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# A low cost approach to synthesize sand like AlOOH nanoarchitecture (SANA) and its application in defluoridation of water



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# ABSTRACT

This paper describes a chitosan template assisted synthesis of nanocrystalline aluminium oxyhydroxide ( $\gamma$ -AlOOH) at an ambient temperature ( $30 \pm 2 \,^{\circ}$ C) and atmospheric pressure. High ability of the composite in removing fluoride from water has been demonstrated. The structural, morphological and compositional characteristics of the composite were studied using various spectroscopic and microscopic techniques. The results showed that the composite has nanoarchitecture comprising a number of  $\gamma$ -AlOOH nanoparticles of size less than 10 nm attached to the fibrils of chitosan. Batch and continuous flow adsorption experiments were conducted to assess the parameters that influence the adsorption process. The parameters investigated include contact time, initial fluoride concentration, adsorbent dose, pH of the solution, co-existing ions in water, and size of the adsorbent granules. The composite showed good affinity to fluoride and the maximum uptake capacity was 13.47 (mg/g) (mg/L)<sup>-1/n</sup> as described by Freundlich isotherm model. The kinetics of adsorption was affected by the size of the granules and the kinetic data followed pseudo-second-order rate equation. Except bicarbonate and sulfate, other competing ions studied did not affect the uptake of fluoride significantly. The high affinity to fluoride, simple and eco-friendly synthesis approach demonstrate the utility of the material for defluoridation of water.

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# Introduction

Fluorosis is a chronic menace affecting large populations across the world [1]. According to statistics, in India, more than 25 million people are affected by fluorosis and approximately 66 million people are at the risk of being affected [2]. Owing to the wide spread occurrence and adverse health impact on humans, many technologies have been developed to remove fluoride from contaminated water [3,4]. Adsorption onto activated alumina (AA) is one among them and is a widely accepted technology in the field [5,6]. However, issues like low fluoride adsorption capacity, competition from other ions, poor kinetics, energy intensive synthesis and difficulty in granulation need to be addressed to improve its practical utility.

Recent studies show that many issues related to the practical application of bulk materials like AA can be improved using nanoscale materials. Nanoparticles (NPs) are one of the important building blocks in the fabrication of nanoscale materials. The large surface area and unusual electronic structure provides new properties to nanoscale materials [7]. To obtain the desired characteristics, nanoscale alumina and other aluminium based oxides with different size, shape and structures have been synthesized. An excellent review on different mesoporous alumina (MA) and their characteristics is reported by Márguez-Alvarez et al. [8]. Lee et al. [9] reported that MA synthesized through the surfactant-assisted route is superior to the commercial AA in removing fluoride from water. Li et al. [10] have synthesized highly ordered MA and calcium-doped alumina through sol-gel route using triblock copolymer Pluronic P123 as the soft template. The materials showed fluoride adsorption capacity as high as 450 mg/g [10]. A recent study by Wang et al. [11] showed that nanoscale AlOOH, a common starting precursor for preparing nanoscale Al<sub>2</sub>O<sub>3</sub>, has fluoride adsorption capacity (3.25 mg fluoride/g of AlOOH) comparable to that of the bulk AA. The preparation of AlOOH is less energy intensive compared to that of Al<sub>2</sub>O<sub>3</sub>. This makes nanoscale AlOOH a good candidate for defluoridation of water. A lot of work has been done on developing various

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nanostructures of AlOOH including nanowires, nanoplates, nanobelts [12,13], nanotubes [14,15], nanofibers [16], nanoflowers [17], nanoflakes [18], and nanosheets [19] by different methods. In these methods, the syntheses are done at hydrothermal conditions at temperatures above 100 °C using non-eco-friendly chemicals such as surfactants [12–19]. This would hamper the large-scale use of the material for application like water defluoridation.

Besides, the purification of water using NPs in powder form have the following practical limitations: (i) low hydraulic conductivity in packed bed, (ii) difficulty in solid/liquid separation in batch operation, (iii) danger of escape of the NPs along with the treated water, and (iv) possible aggregation of NPs due to various ions present in water and reduction in performance. The above limitations are overcome by anchoring the NPs on a suitable matrix or by granulating the NPs using an appropriate binding agent [20–23]. However, such immobilization techniques may reduce the performance due to interactions between the NPs and the supporting matrix. The sustained retention of the NPs in the matrix is also difficult. Maliyekkal et al. [24] reported that a minimum granule size of 0.3 mm is desirable to reduce operational problems in packed-bed adsorption columns. From the review of the literature, it is apparent that though nanoscale materials show enhanced fluoride adsorption capacity, their success in the field is largely decided by the ease of large-scale synthesis, solid-liquid separation, post-treatment handling, and the cost.

