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Chitosan-Fe-Al-Mn metal oxyhydroxides composite as highly efficient fluoride scavenger for aqueous medium

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Graphical abstract

Highlights

- Chitosan helps to improve the fluoride adsorption of metal oxides nanoparticles
- Agglomeration chance of nanoparticles reduce after dispersion into porous polymer
- Interaction among chitoasn and metal oxides reveals by XPS analysis
- Polymeric barrier causes for unaffected adsorption under ionic strength
- Faster adsorption due to less agglomeration and high porosity in polymer matrix

Abstract

Nano-particles are highly efficient fluoride adsorbents, but agglomerate easily due to their high surface activity and difficult to separate from aqueous medium after use. Mixed-metals oxyhydroxides nano-particles were prepared into a natural polymeric matrix of chitosan to
overcome those problems. Hydrous mixed-metal oxyhydroxides, loaded chitosan composite (Fe-Al-Mn@chitosan) was prepared using abundantly available laterite clay and waste from steel industry via co-precipitation method. Fluoride removal using Fe-Al-Mn@chitosan composite followed Freundlich isotherm model which revealed multilayer adsorption on heterogeneous surface sites. Fe-Al-Mn@chitosan exhibited maximum adsorption capacity of 40±0.5 mg/g, while if only the inorganic mass fraction of composite was considered; the value reached 55±0.5 mg/g. Fluoride adsorption on Fe-Al-Mn@chitosan followed the pseudo-second order kinetics with rapid adsorption. No significant effect of other competitive ions was observed on F⁻ adsorption using Fe-Al-Mn@chitosan composite. The composite adsorbent is found to be effective to produce drinking water from fluoride contaminated groundwater.

Keywords: Fluoride removal; clay; mixed oxyhydroxides nano-particles; polymeric-inorganic composite; ferromanganese slag.

1. Introduction
Fluoride contamination in water may occur naturally or anthropogenically. Fluoride contamination of groundwater might be due to disposal of untreated/partially treated industrial effluents, use of excess chemical fertilizers, drilling activities for oil recovery (Viswanathan & Meenakshi, 2010). It is required in a lower concentration (less than 1.5 mg/L) for better bone and dental health of humans (Roy et al., 2017). Many countries or subcontinents including Africa, Asia, and South America are currently facing problems related to excess fluoride concentration in drinking water. In India, out of 29 states, nearly 19 states have been found with excessive fluoride concentrations (0.5 to 48 mg/L) in groundwater. Excess fluoride may cause adverse effects such as a change in the level of thyroid, growth retardation, osteosclerosis, skeletal and dental fluorosis (Biswa, Kumari, Adhikari, & Dutta, 2017). Numerous technologies such as adsorption (Chaudhary, Maiti, & Bhattacharya, 2016; Nagaraj, Sadasivuni, & Rajan, 2017; Raghav & Kumar, 2019), coagulation (Gong, Qua, Liu, & Lan, 2012), electrocoagulation (Hua, Loa, & Kuan, 2003), precipitation (Chaudhary, & Maiti, 2019) and membrane separations (Sehn, 2008) have been used to reduce the fluoride concentration in water. Among all technologies, adsorption has been proven to be the most favourable process for defluoridation. Due to abundance and cost-effectiveness of clay materials, various types of clays such as laterite (Iriel, Bruneel, Schenone, & Cirelli, 2018), modified laterite (Maiti, Basu, & De, 2011), bauxite (Cherukumilli, Maurer, Hohman, Mehta, & Gadgil, 2018), bentonite clay (Mudzielwana, Gitari,
Akinyemi, & Msagati, 2018), organic matter-rich clay (Mobarak, Selim, Mohamed, & Seliem, 2018), have been used previously for defluoridation. Various rare metaloxides/hydroxides composites, such as Ca-Al-La (Xiang, Zhang, Zhang, Tang, & Wang, 2014), Zr-Al-Ca (Dhongde, Wasewar, & De, 2017), and metal with chitosan composites such as Fe-chitosan (Viswanathan & Meenakshi, 2008), Al-chitosan (Swain et al., 2009), Carboxylated chitosan modified ferromagnetic nano particles (Mohammadi et al., 2019), bionanomaterial scaffolds (Kumar, Paul, & Natraj, 2017), La$^{+3}$ impregnated chitosan/β-cyclodextrin (Preethi & Meenakshi, 2018) have also been investigated as fluoride scavenging materials. Numerous studies have also concluded that manganese oxide loaded with base adsorbent materials show much superior fluoride adsorption efficiency compared to base adsorbent material like activated alumina (Ekka, Dhaka, Patel, & Dash, 2017; Maliyekkal, Sharma, & Philip, 2006), tamarind fruit shell (Sivasankar, Ramachandramoorthy, & Chandramohan, 2010), activated carbon (Ma, Wang, Fan, Gong, & Gao, 2009), bentonite (Mudzielwana et al., 2018), disposable earthenware (Sivasankar, Ramachandramoorthy, & Darchen, 2011).

