Elimination of Hazardous Fluoride from Drinking Water using Th–Mn Nanoadsorbent

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Abstract

Herein, we have developed Th–Mn nanoadsorbent for the removal of fluoride from aqueous systems. The adsorbent presented high surface area (156.864 m²/g) and small pore size (13.3 Å) demonstrating the high porosity of the nanoadsorbent. The adsorbent surface morphology has been characterized by XRD, TEM, BET, and Raman techniques. The fluoride adsorption mechanism was confirmed by FTIR studies. The fluoride uptake conditions were optimized using batch studies. The batch results demonstrated maximum adsorption efficiency (85%) at pH 6 within 85 min. The adsorption isotherms were well fitted by the Freundlich isotherm model ($R^2 > 0.870$). The nanoadsorbent presented excellent regenerability (up to 95%) with an alkali solution. The property of regeneration and reusability makes it a smart sustainable material for fluoride removal.

Graphical Abstract

Keywords: Fluoride, adsorption, nanoadsorbent, efficiency

Introduction

Fluorine is the most reactive element in the periodic table. Its high reactivity makes it less abundant in elemental form. It is commonly found as inorganic fluorides (including the free anion F^-) or as organic fluoride compounds (e.g., freons)¹. Weathering of fluorides minerals is considered as the main natural source of inorganic fluorides in water. Volcanoes are also a major natural source in increasing atmospheric fluoride concentration through the release of gases such as hydrogen fluoride²⁻³. Inorganic fluorides commonly remain in water as fluorides in acidic pH, low hardness and in the presence of ion-exchange materials⁴⁻⁸. Aquatic organisms in soft water are more affected by fluoride pollution as compared to organisms in hard or seawaters due to reduced bioavailability of fluoride ions on increasing water hardness⁹. Unpolluted fresh waters have lower fluoride concentrations (0.01–0.3 mg/L) as compared to unpolluted seawaters (1.2–1.5 mg/L)¹⁰⁻¹².

The low fluoride concentration in drinking water is beneficial for human health, while high fluoride intake can cause severe irreversible dental or skeletal fluorosis. Moreover, it has been known to negatively affect the functioning of kidneys, nerves and muscles¹³. Therefore, the prevention of fluorosis is imperative. Precipitation and adsorption are known since times to bring back excessive fluoride content of water to the permissible limit. Adsorption is the most suitable, moderately simple, efficient and inexpensive method for fluoride removal, particularly in small communities. Several conventional and non-conventional adsorbents like activated alumina¹⁴, Fe/Al mixed hydroxides¹⁵, ion exchange resin¹⁶, solid industrial wastes like red mud¹⁷⁻¹⁸, and fly ash¹⁹⁻²⁰ were studied for their fluoride adsorption capacities. Still, most of the adsorbent available for fluoride removal are high-priced and technically non-feasible in rural areas. There is a need to develop easily available adsorbents for fluoride removal which are safe and easy use at small community level. Herein, we have developed a Th–Mn nanoadsorbent by means of simple precipitation process followed by heat treatment to employ it for the efficient fluoride removal from aqueous systems²⁰⁻²³.

Materials and methods

Materials

All reagents like NaF, NaOH, HCl were of analytical reagent grade. The two metal salts like $Th(NO_3)_3 \cdot xH_2O$ and $MnSO_4 \cdot H_2O$ were purchased from E. Merck Ltd. India and utilized without further purification. The standard fluoride stock solution (1000 mg/L) was prepared and different concentrations fluoride solutions for experimental studies were obtained by appropriate dilution²⁴⁻²⁷.

Adsorbent preparation

Both metal salt solutions were prepared by dissolving 5.02 g of $Th(NO_3)_3 \cdot xH_2O$ in 100 mL and 3.02 g of $MnSO_4 \cdot H_2O$ in 100 mL. They were mixed and pH was adjusted to 7.4–7.8 by drop wise addition of 2 M NaOH solution under vigorous stirring, leading to precipitation. The obtained precipitate was filtered and washed many times with distilled deionized water. Further, the precipitate was calcined in a muffle furnace with slow increase of temperature

from 80 to 600 °C for 6 h. Finally, the adsorbent was cooled and then crushed manually into fine powder below 200 meshes²⁸⁻³⁵.

Characterization of adsorbent

The FTIR spectrum of the adsorbent was recorded on a FTIR spectrophotometer (Agilent 660, USA) using KBr pellets³⁶⁻³⁸. FTIR spectra of the adsorbent before and after fluoride adsorption were recorded under experimental conditions in the range of 600–4000 cm^{-1} .