In this study, we demonstrate the high defluoridation capacity of nanocrystalline AlOOH–chitosan composite synthesized via a low cost and eco-friendly approach. The synthesis was done at an atmospheric pressure and at room temperature using chitosan as the template. The template (chitosan) is used because of its high ability of complexation with metal ions. This property helps in reducing the possible agglomeration of the particles during synthesis. The study also demonstrates a green and *in-situ* approach to granulate nanocrystalline AlOOH without the aid of external physical or chemical binding agents. Chitosan fibers are responsible for binding the particle together and form a granular nanoarchitecture. The ability to synthesize stable, granular, nanocrystalline AlOOH composite at room temperature may find wide application for adsorption-based water defluoridation.

# Materials and methods

#### Chemicals

Aluminium nitrate (LR), aluminium chloride (LR), and ammonia (AR) were purchased from Thomas Baker, India. Chitosan flakes were procured from Pelican Laboratories, Kerala, India (detailed specification as obtained from the manufacture is given in Table S1 of Supporting Information (SI)). Stock solution of fluoride (1000 mg/L) was prepared from sodium fluoride (Thomas Baker, India). Samples of required concentrations of the fluoride solutions were prepared by serial dilutions. All chemicals were used as received without further purification. Reagents were prepared in deionized water and adsorption studies were conducted using treated water from a reverse osmosis (RO) plant.

#### Synthesis and granulation of chitosan-AlOOH composite

A soft-chemical synthesis procedure was used to prepare nanocrystalline AlOOH at room temperature and atmospheric pressure. For this, 50 mL of 1 M solution of aluminium nitrate was added slowly into 50 mL of 1% chitosan solution while stirring. After the addition of aluminium nitrate, the stirring was continued for 1 h. Aqueous ammonia (5 M) was added slowly into the aluminium-chitosan complex solution to facilitate the precipitation of the AlOOH-chitosan composites. The precipitation was carried out at three different pHs ( $6\pm0.2$ ;  $7\pm0.2$ ; and  $8.2\pm0.2$ ). The precipitate was separated using a filter cloth, then washed to remove impurities, and dried at various temperatures (30-100 °C). The dried materials were ground to the required granule-size range and stored in clean polypropylene (PP) bottles for further use. The prepared material is similar in appearance to sand and is named as SANA (sand like AlOOH nanoarchitecture).

#### Material characterization

The identification of the phase(s) of the pristine SANA and SANA after contact with fluoride was carried out by X-ray powder diffraction using Cu-K $\alpha$  radiation at  $\lambda$  = 1.5418 Å (Bruker AXS, D8 Discover, USA). A scan step of 1s and step size of 0.10 (in  $2\theta$ ) was applied to record the patterns in the range from 10 to  $90^{\circ}$  (2 $\theta$ ). Surface morphology, elemental analysis and elemental mapping studies were carried out using a scanning electron microscope (SEM) equipped with energy dispersive analysis of X-rays (EDAX) (FEI Quanta 200). high resolution transmission electron microscopy (HRTEM) images of SANA were recorded with JEM 3010 (JEOL, Japan). Samples were spotted on amorphous carbon films supported on copper grids and dried at ambient conditions. Xray photoelectron spectroscopic (XPS) analysis was done using ESCA Probe TPD of Omicron Nanotechnology. Polychromatic Mg K $\alpha$  was used as the X-ray source (*hv* = 1253.6 eV). Spectra were collected in the required binding energy range and an average was taken. X-ray flux was adjusted to reduce the beam-induced damage on the sample. Binding energies were calibrated with respect to C 1s at 284.5 eV. Attenuated total reflectance infrared (ATR-IR) spectra of pristine SANA and SANA after contact with fluoride were collected (650–4000 cm<sup>-1</sup>) using Spectrum 100 (PerkinElmer, USA).