Studies show that MnO$_2$ has great affinity to adsorb fluoride ions, but there are difficulties in its separation from aqueous medium after use and using MnO$_2$ alone as a filter bed media poses high pressure drop. Also, it is well known that mixed metal adsorbents generally are more amorphous in nature than single metal adsorbents. This is because, amorphous metal oxides generally show high BET surface area, pore volume, and subsequently shows higher adsorption capacity. Literature shows that nano-particles are highly efficient fluoride adsorbents, but agglomerate easily due to their high surface activity and are difficult to separate from aqueous medium after use. Natural polymeric matrix of chitosan has unique properties such as solubility in acidic aqueous medium and affinity for negatively charged surfaces. So, it can be used to prepare homogeneously dispersed nanoparticles inside of chitosan to overcome the problems of nano-particles alone. The systematic study of nano-mixed-metaloxyhydroxides loaded chitosan composite prepared from clay and industrial waste is not currently available in the literature. Thus, two low cost materials, namely abundant laterite (the source for Al and Fe) and ferromanganese slag from steel industries (the source for Mn and Al) are used to prepare highly efficient novel mixed oxides adsorbent dispersed in chitosan polymer matrix to remove fluoride from water. A comparison performance of both adsorbents (with and without chitosan) was carried out using batch experiments, and further detailed study on superior adsorbent was performed. The chitosan composite prepared in present study was highly efficient as defluoridating agent and easily separable from aqueous medium.
2. Material and methods

2.1 Materials

Chitosan (with degree of deacetylation: 75±5 %) was purchased from Hi-media, India and average molecular weight was estimated around 2.2*10^5 g/mol (Supplementary Fig. 1S). Sodium hydroxide (NaOH) (99.5% pure) was purchased from Rankem, India. Only analytical grade chemicals were used for all experiments and analysis. Laterite soil collected from Jhargram, West Bengal, India was used as a source of iron and aluminium while Mn-slag collected from a steel manufacturing industry was used as a source of aluminium and manganese.

2.1.1 Preparation of adsorbent

Acid leaching was performed on 50g laterite and 50g Mn slag separately using 200 mL of 5 N HCl. The concentration of Fe, Al and Mn ions in acid leached solutions were determined using ICP-OES. Al, Fe ions containing leached solution from laterite clay (14 g/L Fe ions and 1.5 g/L Al ions) and Al, Mn ions containing leached solution from industrial waste (25 g/L Mn ions and 21 g/L Al ions) were mixed in equal proportions. The leached solution containing metal ions and 1% chitosan solution were mixed in 1:1 ratio (v/v). Afterwards, ammonium hydroxide (0.5M) was added drop wise to the solution of mixed metal ions until pH 8.5 reached and the solution was left for 24h at 1000 rpm for homogeneous dispersion of Al-Fe-Mn precipitate in chitosan matrix. Thereafter solvent evaporation was carried out at 333 K for 15 h. The mixed-metal oxyhydroxides chitosan composite so obtained was washed using double distilled water and subsequently dried at 333 K for 12h. The synthesized composite adsorbent (Fe-Al-Mn@chitosan) consists of chitosan and mixed metal oxyhydroxides in the mass ratio of 30:70. The procedure described above was also used to prepare Al-Fe-Mn mixed-metal oxyhydroxides composite in the absence of chitosan.

2.2 Characterization

Surface morphologies of Fe-Al-Mn mixed-metal oxyhydroxides composite and Fe-Al-Mn@chitosan composite were analyzed by FE-SEM (TESCANMira3). XRD spectrum of both adsorbents was acquired by means of RigakuUltima IV XRD diffractometer in the range between 15° to 80°. Chitosan and mixed-metal oxyhydroxides loaded chitosan were also characterized by FTIR spectrophotometer (PerkinElmer, USA) through diamond attenuated total reflectance.
(ATR) method. The pH_{zpc} of Fe-Al-Mn@chitosan composite adsorbent was investigated using potentiometric titration method (Chaudhary et al., 2016).

