the nano-biosorbents were functionalized so as to enable them to adsorb fluoride ions more efficiently from water. FNPSA and FNPSOPR exhibited a maximum sorption capacity of $58.24 \text{ mg} \cdot \text{g}^{-1}$ and $80.33 \text{ mg} \cdot \text{g}^{-1}$ respectively, and followed the Langmuir model of isotherm which explains monolayer adsorption of fluoride. Moreover, both the sorbents followed pseudo first order reaction. It could be suggested that electrostatic interaction and ion exchange are the possible mechanisms for fluoride uptake. This is the first kind of study on the sorption of fluoride ions from aqueous phase by Fe_3O_4 nanoparticle immobilized in surface modified sorbent matrix.

FNPSA exhibits higher fluoride sorption capacity than the earlier reports by aluminum loaded saponified orange juice residue, Fe (III) loaded carboxylated chitosan beads, and glutaraldehyde crosslinked calcium alginate matrix [16,19,34]. However, FNPSOPR exhibited a higher sorption capacity, and has a good reusability of 76.53% after 5 cycles of alternative adsorption–desorption.

The major objective of this manuscript is to study the fluoride removal capacity of the sorbents with synthetic fluoride solution prepared in laboratory conditions as a pilot study. According to Ashwini *et al.*, it is estimated that the fluoride concentration in drinking water in India, is about $0.5 \text{ mg} \cdot \text{L}^{-1}$, however it may range from 3 to $12 \text{ mg} \cdot \text{L}^{-1}$ in fluoride endemic areas [46]. In such a case, there was an increase in adsorption capacity of FNPSOPR in this range of fluoride concentrations. Hence it can be concluded that FNPSOPR can be used as an effective sorbent remove fluoride from water and bring down its concentration within the permissible limits in when used in fluoride prevalent areas.

Nomenclature

DLS	dynamic light scattering
EDX	energy dispersive X-ray spectroscopy
FNPSA	functionalized Fe_3O_4 nanoparticle immobilized calcium alginate nano-biocomposite matrix
FNPSOPR	functionalized Fe_3O_4 nanoparticle and saponified orange peel residue immobilized calcium alginate nano-biocomposite matrix
FT-IR	Fourier transform-infra red spectroscopy
HR-SEM	high resolution scanning electron microscopy
MIONS	magnetic iron oxide nanoparticles
SOPR	saponified orange peel residue
VSM	vibrating sample magnetometry