# Adsorption studies

The batch adsorption studies were performed in 250 mL PP conical flasks at room temperature  $(30 \pm 2 \circ C)$ . The working volume of the solution was fixed at 100 mL and required quantity of the SANA was added. The flasks were shaken at  $80 \pm 5$  rpm in an orbital shaker (Remi Instruments, India). Samples were withdrawn at predetermined time intervals and analyzed for residual fluoride concentration. Fluoride analyses were carried out using ion chromatography (IC, Basic Plus, Metrohm). Time dependent adsorption studies were done at two fluoride concentrations of  $\sim$ 10 and  $\sim$ 5 mg/L. The kinetic studies were performed using two different size ranges of granules of SANA (i.e., <0.3 mm and 0.3–1.18 mm). Isotherm studies were performed at a neutral pH  $(7\pm0.2)$  and at room temperature. The fluoride concentrations were varied over a range of  $\sim$ 5–90 mg/L. Defluoridation studies were also carried out as a function of pH, adsorbent dose, and size of the adsorbent granules. The pHs of the samples were adjusted using dilute NaOH or HCl solutions. Except kinetics, all adsorption studies were conducted at an equilibrium condition, at neutral pH, at an initial fluoride concentration of  $\sim$ 10 mg/L, and at the granule size range of 0.3-1.18 mm, unless otherwise specified.

Continuous removal of fluoride by SANA was studied in fixed-bed glass columns (length = 400 mm; internal diameter = 20 mm). The photographic image of the reactor setup is shown in Fig. S1 of the SI. The columns were initially saturated with fluoride to avoid any possible adsorption by glass. The studies were performed at two adsorbent bed heights of 4 and 8 cm in the down-flow mode. The feed-flow rate was maintained at  $\sim$ 3 mL/min (0.57 m<sup>3</sup>/m<sup>2</sup>/h). The results were compared with that of AA (grade: AD 101F).

#### **Results and discussion**

#### Material synthesis

# Effect of drying temperature

The schematic diagram of the formation of SANA is shown in Fig. 1A. The photographs of the sample dried at various temperatures are given in Fig. 1B. The results show that SANA is sensitive to the drving temperature. An inverse relationship was observed between drying temperature and the stability of SANA in water. The sample dried at an ambient temperature  $(30 \pm 2 \degree C)$  showed an excellent stability and no sign of disintegration for prolonged soaking in water (>60 days). On the contrary, the samples dried at higher temperatures (>50 °C) disintegrated within 24 h of soaking in water. The stability of the SANA in water as a function of drying temperature was quantified using a factor called swelling index (SWI). For estimating SWI, a known quantity of the sample was immersed in deionized water (conductivity  $< 10 \,\mu$ S) for 24 h under ambient condition. The sample was filtered carefully and blotted with filter paper followed by blowing with nitrogen (5 min) to remove surface absorbed water. The mass of the saturated and the surface dried samples were determined. SWI is calculated using Eq. (1) and the data are presented in Fig. 1C.

SWI (%) = 
$$\left(\frac{M_{\rm w} - M_{\rm d}}{M_{\rm w}}\right) \times 100$$
 (1)

where  $M_d$  and  $M_w$  are dry and wet mass (g) of the adsorbent, respectively; SWI is the percentage of the water absorption

capacity of the material. From the data, it is clear that there is a direct relationship with drying temperature and the percentage water absorption. Higher the temperature, more is the water absorption capacity of SANA. This behavior is due to the presence of chitosan in the material. Chitosan in solution exists in the form of quasi-globular conformation stabilized by extensive intra- and inter-molecular hydrogen bonding [25]. The hydrogen bonding in chitosan chains is due to the presence of the amine and hydroxyl groups. The number of intermolecular hydrogen bonds affects the rigidity of the polymer [26]. The extent of dissociation of the hydrogen bonds plays an important role in the swelling behavior of the chitosan. At pH below  $pK_a$  (chitosan is a weak base with a  $pK_a$  of around 6.4), the hydrogen bonding dissociates due to the protonation of the  $NH_2$  groups to  $NH_3^+$ . The cationic ammonium ion in the protonated chitosan makes the fibers repel each other, leading to more swelling. At a higher temperature, it is likely that more of the hydrogen bonds break, leading to greater degree of swelling and hence disintegration of the granules.