X-ray diffraction (XRD) patterns of adsorbent were obtained using Bruker D8 ADVANCE X-ray diffractometer, Germany with Cu $K\alpha$ radiation. The scanning speed was maintained at 0.5 sec/step in the range of 10–80 °C with a scan step of 0.02 °C at 80 °C³⁹⁻⁴².

Transmission electron microscopy (TEM) micrographs before and after adsorption were obtained using a Philips CM 200 FEG microscope recorded at 200 KeV⁴³⁻⁴⁵. Raman spectral analysis was carried out on an Instrument Advantage 532 (Raman). Excitation was achieved using 514.5 nm line of argon ion laser with an output power⁴⁶⁻⁴⁸.

The specific surface area of the nanoadsorbent was determined by Nova 2000e, Quantachrome Instruments Limited, USA by recording nitrogen adsorption isotherms at 77.35 K. The obtained data were processed using Brunauer, Emmett and Teller (BET) method to evaluate specific surface area using BET equation shown below.

$$1/(W((p/p_o)(p-1))) = 1/(W_{(m)}C) + (C-1)/(W_{(m)}C)(p/p_o)$$

A linear plot of $1/[W(p/p_o)-1]$ against p/p_o gives a straight line where W is the quantity of the gas adsorbed, p/p_o is the relative pressure, $W_{(m)}$ is the quantity of adsorbed monolayer gas and C is the BET constant⁴⁹⁻⁵¹.

Batch adsorption experiments

Batch adsorption experiments were conducted to study the adsorption isotherms. For that, 1.2 g adsorbent was added in 50 mL fluoride solutions of different concentration and with a continuous stirring at 29 °C with 180 min of contact time except where the contact time parameter was studied⁵²⁻⁵⁴. The pH was adjusted by using 0.1 M HCl/NaOH solution. The adsorbent was filtered from the solution after the adsorption experiments and residual fluoride concentration was determined by fluoride meter (Thermo Orion, USA).

Adsorbent optimization

Effect of pH

The solution pH is a key parameter that influences the adsorption phenomena at the solid–water interface. The effect of pH was studied in the range of solutions having pH from 1 to 10 with an adsorbent dose of 1.2 g/50 mL, temperature 29 °C and the contact time of 145 min. The results indicate that fluoride adsorption increases markedly with increasing pH from 1 to 6 (Fig. 1a). The rate of adsorption increased up to pH 6 due to highly protonated adsorbent surface in acidic medium which gradually increased the attractive forces between positively charged adsorbent surface and negatively charged fluoride ions. The adsorbent demonstrated

highest efficiency (~85%) at pH 6 as a result of ligand exchange interactions between F^- and OH^- groups which is further supported by FTIR studies. Further rise in pH after 6 caused reduction in the adsorption efficacy as a result of the increased hydroxyl ions concentration which can compete with F^- ions for adsorption active sites. Also, it may be a result of development of negative surface charge on adsorbent.

Fig. 1. Influence of the pH (a) and contact time (b) on fluoride adsorption capacity.

Effect of contact time

The effect of the contact time on adsorption efficiency was studied at normal room temperature (29 °C) by changing the contact time from 2 to 180 min under similar experimental conditions as described above. Fluoride adsorption (Fig. 1b) was rapid during the first 145 min, where maximum adsorption occurred (85%). However, the adsorption rate slowed down after 145 min possibly due to the attainment of the equilibrium and later on became almost constant at the later stage of adsorption. Similar results have been reported in the literature⁵⁶⁻⁵⁸.

Effect of adsorbent dose

The effect of adsorbent dose on fluoride adsorption was determined by varying the adsorbent dose from 0.1 to 1.5 g/50 mL. The results demonstrated that the removal percentage increased with increase in adsorbent dosage (Fig. 2a) because of the availability of more number of active sites with dose. Further, increase in adsorbent dose not considerably raises the adsorption rate due to the presence of numerous available adsorbent sites as compared to fluoride ion concentration. Therefore, Th-Mn nanoadsorbent shows maximum fluoride removal efficiency at 1.2 g/50 mL⁵⁹⁻⁶⁰.