2.3 Methodology

2.3.1 Comparison of Fe-Al-Mn with Fe-Al-Mn@chitosan

Fe-Al-Mn mixed-metal oxide hydroxides adsorbent and Fe-Al-Mn@chitosan composite were compared by performing batch study with zero and 0.1 M NaCl ionic strength. A known amount (0.1 g/100 mL) of each adsorbent was used with solutions of varied fluoride concentration (5 to 30 mg/L). Initial pH and temperature for these experiments were 6.7 and 298 K, respectively. Spent Fe-Al-Mn and Fe-Al-Mn@chitosan adsorbents were separated by ordinary filter paper. For constant adsorbent (0.5 g/L) and adsorbate dose (10 mg/L), fluoride removal rate of both adsorbents was also compared. A known volume of sample (2 mL) was taken out from each solution at different time intervals to determine fluoride concentration after filtration using 0.22 µm syringe filter. The experimental conditions (temperature: 298 K, initial pH: 6.7, and stirring speed: 200rpm) were kept same for both adsorbents. Both adsorbents were then compared in terms of their fluoride removal capacity.

2.3.2 Detailed F⁻ adsorption study on Fe-Al-Mn@chitosan composite

Various adsorption experimental condition optimization (effect of pH, dose, and anions effect), adsorption isotherm and kinetic studies, reusability study of adsorbent were carried out using nano-Fe-Al-Mn@chitosan composite. The details experimental methodology employed in this study has been discussed in supplementary information.

3. Results and discussion

3.1 Characterization

Fe-Al-Mn@chitosan and Fe-Al-Mn were characterized using FE-SEM, TEM, EDAX, XRD, and FTIR. Average grain sizes of mixed metal oxide and mixed metal oxide loaded chitosan composite were analyzed using Brookheaven ZetaPALS (Zeta potential analyzer) and were found to be 0.94 µm and 1.5 µm, respectively (Fig. 2S in SI). FE-SEM images of both the adsorbents show different surface morphologies. FE-SEM image of chitosan (Fig. 1a) shows smooth outer surface of chitosan, Fe-Al-Mn@chitosan (Fig. 1b &c) shows porosity in the outer surface of mixed-metal oxide hydroxides impregnated chitosan composite while mixed-metal oxide hydroxides composite without chitosan can be seen with having the agglomerated
morphologies (Fig. 1d). These findings were further confirmed by TEM analysis of both the adsorbents. Comparison of TEM images (Fig. 2) confirm the homogeneous dispersion of mixed metal oxyhydroxides sphere particle in size range of 20-30 nm (diameter) inside chitosan matrix while mixed metal oxide without chitosan shows agglomeration TGA analysis of chitosan and nano-Fe-Al-Mn@chitosan was carried out to compare the thermal stability of mixed metal loaded chitosan composite. TGA analysis (Fig 3S in SI) reveals that composite adsorbent loses more weight at lower temperature due to removal of water from inorganic oxyhydroxide and is more stable at very high temperature than chitosan alone. Porous outer surface and homogeneously dispersed mixed metals oxyhydroxides of chitosan composite makes F ions easily accessible to active sites for adsorption. This might also increase the diffusion of fluoride ions inside the composite matrix and hence might be the reason for better fluoride scavenging properties of Fe-Al-Mn@chitosan as compared to mixed-metal oxyhydroxides alone. EDAX analyses of the virgin and spent Fe-Al-Mn@chitosan (Table 1S and Fig. 4S) confirm presence of iron, aluminium and manganese in chitosan matrix in virgin adsorbent, while the presence of fluoride (4.7 % in wt.)also confirms in spent adsorbent in addition to Fe, Al and Mn. Easy access of the adsorption sites by F ions leads to faster adsorption kinetics of Fe-Al-Mn@chitosan composite. XRD patterns of virgin and spent Fe-Al-Mn@chitosan confirm the various main diffraction peaks corresponding to Mn$_2$O$_3$ (JCPDS 00-041-1442) and Fe$_2$O$_3$ (JCPDS 00-033-0664), FeO(OH) (JCPDS 00-044-1415), MnO(OH) (JCPDS 00-041-1379), AlO(OH) (JCPDS 00-049-0133).The peaks corresponding to the formation of various forms of iron, aluminium and manganese oxides inside chitosan matrix have been shown in Fig. 3a. The intensity of peaks was decreased in spent adsorbent which might be due to increase in amorphous nature through surface co-precipitation during adsorption of fluoride ions (Lu et al., 2013). The FTIR spectrum of commercially available chitosan, virgin and spent Fe-Al-Mn@chitosan were compared (Fig.3b). As displayed in Fig.3b, most absorption bands were found same for both chitosan and mixed-metal oxyhydroxides loaded chitosan composite except in the range of 400 to 1100 cm$^{-1}$. The absorption band appeared in 400 to 1100 cm$^{-1}$ region (580, 650, 1013 cm$^{-1}$) are due to the vibrations of multicentered Fe, Al, Mn metal oxyhydroxides (Kahani & Jafari, 2009; Qin, Wang, Fu, & Ma, 2011; Trombetta, Busca, & Willey, 1997). The pH$_{ZPC}$ values of the virgin adsorbent in distilled water and in the presence of 10 mg/L of fluoride ions were found as 5.5 and 6.6, respectively (Fig. 4a). This shift in pH$_{ZPC}$ can be attributed to the hydroxyl ions released into aqueous solution due to replacement of –OH ions on adsorbent surface by fluoride ions. Prepared adsorbent shows better fluoride removal in wider pH range (pH > pH$_{ZPC}$). Various adsorbents,
showing better adsorption performance at pH > pH\textsubscript{ZPC}, are also reported by other researchers (Zhang, Yang, & Huang, 2003; Zhang, Yang, Dou, He, & Wang, 2005).