#### Effect of synthesis pH

pH plays an important role in deciding the surface charge and the adsorption of fluoride by SANA. Synthesis pH can also affect the settling characteristics of the product (AlOOH–chitosan composite gel). These two aspects were investigated in this study. It was observed that the material synthesized at pH  $8.2 \pm 0.2$  and above showed lesser fluoride uptake capacity compared to the material synthesized at lower pHs (pHs  $7.2 \pm 0.2$  and  $6.2 \pm 0.2$ ). This can be attributed to the possible change in the surface charge of the



**Fig. 1.** (A) A schematic representation showing the formation of AlOOH–chitosan composite. Inset shows the photographs of the composite gel synthesized at various pHs. (B) SANA produced at various drying temperatures ('a': surface dried at room temperature (RT); 'b': oven dried at  $50 \pm 2$  °C, 'c': oven dried at  $60 \pm 2$  °C; 'd': oven dried at  $105 \pm 2$  °C). (C) The stability of granules of SANA (produced at various drying temperatures) after 24 h soaking in water.

adsorbent. At higher synthesis pH ( $8.2 \pm 0.2$ ), it is likely that the surface of the product will be more negative and thus show less affinity towards anions such as fluoride. However, no significant change in adsorption capacity was observed between the materials synthesized at pH 7 and pH 6.

On the other hand, at pH 7 and above, the products showed rapid settling compared to the composite synthesized at the acidic pH (data are shown in the inset of Fig. 1C). Hence, unlike conventional NPs, no expensive filtration or centrifugation is needed to separate the product from the aqueous medium. The enhanced settling may be due to the attached AlOOH NPs on the fibrils of the protonated chitosan. Further, high degree of cross-linking of the chitosan at an elevated pH would have resulted in the formation of dense floc (gel) and hence, accelerated the settling characteristics. It is known that the increase in pH enhances deprotonation, and the amino groups on the chitosan become more available for H-bridges. At a critical pH value, the chitosan molecules develop sufficient H-bridges to give rise to a gel [27].

# Material characterization and mechanistic details of surface binding

The SEM and HRTEM analyses were carried out to understand the structure and morphology of SANA. HRTEM images (Fig.  $2A_1$ and  $A_2$ ) show that each microarchitecture is constructed of a number of nanoparticles of size <10 nm and they align themselves to form a structure similar to peppercorn. The fibrils are due to the chitosan and the particles are due to the AlOOH nanoparticles. Fig. 2B shows the EDAX spectrum of SANA after exposure with water containing dissolved fluoride. The spectrum confirms the presence of adsorbed fluoride along with the principal elements, Al and O. The EDAX and elemental mappings of the pristine SANA are shown in Fig. S2 of the SI. From the elemental map, it is clear that the principal elements, Al and O are uniformly distributed. This indicates the formation of a composite.

The XRD pattern of the biopolymer template, chitosan, is shown in Fig. 3A. The figure shows two distinctive peaks ( $2\theta$  = 10.5 and



**Fig. 3.** (A) XRD patterns of pristine SANA and fluoride adsorbed SANA. (B) XRD patterns of chitosan used in the study. (C) ATR-IR spectra of pristine SANA and fluoride adsorbed SANA. (D) Expanded view of the 650–2000 cm<sup>-1</sup> spectral region. 'a': represents pristine SANA and 'b' represents fluoride adsorbed SANA. The traces are shifted vertically for clarity. Inset of panel B shows the standard index planes of orthorhombic-AlOOH (JCPDS#21-1307).

20.1°) of chitosan prepared from shrimp shells. These peaks are typical fingerprints of semi-crystalline chitosan and can be attributed to the crystal I and crystal II in chitosan structure [28,29]. The XRD patterns of SANA before and after contact with fluoride are shown in Fig. 3B. The material shows broad peaks corresponding to (020), (120), (031), (200), (231) and (251) planes. The peaks are indexed as orthorhombic-AlOOH (JCPDS 21-1307). The broad XRD patterns show that the size of AlOOH particle is in the nanoregime. The XRD patterns also show that the material retains its phase purity even after fluoride adsorption. The