Effect of initial fluoride concentration

The effect of fluoride ion concentration was studied by varying the initial fluoride ion concentration from 10.0 to 45.0 mg/L under

Fig. 2. Influence of the adsorbent dose (a) and initial fluoride concentration (b) on fluoride adsorption capacity.

present experimental conditions (Fig. 2b). The F^- adsorption decreased with increase in initial fluoride ion concentration and later on became almost constant at higher fluoride concentrations as a result of availability of fewer adsorption active site then available fluoride ions concentrations. The maximum adsorption capacity (85%) was observed at the initial fluoride concentration of 10 mg/L⁶¹⁻⁶⁴.

Results and discussion

FTIR studies of adsorbent

FTIR spectrum of adsorbent before fluoride adsorption shows the transmission band at 3392 cm^{-1} due to H_2O stretching and a transmission peak of high intensity at 1634 cm^{-1} due to bending vibrations of H_2O (Fig. 3). Further, the FTIR peak at 1050 cm^{-1} corresponds to metal hydroxyl group (M-OH) bending vibrations (Fig. 3). A slight broadening of $-OH$ stretching vibration band at 3504 cm^{-1} after fluoride adsorption corresponds to the formation of O-H-F (Fig. 4). It could be seen that the disappearance of peak at 1050 cm^{-1} after adsorption demonstrates the hydroxyl group exchange with the fluoride ions⁶⁵⁻⁷⁰. The appearance of a new broad band in the region 500–800 cm^{-1} after fluoride adsorption can be attributed to the complexation of fluoride ions with nanoadsorbent (Fig. 4).

Fig. 3: FTIR spectrum of Th-Mn nanoadsorbent before fluoride adsorption.

Fig. 4: FTIR spectrum of Th-Mn nanoadsorbent after fluoride adsorption

XRD studies

The presence of XRD peaks at 2θ 17.6°, 29.09°, 44.2° supports the presence of MnO₂ species (Fig. 5 (a)). The presence of ThO₂ in lesser amount made its phase hard to detect. It could be due to the formation of Th–Mn solid species where Th species entered the lattices of MnO₂.

Adsorption of fluoride caused reduction of the peak intensity and depletion was found in peak 19.5° and 29° 71-74 (Fig. 5 (b))

Fig. 5. XRD pattern of Th-Mn nanoadsorbent before (a) and after (b) fluoride adsorption.

TEM analysis

The TEM image (Fig. 6a) demonstrates agglomerated particles with not well defined shapes⁷⁵⁻⁷⁸. The average size of particle increased after fluoride adsorption due to accumulation of fluoride ions on the surface of the nanoadsorbent (Fig. 6b) (Table 1).

Table 1

Average particle size of nanoadsorbent before and after fluoride adsorption

Adsorbent	Average Particle size (nm)	
	Before fluoride adsorption	After fluoride adsorption
Th–Mn nanomaterial	15.3	26.6

Fig. 6. TEM images of nanoadsorbent before (a) and after (b) fluoride adsorption.

Raman spectroscopy

The involvement of ion exchange between F[–] and OH[–] ions was further confirmed by the Raman spectra of nanoadsorbent before and after fluoride adsorption (Fig. 7 and 8). The peak at 497 cm^{–1} was attributed to characteristic peak of Th–O vibrations, and the reduced intensity of the present peak after adsorption may be due to fluoride adsorption⁷⁹⁻⁸⁰.

Fig.7. Raman spectrum of Th-Mn nanoadsorbent before fluoride adsorption.

Fig. 8. Raman spectrum of Th-Mn nanoadsorbent after fluoride adsorption.

BET analysis

The specific surface area is an imperative characteristic of adsorbents, and BET specific surface area of the nanoadsorbent before and after fluoride adsorption were determined using nitrogen adsorption/desorption at 77 K, Fig. 9. The data is presented in Table 2. The pore size distribution and pore characteristics were analyzed based on Dubinin–Astakhov (D–A) equation, and the plot is shown in Fig. 10. The increase in surface area decreased the

pore radius as found in the present study (Table 2). The increase in surface area supports the view that a major structural change occurred during the adsorption of the fluoride ions Table 2. Higher adsorption capacity results in an extensive fluoride adsorption both on the exterior adsorbent surface and inside of the pores. Therefore, the BET surface area of adsorbent is dominated by the surface area of adsorbate. The small size of adsorbate (fluoride) presents high surface area thereby increasing the overall surface area of adsorbent⁸¹⁻⁸³.