Fig. 1. FE-SEM images of chitosan (a), Fe-Al-Mn@chitosan (b and c) and Fe-Al-Mn mixed metals oxyhydroxides (d)
Fig. 2: TEM images and diffraction pattern of Fe-Al-Mn@chitosan (a, b, c) and Fe-Al-Mn (d, e, f)

Fig. 3: a) XRD diffraction pattern of virgin and spent Fe-Al-Mn@chitosan and b) Comparison of FTIR spectrum of chitosan, fresh and spent Fe-Al-Mn@chitosan composite.

3.2 Comparison of Fe-Al-Mn and Fe-Al-Mn@chitosan
A comparative adsorption study was carried out to determine the more efficient adsorbents among the two stated above. Fe-Al-Mn@chitosan composite was found to be a superior adsorbent for fluoride when compared to mixed-metal oxyhydroxides adsorbent without chitosan (Fig. 4b) at the same adsorbent dosing. It is also to be noted that the amount of oxyhydroxide of mixed-metals is higher in mixed-metal oxyhydroxides compared to Fe-Al-Mn@chitosan composite. As
shown in Fig. 4b, Fe-Al-Mn@chitosan composite has shown almost constant percentage fluoride removal (from 5 to 30 mg/L) while mixed-metal oxyhydroxides composite without chitosan has shown descending rate of fluoride removal in %. Thus, for the same amount of adsorbent, Fe-Al-Mn@chitosan has shown higher adsorption site density to absorb more fluoride ions compared to mixed-metals oxyhydroxides without chitosan. Also, Fe-Al-Mn@chitosan composite was unaffected by the increased ionic strength, while mixed-metal oxyhydroxides composite without chitosan has shown a decreasing trend of fluoride removal in % (Fig. 4b). This is because the formation of an electric double layer surrounding the adsorbent is more prominent for mixed-metal oxyhydroxides without chitosan under high ionic strength solution. Hence, the electric double layer hinders the fluoride transport and hence the reduced rate of adsorption. But, Fe-Al-Mn@chitosan might not be affected by such strong electric double layer under high ionic strength solution. This can be explained by the possibility of the presence of polymeric barriers between the external surface of mixed-metal oxyhydroxides nanoparticles and external electrolytic solution. The Fe-Al-Mn@chitosan has not shown any decreasing trend of fluoride adsorption under high ionic strength solution which implies better applicability of this adsorbent for contaminated water with high ionic loadings. The fluoride removal rate for both adsorbents was also compared (Fig. 4c). The fluoride removal rate for Fe-Al-Mn@chitosan composite was found to be much higher than Fe-Al-Mn oxyhydroxides without chitosan. The Fe-Al-Mn@chitosan composite has shown 47.6 % fluoride removal within 1 min of contact time while Fe-Al-Mn oxyhydroxides without chitosan has shown only 22.6 % fluoride removal (Fig. 4c).