**Fig. 2.** A<sub>1</sub> and A<sub>2</sub> show HRTEM images of SANA at two different magnifications. Schematic representation of the AlOOH nanoparticles embedded onto the fibrils of chitosan is shown in the inset. (B) EDAX spectrum of fluoride adsorbed SANA. Inset shows the elemental composition of SANA (right to panel A<sub>2</sub>).

standard index-planes of orthorhombic-AlOOH (JCPDS 21-1307) are also shown to validate the structure of the sample (inset of Fig. 3A). A change in the intensity pattern can be seen by comparing the index-planes of the standard and the SANA. This can be due to the effect of the chitosan template. The shoulder peak at ~20.2° (2 $\theta$ ) is due to the chitosan in the sample. Unlike the standard sample, the intensity of the higher index planes is more in SANA. Studies have shown that the high-index planes exhibit much higher catalytic activity than that of common and stable low-index planes [30,31].

Fig. 3C shows the ATR-IR spectra of SANA and fluoride adsorbed SANA in the range  $650-4000 \text{ cm}^{-1}$ . An enlarged view of the  $650-2000 \text{ cm}^{-1}$  spectral region is shown in Fig. 3D. All the absorption bands are consistent with literature values of  $\gamma$ -AlOOH [13,15]. The band at  $1642 \text{ cm}^{-1}$  and the broad band at  $3426 \text{ cm}^{-1}$  can be ascribed to the bending and the stretching modes of adsorbed water. The broad shoulder bands at  $3100 \text{ and } 3310 \text{ cm}^{-1}$  are assigned to OH stretching vibrations. The bands at  $1073 \text{ and } 1155 \text{ cm}^{-1}$  are due to the symmetric and asymmetric stretching frequencies of Al–O–H.

The XPS survey spectra of the material before and after fluoride adsorption are shown in Fig. 4A. These spectra clearly show the existence of adsorbed fluoride along with the key elements Al, O, C and N of the composite. The presence of N is due to chitosan and Al and O are due to AlOOH. The new F 1s peak in SANA after contact with fluoride is due to adsorbed fluoride. For understanding the chemical form of the pristine and fluoride adsorbed SANA, detailed scans of specific regions of key elements (Al 2p, O 1s) and adsorbed element (F 1s) were carried out and are shown in Fig. 4B-D. The spectrum of Al 2p shows a peak at 74.4 eV, which is in agreement with Al in AlOOH. Though pristine and fluoride adsorbed sample do not show significant shift in the position of the center of the peaks (Al 2p), it is clear that Al 2p peak area increased after fluoride adsorption, indicating the merging of more than one peak. On convolution, we could clearly see two peaks, one centered at 74.4 eV and another centered at 75.1 eV. The lower binding energy peak is due to Al in AlOOH and higher biding energy peak is due to Al is AlF. This ligand exchange is one of the reasons for removal of fluoride and the reaction is shown in chemical Eq. (R1) [10,11]. A



**Fig. 4.** XPS spectra of pristine SANA and fluoride adsorbed; panel 'A' shows the survey spectra. Panels 'B–D' show the spectra of various regions (Al 2p, and O 1s). 'a' represents pristine SANA and 'b' represents fluoride adsorbed SANA. Inset of 'C' shows the spectrum of F 1s. 'a' represents pristine SANA and 'b' represents fluoride adsorbed SANA.

reduction in the surface positive charge is seen in O 1s, as a result of which it appears at a lower binding energy. This may be due to the exchange of fluoride with hydroxyl group and possible formation of AIF.

$$AI - OH + H^+ + F^- \leftrightarrow \equiv AIF + H_2O \tag{R1}$$

The spectroscopic and microscopic studies show that the current synthetic approach yields nanocrystalline AlOOH at room temperature and atmospheric pressure. Interestingly, most of the reported syntheses of nanoscale AlOOH are done in hydrothermal conditions at temperatures above 373 K [13,16,18]. The formation of nanocrystalline AlOOH at room temperature may be due to the presence of large oxygen dense functional group in protonated chitosan. These groups (-O - and - OH) act as nucleation centers for the formation of AlOOH nanocrystals [32]. Maliyekkal et al. [33] have reported that the presence of an oxygen dense template (cellulose) influences the oxidation state of manganese in the synthesis of nanoscale manganese oxides. In the presence of cellulose, manganese in manganese oxide was found in Mn(III) form. On the contrary, a higher oxidation state of Mn(IV) was observed when no cellulose was used as a template. These observations also suggest that oxygen dense templates like chitosan and cellulose can influence the mineral phases of metal oxide during synthesis.