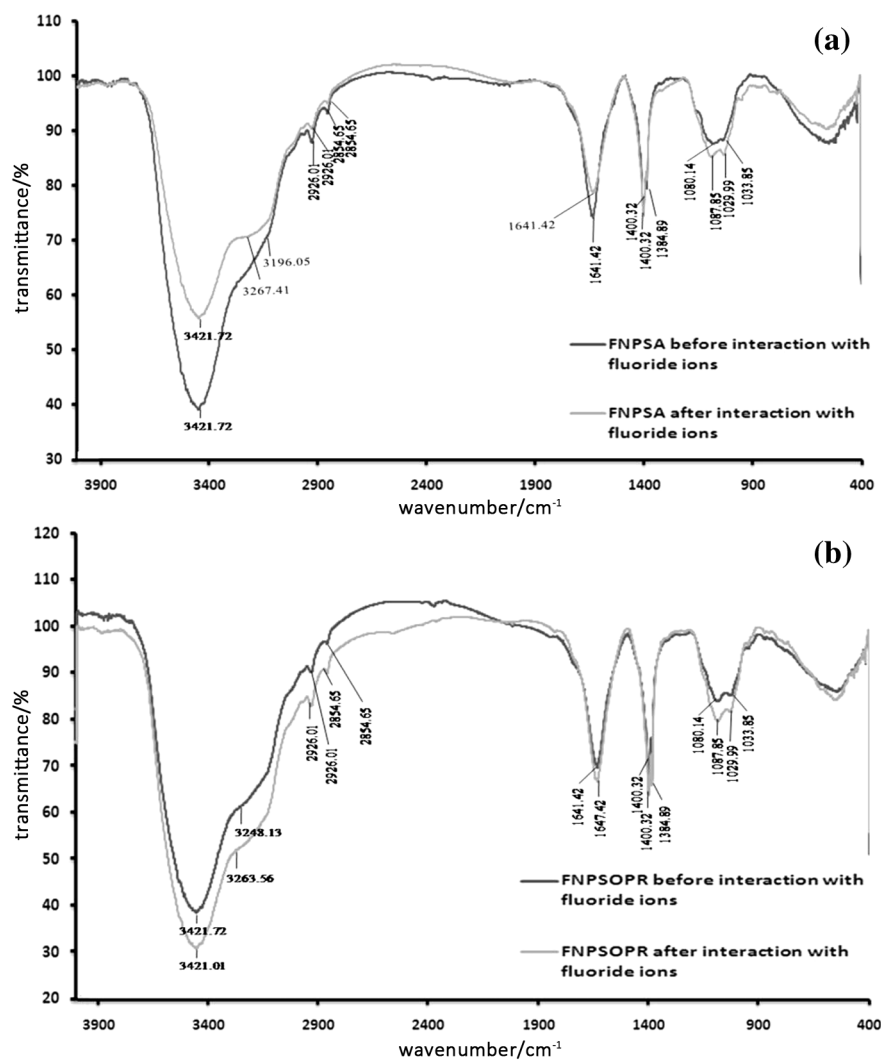


Fig. 6. FTIR pattern of (a) FNPSA and (b) FNPSOPR before and after interaction with fluoride ions.

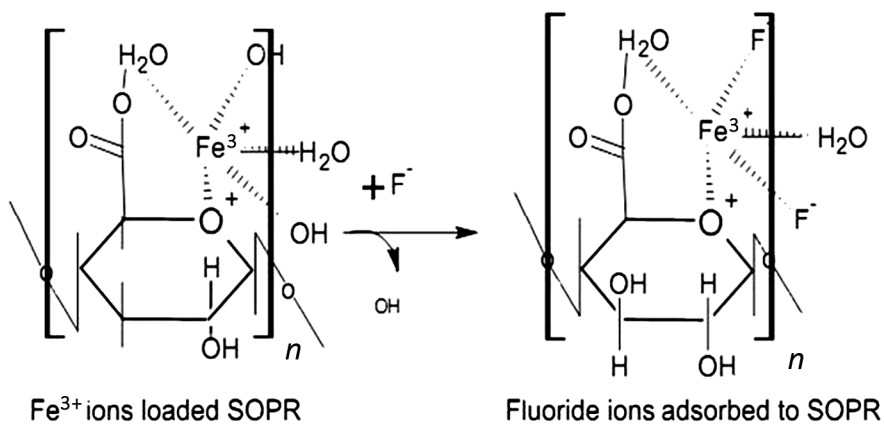
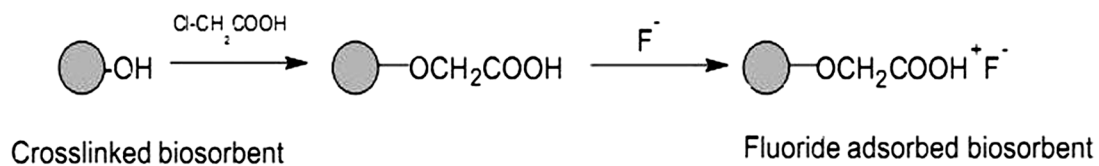


Fig. 7. Possible mechanism of fluoride sorption by the sorbents FNPSA and FNPSOPR.

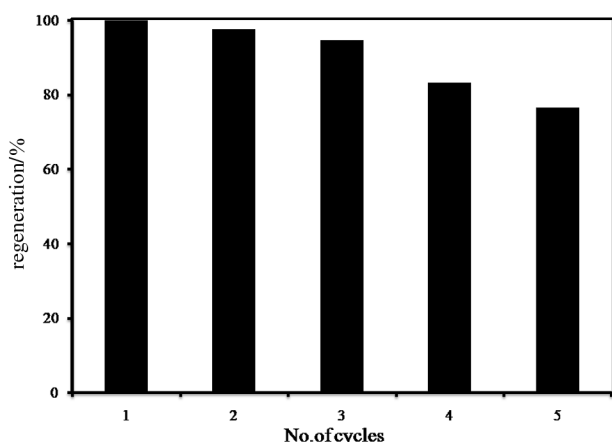


Fig. 8. Regeneration of the sorbent FNPSOPR.

WHO world health organization
XRD X-ray diffraction

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