Due to higher porosity of Fe-Al-Mn@chitosan composite, the mass transfer rate of fluoride ions from bulk to the composite surface was much higher compared to mixed-metals oxyhydroxides alone. The better fluoride removal performance of Fe-Al-Mn@chitosan might be due to the homogeneous dispersion of Fe-Al-Mn oxyhydroxides within the highly porous chitosan matrix (Fig. 2). This finding was further supported by nitrogen adsorption/desorption isotherms and the DFT average pore diameters of mixed metal loaded chitosan composite (Fig. 5a) and Fe-Al-Mn oxyhydroxides (Fig. 5b). Fe-Al-Mn@Chitosan exhibits higher BET surface area (41.6 m$^2$/g) as compared to Fe-Al-Mn oxyhydroxides (21.1 m$^2$/g). Pore volumes of these two adsorbents were 0.019 and 0.022 mL/g, respectively. DFT average pore diameter of Fe-Al-Mn@chitosan composite and Fe-Al-Mn were found to be as 0.92 and 1.19 nm, respectively. As the radius of F$^-$ is 0.133 nm which makes it possible for fluoride to penetrate into pores of both of the adsorbents (Chen et al., 2010).
Fig. 5S (elemental mapping of spent adsorbent) also revealed that fluoride ions were evenly distributed inside composite matrix. Homogeneous dispersion of mixed-metal oxyhydroxides in Fe-Al-Mn@chitosan prevents the agglomeration among the nanoparticles (Fig. 2) and exposes more active sites for fluoride adsorption than agglomerated Fe-Al-Mn mixed-metal oxyhydroxides composite.

Nanoporous morphology of chitosan matrix might also facilitate faster diffusion of fluoride ions inside of the adsorbent matrix when compared to mixed metal oxyhydroxides adsorbent in the absence of chitosan polymer. Based on the comparative study, the Fe-Al-Mn@chitosan composite emerged as the superior adsorbent for fluoride ions and hence, was considered for subsequent study.

![Figure 4](image)

**Fig. 4:** a) pH ZPC of virgin and spent Fe-Al-Mn@chitosan composite, b) Comparative study on fluoride removal performance and c) fluoride removal with time using Fe-Al-Mn@chitosan and Fe-Al-Mn adsorbents.
Fig. 5: N\textsubscript{2} adsorption/desorption isotherm and DFT pore diameter of Fe-Al-Mn@chitosan composite (a) and Fe-Al-Mn oxyhydroxide (b).

### 3.3 Fe-Al-Mn@chitosan dose, initial solution pH and pH\textsubscript{ZPC} effect

Effect of Fe-Al-Mn@chitosan dose and initial pH was investigated to identify optimum condition for batch adsorption study. Fe-Al-Mn@chitosan shows maximum adsorption capacity at 0.5 g/L dose (Fig. 6a) and was considered as the optimum dose in the subsequent study. Fig. 6b shows that initial pH has no significant effect on adsorption from initial pH 3.4 to pH 8. Fig.6b shows that fluoride removal performance of the composite is affected by the increase in pH only beyond pH 8. The effect of pH\textsubscript{ZPC} has been discussed in supplementary information.

Table 1: Equilibrium adsorption isotherm constants for Fe-Al-Mn@chitosan composite and comparison between different kinetic parameters for fluoride adsorption.
3.4 Adsorption isotherm and thermodynamic feasibility studies

Experimental maximum adsorption capacities of Fe-Al-Mn@chitosan composite at 283 K, 298 K, and 313 K were found to be 35.6, 39, and 41 mg/g, respectively. Experimental data obtained from fluoride removal experiments were used to fit Langmuir (Langmuir, 1918), Temkin (Foo & Hameed, 2010) and Freundlich (Freundlich, 1906) isotherm models. Table 1 and Fig. 6c show that fluoride adsorption using Fe-Al-Mn@chitosan adsorbent at room temperature (298 K) follow Freundlich isotherm model ($R^2 = 0.99$) with following descending order of fitting, i.e.,

Freundlich isotherm model $>$ Temkin isotherm model $>$ Langmuir isotherm. Adsorption isotherm modelling suggests multilayer adsorption on the heterogeneous surface (heterogeneity developed through mixed-metal oxides: surface active sites with varying energy levels). This finding was also supported by Temkin model fitting ($R^2 = 0.98$) which states that free energy in sorption process works as a function of adsorbent surface remaining available and after initial sorption chances of adsorption reduce, and later stage it takes place on the non-uniform surfaces. In this