In the adsorption process, an adsorbent in powder form offers several operational problems. Granulating the powder helps in reducing such problems. In the current synthesis, the use of protonated chitosan as a template also helped in granulating the AlOOH without any external physical or chemical agents. So, expensive pan coating or binding with polymers and heating can be avoided. Considering these factors, the developed synthetic approach is simple, less energy intensive and green compared to the existing methods of synthesis of nanoscale AlOOH.

## Fluoride adsorption studies

In order to assess the fluoride uptake capacity of the material under various conditions, the following adsorption studies were conducted in batch and continuous fixed-bed reactors.

#### Effect of adsorbent dose

The effect of adsorbent dose on the removal of fluoride by SANA was studied and the data are shown in Fig. 5A. As expected, the adsorption increases with an increase in adsorbent dose up to a certain dose of adsorbent. This can be attributed to the increase in available reaction sites due to an increase in the dose of SANA. On further increase in adsorbent dose, no considerable change in fluoride uptake is observed. This less proportionate increase in fluoride adsorption may be due to the limited fluoride ions present as compared to the available adsorbent sites [34].

#### Effect of pH

pH of feed water plays a significant role in the adsorption of fluoride by metal oxides, since pH can influence the chemical speciation of the target pollutant as well as the surface properties of the adsorbent. This study was conducted to quantify the effect of pH on fluoride adsorption by SANA. The results of the study are shown in Fig. 5B. The data show that the adsorption of fluoride is more favored between pH 6–7 and a reduction in the uptake capacity is observed at pH below 5 and pH above 8.0. At higher pHs, the reduced uptake may be attributed to a greater competition from OH<sup>-</sup> ions for the active adsorption sites. Reversal of the surface charge of the adsorbent and thus, the repulsion of an anion like fluoride may be one of the reasons for the reduced uptake. The possible formation of HF may be the reason for the reduced uptake at a lower pH. Higher dissolution of



**Fig. 5.** (A) Effect of adsorbent dose on the removal of fluoride by SANA. Inset shows the photographs of SANA of different granules sizes (A<sub>1</sub> – granules sizes < 0.3 mm; B<sub>1</sub> – granules sizes between 0.3 and 1.18 mm). (B) Effect of pH on the removal of fluoride by SANA. (C) Pseudo-second-order kinetic plots for the adsorption of fluoride by SANA (granules sizes: <0.3 mm). D. Pseudo-second-order kinetic plots for the adsorption of fluoride by SANA (granules sizes: 0.3–1.18 mm); legend 'E' represents experimentally obtained data and 'P' represents model predicted data.

SANA at extreme pH values can also reduce the uptake. It is known that aluminium oxide is soluble in water under both acidic (pH < 4) and alkaline (pH > 9) conditions [35].

# Adsorption kinetics

The time dependent removal of fluoride by SANA is shown in Fig. 5C. The study was conducted at different granules sizes of SANA (0.3–1.18 mm and < 0.3 mm) and at initial fluoride concentrations of 4.9 and 9 mg/L. Irrespective of the size of the granules, fluoride removal was rapid in the initial contact period (Fig. S3 of the SI). However, in the case of smaller granules (<0.3 mm), the system reached pseudo-equilibrium in less than 2 h of contact time. In the case of bigger granules (0.3–1.18 mm), the system took around 5 h to reach pseudo-equilibrium.

Theoretically, adsorption kinetics is controlled by different mechanisms and it is essential to use mathematical models to better understand the adsorption process. In this regard, the data were analyzed using Lagergren pseudo-first-order [36] and Ho's pseudo second-order reaction rate [37] models. The mathematical representations of these models are given below. Pseudo-first-order equation:

$$q_t = q_e (1 - e^{-k_1 t})$$
(2)

Pseudo- second-order equation:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

where  $q_e$  and  $q_t$  (mg/g) are the amount of metal ion adsorbed at equilibrium and at time t (h), respectively.  $k_1$  (1/h) and  $k_2$  (g/mg/h) are the first-order and second-order rate constants, respectively.