Table 2 Surface area and D–A pore size of nanoadsorbent

Adsorbent		Surface area (m ² /g)	D–A (Pore Size) Å
Th–Mn nanoadsorbent	before fluoride adsorption	156.864	13.30
	after fluoride adsorption	182.582	10.40

Fig. 9. BET surface area plots where, pink line presents before fluoride adsorption, blue line presents after fluoride adsorption.

Fig. 10. D–A plots for pore radius where, pink line presents before fluoride adsorption, blue line presents after fluoride adsorption.

Adsorption isotherm

Equilibrium adsorption isotherms for fluoride adsorption were determined in batch mode at pH 6.0 and 298 K. The adsorption capacity of nanoadsorbent was determined by means of following equation 84-85:

$$Q_m = (C_o - C_e) V / M_s$$

Where, Q_m is the adsorption capacity (mg/g),

C_o is the initial fluoride concentration (mg/L),

C_e is the equilibrium fluoride concentration (mg/L),

V is the volume of solution (L),

M_s is the mass of the adsorbent (g).

The Langmuir and Freundlich isotherm models were employed to analyze the experimental adsorption equilibrium data (Fig. 11 and 12).

Langmuir Isotherm model

Langmuir model presumes monolayer mode of adsorbate molecules binding on that the surface valence active site of the adsorbent and homogenous adsorption of adsorbate molecules⁸⁶. The experimental data agreed with the equations of the Langmuir adsorption isotherm as shown below

$$Q_e = Q_o b C_o / (1 + b C_o)$$

$$1/Q_e = 1/Q_o + 1/b Q_o C_o$$

where, Q_e is saturation adsorption capacity (mg/g),

C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L),

Q_o and b are equilibrium constants.

Freundlich Isotherm model

In Freundlich adsorption isotherm, the curve demonstrates the relation between concentration of contact, this model becomes invalid at high pressure conditions where as the Langmuir model relates the adsorption of molecules on the adsorbent surface to the concentration of solution at a fixed temperature. The empirical Freundlich isotherm model and its linear form can be expressed

as follows:

$$Q_e = K_f C_e^{(1/n)}$$

$$\log Q_e = \log K_f + 1/n \log C_e$$

where K_f and n are constants whose values are calculated by linear fitting of $\log Q_e$ vs. $\log C_e$. All the parameters are calculated and are tabulated in Table 3. Evaluation of the parameters demonstrates that the Freundlich model presents higher correlation coefficients $R^2 = 0.870$ as compared to that of Langmuir model (Fig. 6 and 7) ($R^2 = 0.82$).

Fig. 11. Linear model of Langmuir isotherm.

Fig. 12. Linear model of Freundlich isotherm

Table 3 The Langmuir and Freundlich constants

Adsorbent	Langmuir Constants			Freundlich Constant			
	Q_o	$1/b$	R^2	K_f	$1/n$	N	R^2
Th–Mn	1.194	0.223	0.820	0.967	0.043	23.250	0.870

Regeneration and Reusability

Fig. 13. Fluoride desorption (a) and regeneration (b) studies.

Regeneration and reusability of the nanoadsorbent was checked in several adsorptions and desorption cycles⁹⁰⁻⁹⁷. The used nanoadsorbent was regenerated by means of 2 M HCl and 2 M NaOH. Desorption of nanoadsorbent was moderate in acidic pH, while efficient desorption (96%) occurred in alkaline pH (Fig. 13a).

Further, 5 times adsorption–desorption cycles were performed and the adsorbent showed reduced adsorbent capacity in fifth cycle (59%) (Fig.13b). Therefore, the study revealed efficient regeneration and reusability of the nanoadsorbent up to five cycles with considerable efficiency⁹⁸⁻¹¹¹.

Conclusion

In this study, a novel nanocomposite of Th–Mn developed using a co–precipitation process for efficient fluoride uptake from drinking water. The adsorbent presents efficient fluoride adsorption (85%) at room temperature with contact time of 85 min, pH 6, and 1.25 g adsorbent dose in 10 mg/L (50 mL) initial fluoride concentration. The rate of fluoride adsorption increased with contact time and adsorbent dose. The adsorption of fluoride is efficiently followed by Freundlich isotherm. FTIR studies which confirmed the involvement of hydroxyl groups in fluoride adsorption in the form of anion exchange processes and electrostatic interaction. BET analysis demonstrated the high surface area favourable for fluoride

adsorption. Adsorption experiments revealed potential of Th–Mn nanoadsorbent for fluoride removal from drinking water.

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