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Langmuir isotherm data</th>
<th>Freundlich isotherm data</th>
<th>Temkin Isotherm data</th>
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<tr>
<td></td>
<td>$Q_m$</td>
<td>$b$</td>
<td>$R^2$</td>
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<td>298</td>
<td>40.5</td>
<td>0.17</td>
<td>0.97</td>
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<table>
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<tr>
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<th>Pseudo first order kinetic data</th>
<th>Pseudo second order kinetic data</th>
<th>Intraparticle diffusion model kinetic data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$(mg/g)</td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>16.9</td>
<td>15.54</td>
<td>0.84</td>
<td>0.95</td>
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</tbody>
</table>
study, the thermodynamic feasibility of fluoride removal process was also investigated. Standard free energy ($\Delta G^0$) was found to be -18.33, -20, -22.09 KJ/mol at 283 K, 298 K and 313 K, respectively which indicates that adsorption is spontaneous and thermodynamically favourable (Table 2S).

Van’t Hoff Plot (Fig.6S) was used to calculate standard enthalpy and standard entropy change. Table 2S shows the changes of standard enthalpy (17.06 kJ/mol) and entropy (124.5 J/mol.K) in this adsorption process. $\Delta H^0$ predicts fluoride removal process is endothermic and favourable to adsorption, while $\Delta S^0$ predicts the thermodynamically favorability. Process performance of Fe-Al-Mn@chitosan composite was also compared with other materials such as mixed-metal, clay-based composites and single metal-oxide based chitosan adsorbent (Table 2) and studied material here was found much superior.

3.5 Adsorption kinetics study

Fe-Al-Mn@chitosan composite has shown very fast fluoride adsorption kinetics. It removes more than 50% of the initial fluoride ions ($C_0$: 10mg/L) within 1 min while equilibrium was achieved within 45 min. Pseudo-first order (Lagrgren, 1898), pseudo-second order (Ho & McKay, 1999), and intraparticle diffusion models were fitted. Graphs obtained and model best fitting parameters have been shown in Fig. 7a-b and Table 1, respectively. Further, the adsorption kinetics depends on both loadings of adsorbent and adsorbate concentration. Best fitting of pseudo-second order kinetic model ($R^2 = 0.99$) indicates that the fluoride removal mechanism is
chemisorption in nature (Wanga et al., 2017). Experimental $Q_m$ (16.9 mg/g), observed during kinetics, was very close to pseudo-second order predicted $Q_m$ (16.6 mg/g).

In intra-particle diffusion model fitting ($q_t$ vs $t^{1/2}$), a linear plot is indicative of one governing mechanism while, multi-linearity implies that the adsorbate removal process is governed by multiple mechanisms (Fierro, Fernandez, Montane, & Celzard, 2008). Fig. 7b shows that intraparticle diffusion model fitting was represented by two straight lines which imply that the removal on the heterogeneous adsorbent surfaces is governed by more than one mechanism. As shown in Table 1, intra-particle pore diffusion constants for first and second step were 3 and 0.67 mg/g min$^{1/2}$ respectively. Initially in first step, fluoride adsorption might occur rapidly through film diffusion by external mass transfer control while in second step intraparticle or diffusion might be a contributing mechanism for fluoride removal (Wanga et al., 2017). In the first step, the external mass transfer is faster as the concentration difference of fluoride between bulk and adsorbent pore surfaces is higher. So the slope of the first step is much higher compared to the second step.

### 3.6. Effect of competing ions and desorption study

As it is known that groundwater contains various ions. Anions (phosphate ($\text{PO}_4^{3-}$), sulphate ($\text{SO}_4^{2-}$) and bicarbonate ($\text{HCO}_3^-$)) may hinder fluoride removal. So, effect of these anions (10 mg/L) on fluoride removal capacity of Fe-Al-Mn@chitosan composite was also investigated. In presence of competitive ions, Fe-Al-Mn@chitosan composite exhibited excellent fluoride removal performance. No significant effect of negative competitive ions on Fe-Al-Mn@chitosan composite was observed even in the presence of positive ions (iron, magnesium), a slight higher fluoride removal was observed probably due to increase in overall positive surface charge after adorption of multivalent cations ($\text{Mn}^{2+}$)(Fig. 7c). Desorption study carried out using basic solution having pH 12.4 and 90% desorption was achieved, but fluoride removal performance of spent adsorbent was reduced to 70 to 80% in two successive adsorption/desorption cycles compared to the fresh adsorbent capacity ($C_0$: 10 mg/L).
3.7 Fluoride removal from groundwater samples