Pseudo-second-order fits along with the experimental data are shown in Fig. 5C and D. The corresponding pseudo-first-order fits are shown in Fig. S4 of the SI. The kinetic parameters obtained from these model fits are summarized in Table 1. The model fits with pseudo-second-order equation is better as evident from low RMSE (root mean squared error) and Chi-square values ( $\chi^2$ ). The pseudosecond-order expression has been widely used to describe the adsorption of ions onto metal oxide surfaces [38]. The data also reveals that adsorption is faster in the case of smaller size granules.

#### Table 1

Estimated pseudo-first-order and second-order rate parameters for the adsorption of fluoride by SANA.

Model	Particle size (mm)	Fluoride concentration (mg/L)	k1 (L/min); k2 (g/mg/h)	q <sub>e</sub> (mg/g)	RMSE	$\chi^2$
Pseudo-first-order	<0.3	4.9	0.041	9.09	1.31	3.83
	0.3-1.18	4.9	0.032	9.23	0.58	0.68
		9.0	0.026	15.52	1.27	1.15
Pseudo-second-order	<0.3	4.9	0.012	9.66	0.52	0.32
		9.0	0.004	17.67	0.46	0.13
	0.3-1.18	4.9	0.005	9.94	0.41	0.26
		9.0	0.001	19.9	0.56	0.44

This may be attributed to increased exposure of active sites and a shorter diffusion route. This limitation may be overcome by introducing more structured pores in SANA through appropriate modification of the synthesis process. Further studies are required to prove the same.

#### Equilibrium studies

The equilibrium adsorption study of fluoride by SANA was carried out at  $30 \pm 2$  °C and at neutral pH. The initial fluoride concentration was varied over a range of ~5–90 mg/L. It was observed that with an increase in the initial fluoride concentration, fluoride adsorption capacity was increased. This may be due to the increase in the driving force provided by the concentration gradient. The data obtained from this study was analyzed using well known Langmuir [39], Freundlich [40] and Sips [41] isotherm models. The mathematical equations of the models are given below.

Langmuir model:

$$q_{\rm e} = \frac{q_{\rm L} b_{\rm L} C_{\rm e}}{1 + b_{\rm L} C_{\rm e}} \tag{4}$$

Freundlich model:

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{5}$$

Sips model:

$$q_{\rm e} = \frac{q(K_{\rm S}C_{\rm e})mS^{m_{\rm s}}}{1 + (K_{\rm S}C_{\rm e})^{m_{\rm s}}} \tag{6}$$

where  $q_e$  is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g);  $C_e$  is equilibrium concentration of the adsorbate in the solution (mg/L);  $K_F$  is the Freundlich isotherm constant ((mg/g)(mg/L) <sup>-1</sup>/n);  $q_L$ , and  $q_{mS}$  represent maximum



**Fig. 6.** (A) Comparison of various isotherm models for the adsorption of fluoride by SANA at room temperature (temperature  $-30 \pm 2$  °C). (B) Effect of various competing ions in water on the removal of fluoride by SANA.

specific uptake capacities at equilibrium of Langmuir and Sips isotherms, respectively (mg/g);  $b_L$ , and  $K_{S_c}$  are the Langmuir and Sips isotherm constants, respectively (L/mg);  $n_F$ , and  $m_S$  are Freundlich and Sips isotherm exponents, respectively.

Isotherm plots are shown in Fig. 6A. The isotherm parameters obtained from the models are summarized in Table 2. It is evident from the low RMSE and  $\chi^2$  values that the Freundlich equation is more appropriate to describe the experimental equilibrium data. Langmuir theory assumes that the surface of the adsorbent is homogeneous and may not be appropriate to predict the adsorption of fluoride on a heterogeneous surface like SANA. SANA showed around 17 times higher adsorption capacity compared to nanoscale AlOOH in removing fluoride from water [11].

#### Effect of co-existing ions

The effects of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup> and Fe<sup>3+</sup> on the fluoride uptake by SANA were studied. The Fig. 6B shows that the chloride, nitrate and cations studied have insignificant effect on fluoride removal by SANA. However, the bicarbonate and phosphate ions affected the fluoride uptake. To understand the effect of combination of ions on the fluoride uptake by SANA, the study was performed in tap water spiked with fluoride. The data (Fig. 6B) shows around 25% reduction in fluoride uptake capacity compared to the reference. This shows the feasibility of using the material in the field condition without significant compromise in the adsorption capacity.