Initially, all experiments were carried out with double distilled water having an initial pH 6.7 and zero ionic strength solution. The Fe-Al-Mn@chitosan composite material was also applied to remove fluoride from drinking water (initial pH 7.6 and conductivity 250 μs/cm) spiked with fluoride concentration to 5 mg/L. Groundwater may contain a high concentration of competitive ions, so the feasibility of developed adsorbent in real water was also examined. As shown in Fig. 7d, at 1.3 g/L Fe-Al-Mn@chitosan dose, equilibrium concentration ($C_e$) was within the maximum acceptable limit. To estimate the leaching of various metals in treated water, treated water was analyzed using ICP-OES. As shown in Table 4S in SI, Fe, Al, Mn concentrations were found to be below the maximum permissible limit specified by BIS -2015 (Bureau of Indian standards) for drinking water. It reveals that Fe-Al-Mn@chitosan adsorbent developed in the present study can be used to remove from real fluoride contaminated groundwater.
Table 2. Comparison of Fe-Al-Mn@chitosan composite with other materials.

3.8. Fluoride removal mechanism

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylated Chitosan</td>
<td>11.11</td>
<td>(Viswanathan et al., 2009)</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1.39</td>
<td>(Sahila et al., 2007)</td>
</tr>
<tr>
<td>Al-Chitosan</td>
<td>1.7</td>
<td>(Swain et al., 2009)</td>
</tr>
<tr>
<td>Fe-Chitosan</td>
<td>15.38</td>
<td>(Viswanathan et al., 2008)</td>
</tr>
<tr>
<td>Ca-Al-La</td>
<td>29.3</td>
<td>(Xiang et al., 2014)</td>
</tr>
<tr>
<td>Laterite soil</td>
<td>0.5</td>
<td>(Iriel et al., 2018)</td>
</tr>
<tr>
<td>Mn2+ bentonite</td>
<td>2.4</td>
<td>(Mudzielwana et al., 2018)</td>
</tr>
<tr>
<td>La3+ bentonite/Chitosan beads composite</td>
<td>2.31</td>
<td>(Yi et al., 2014)</td>
</tr>
<tr>
<td>Fe-Al-Mn@chitosan (prepared using Laterite and Industrial waste as raw materials)</td>
<td>40±0.5</td>
<td>Present study</td>
</tr>
<tr>
<td>Fe-Al-Mn (after excluding chitosan matrix)</td>
<td>55±0.5</td>
<td>Present study</td>
</tr>
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XPS and FTIR analysis of the virgin and spent adsorbents were performed to determine the fluoride removal mechanism in the present study. Comparisons of XPS spectra obtained from virgin and spent adsorbent have been shown in Fig. 8a which confirms the loading of fluoride on mixed-metal oxyhydroxides loaded chitosan composite adsorbent. The Deconvoluted curves of C1s for fresh Fe-Al-Mn@chitosan composite adsorbent was found to be in good agreement with XPS spectra of chitosan with two small peaks (283.9 eV and 285.4 eV) (Zheng et al., 2009) (Fig. 8c) and the slight increase in binding energy from 286.9 eV (for –OH) to 287.06eV was observed for fresh Fe-Al-Mn@chitosan composite adsorbent compared to chitosan alone which might be due to the formation of the organometallic compound (C-O-M). This finding was also confirmed via analysis of the FTIR spectrum of fresh adsorbent. In the FTIR spectra of chitosan, the absorption band at 3426 cm⁻¹ can be seen which is corresponding to stretching vibrations of NH₂ and OH functional groups. This band disappeared in Fe-Al-Mn@chitosan composite and reappears at 3135, and 3032 cm⁻¹ which reveal that NH₂, OH and metal complexation can not be ruled out (Wang, Du, Fan, Liu, & Hu, 2005).
The chitosan FTIR spectrum at 1636 cm\(^{-1}\) was slightly relocated to 1552 cm\(^{-1}\) in Fe-AL-Mn@chitosan composite. This shifting and reappearance of absorption bands in both cases reveal that this is not a simple mixture of mixed-metal oxyhydroxides and chitosan; rather it might be because of the formation of multi-centered metal hydroxyl functional groups. Fig. 8c-d showed lowering the peak intensity of –NH\(_2\) using the high-resolution XPS scan of spent adsorbent. Comparative densities of the functional group correspond to the relative area of sub-peaks have been explored previously (Dhillon, Sapna, Choudhary, Kumar, & Prasad, 2018). So decrease in NH\(_2\)-sub-peak intensity might be due to adsorption of F\(^-\) ions with NH\(_2\). This finding was further confirmed by deconvolution of Fls in the spent adsorbent. As shown in Fig. 8b, a high-resolution scan of Fls shows three sub-peaks. The sub-peaks of Fls at 684, 687.8 and 689.9eV binding energy confirm the formation of metal-F (Wagner, Riggs, Davis, Moulder, & Muilenberg, 1979), Aluminum tri fluoride AlF\(_3\) (Kemnitz, Kohne, Grohmann, Lippitz, & Unger, 1996) and organopolymeric compound (Clark, Feast, Kilcast, & Musgrave, 1973). The metal-F bond formation might be formed between Mn and fluoride ions by replacing –OH bond. Deconvolution of Fls also reveals that chitosan bound aluminium and MnO\(_2\) contribute significantly to remove fluoride by making possibly aluminium trifluoride and Mn-F bond. The role of OH groups is investigated in the fluoride removal process through comparative study of the O 1s spectrum of virgin and spent adsorbent (Fig. 8e-f). It shows the three peaks of O1s spectrum, one assigns to metal oxide (M-O-M) and other two assign metal oxide bounded to hydroxyl functional group (M-OH) and adsorbed water (H\(_2\)O) respectively (Wang et al., 2013). As shown in Fig. 8e–f, the area covered by hydroxyl functional group (M-OH) decreases (from 62 % to 45 %) after fluoride adsorption which indicates that fluoride exchanges with metal hydroxyl group might be the main mechanism of the fluoride removal in this study.
Fig. 8. XPS spectra of virgin and spent mixed metal loaded chitosan composite (a), fluoride 1s of spent adsorbent (b), C1s for virgin (c) and spent adsorbent (d), O1s for virgin (e) and spent adsorbent (f).