#### Column experiment

The breakthrough profiles for SANA and AA are shown in Fig. 7A and B, respectively. As expected, at lower bed depths, the breakthrough curves were steeper for both AA and SANA, indicating a faster exhaustion of the adsorbent beds. This can be attributed to the different contact times available at various bed depths. At a lower bed depth, fluoride does not have enough time to diffuse into the adsorbent mass. The breakthrough data were analyzed using a well known kinetic model proposed by Thomas [42]. The model in its original form is given in Eq. (7).

$$\frac{C_t}{C_0} = \frac{1}{1 + e(k_{\rm Th}q_0m/Q - k_{\rm Th}C_0t)}$$
(7)

where  $C_0(\text{mg/L})$  is the feed concentration of the fluoride,  $C_t(\text{mg/L})$  is the outlet concentration of fluoride at time t(min),  $k_{\text{Th}}(\text{L/mg/min})$  is the Thomas adsorption rate, m (g) represents the mass of the adsorbent,  $q_0$  (mg/g) is the adsorption capacity and Q (mL/min) is the flow rate of the feed solution.

Table 2				
Isotherm parameters	obtained for	the adsorption	of fluoride	by SANA.

Isotherm model	Model parameters	Estimated parameters
Freundlich	$K_{\rm F} ({\rm mg/g}) ({\rm mg/L})^{-1/n}$ N RMSE $\chi^2$	13.47 2.26 4.51 2.80
Langmuir	$q_m (mg/g)$ b (L/mg) RMSE $\chi^2$	70.58 0.13 4.14 16.88
Sips	$q_m (mg/g)$ $K_s (L/g)$ mS RMSE $\chi^2$	91.40 0.067 0.74 3.62 5.01



Fig. 7. Comparison of experimental and Thomas model predicted breakthrough curves for the adsorption of fluoride by (A) SANA and (B) AA.

 Table 3

 Thomas model parameters obtained for the adsorption of fluoride by SANA and AA.

_	Adsorbent	Bed depth (cm)	C <sub>0</sub> (mg/ L)	Q (mL/ min)	k <sub>Th</sub> (L/mg/min)	q <sub>0</sub> (mg/ g)	<i>R</i> <sup>2</sup>
	SANA SANA AA	4.0 8.0 4.0	10.0 10.0 10.3	3.0 3.0 3.0	0.00007014 0.00004928 0.00060821	31.58 20.80 1.50	0.93 0.88 0.83
	AA	8.0	10.3	3.0	0.00025214	1.93	0.96

A non-linear approach was used for modeling the experimental data. Non-linear methods offer a better way to obtain the model parameters because they do not alter the error structure, error variance and normality assumption of the standard least square. This was done using Microsoft Excel software, solver add-in option [43]. The model fits are shown in Fig. 7A and B. The characteristic parameters obtained from this model are summarized in Table 3. The data show that as bed depth increases,  $K_{Th}$  values decreases for both SANA and AA. A direct relation is observed between  $q_0$  and bed depth for AA. Ayoob and Gupta [44] have observed a decrease in  $K_{Th}$  and increase in  $q_0$  values with an increase in bed depth for the adsorption of fluoride by alumina cement granules (ALC). The observed reduction in  $q_0$  of SANA at higher bed depth was unexpected. This may be due to some localized channeling or uneven flow patterns developed in the adsorbent bed.

# Conclusions

The study reports an eco-friendly and facile *in-situ* approach for the synthesis of a granular adsorbent composite (SANA) comprising nanocrystalline AlOOH and a biopolymer template, chitosan. Unlike conventional methods of synthesis of nanoscale AlOOH, the SANA was synthesized at room temperature and atmospheric pressure. No compressive pressure, external binder or high temperature sintering is required for the granulation of SANA. The SANA showed good stability in wet and dry conditions.

Application of SANA for defluoridation of water was investigated. The study revealed the excellent ability of SANA to remove fluoride in water. The fluoride uptake capacity was superior to that of other aluminum-based adsorbents reported in literature. The kinetic data followed a pseudo-second-order rate equation. The equilibrium data were well described by Freundlich model. The results of this study indicate that SANA can be considered as a replacement of the commercial AA for defluoridation of water.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jece.2014.11.030.

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