4. Conclusions

The fluoride removal performance of hydrous metal oxides Fe-Al-Mn@chitosan composite was compared with Fe-Al-Mn mixed-metal oxyhydroxides. The Fe-Al-Mn@chitosan based composite material was found to be superior in terms of both adsorption capacity as well as adsorption rate. Better dispersion of mixed-metal oxyhydroxides in the porous chitosan matrix and probable metallic-organic complexation were the main reasons for the excellent fluoride adsorption behaviour of Fe-Al-Mn@chitosan composite material compared to mixed-metal oxyhydroxides alone. In the absence of chitosan matrix, the agglomeration of nanoparticles cannot be ruled out which is the main reason for inferior fluoride adsorption behaviour of the mixed-metal oxyhydroxides. A detailed study on Fe-Al-Mn@chitosan composite reveals that prepared material was very effective for broad pH range of 3.5 to 8.5 and shows minimal effect of competitive anions. Experimental data was found better fitted with the Freundlich isotherm model ($R^2 = 0.99$) with following the descending order i.e., Freundlich isotherm model $>$ Temkin
isotherm model > Langmuir isotherm. Adsorption isotherm modelling suggests that multi layered fluoride adsorption is taking place on the heterogeneous adsorbent surfaces. Fluoride removal using composite materials followed pseudo-second order kinetics. This process was found to be thermodynamically feasible and endothermic. Adsorption results confirm that the hydrous Fe-Al-Mn mixed-oxide chitosan composite is capable of removing fluoride from the water quite efficiently and can be used as a fluoride scavenging material in a household filter. Further, the composite spent adsorbent can be easily separated from the aqueous medium after use due to its larger particle size. The pressure drop in fixed bed column application would be very low, hence overhead tank could be sufficient to obtain desire flow rate of treated water through fixed bed column. The chitosan polymer is not making just a support material to make homogenously dispersion of nano-particle within it, an interaction among functional groups like amine with inorganic metals oxides has been revealed through XPS study. The interactions between polymeric materials and inorganic composite largely help to improve the overall scavenging capacity of composite materials. Study suggests that Fe-Al-Mn@chitosan can efficiently remove fluoride from contaminated groundwater.

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References


