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3D Printed Microchannel Loaded with Hematite Nanoadsorbent for Fluoride Removal from Water

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Abstract

3D printed microchannels were loaded with α-Fe_2O_3 nanoparticles for fluoride removal from water. Devices having 35 microchannels of 2 and 1.5 mm diameter were fabricated and loaded with 4 and 3 g of nanoadsorbent respectively. Hematite nanoadsorbent used shown good fluoride removal efficiency with a defluoridation capacity of 2.5 mg/g (3 mg/L fluoride concentration, 4 g adsorbent, 1 mL/min flow rate at 25°C and 7 pH). The customized and compact 3D devices could be an alternative for traditional columns being used for effective fluoride removal from water.

Keywords: 3D printing, Nanoparticles, Microstructure, Fluoride, Water, Adsorption

1. Introduction

Various forms of fluoride (Sellaite, Fluorspar, Cryolite, and Fluorapatite) are released through interaction with rocks, recharge of groundwater and various anthropogenic activities [1]. Excessive fluoride intake can lead to diseases like dental and skeletal fluorosis.

Elimination can be achieved through cation exchange resin, membrane separation, electrodialysis. However, oxides and hydroxides of Al, Mg, Ti, Zr, Ce, La, and Fe [2-4] have been reported to remove fluoride in the range of 75-90% at comparatively low cost [5]. To optimize the adsorption capacity, 3D printed microchannels were loaded with metal oxide nanoparticles have been prepared and tested in the present approach that has the potential to be a directly applicable system for fluoride removal.

2. Experimental Procedure

α-Fe_2O_3 nanoparticles were synthesized by using iron (III) nitrate nonahydrate and sodium hydroxide was purchased from Sisco Research Laboratories Pvt. Ltd.. 0.1 M solution of $Fe(NO_3)_3.9H_2O$ in distilled water was sonicated for 10 min. until it forms a clear solution (a). 1M solution of NaOH was separately prepared (b). After neutralization of (a) through dropwise addition of (b), till it reached pH 7.5, the prepared precipitate was dried in a hot air oven at 80°C until it gets completely dried. The material formed was then powdered and sintered at 400°C in a muffle furnace (Nabertherm) for 4 hours. Brunauer-Emmett-Teller (BET) surface area, pore size distributions, pore volumes, and average particle size were measured by nitrogen adsorption/desorption isotherm at -195.85°C (77.3 K) using Accelerated Surface Area and Porosimetry System, Micromeritics, ASAP 2020. Samples were analyzed through X-ray diffraction analysis (Bruker D8 ADVANCE ECO), Fourier Transform Infrared Spectroscopy (Perkin Elmer Frontier) and Field Emission Scanning Electron Microscope (JEOL JSM-7600F).

The 3D microchannel (Figure 1) was designed by using SolidWorks software and printed using MiiCraft 3D printer (PN#95.LF800G004). The printing machine was based on stereolithography (SLA), minimum resolution across the XY axis and Z axis are 56 microns and 50 microns respectively. Transparent resin (Clear Resin BV-003) was used having boiling point and a specific gravity of 150°C and 1 g/mL respectively at 25°C. The resin curing technique was dependent on the printing mode that was bottom-up [6].

Actual images of 3D printed microchannels with specifications are presented in Figure 1 a having 2 and 1.5 mm diameter. These channels are loaded with the suspension of 4 (2 mm) and 3 (1.5 mm) g of nanoparticles followed by repeated drying at 45°C for 2 hrs. These loaded microchannels were tested to study their efficiency in removing fluoride of different concentrations (3, 6, and 10 mg/L). The flow rate for the complete experimental process was 1 mL/min. Final printed channels are shown in Figure 2. The total amount of adsorbent effectively loaded in the microchannel device was calculated using the below equation 1:

$$\text{Total adsorbent dosage} = \text{Device mass with adsorbent} - \text{Device mass without adsorbent} \qquad (1)$$

Spiked water was prepared by dissolving 22.1 mg sodium fluoride (NaF) in 100 mL of double distilled water. Subsequent concentration of 3, 6 and 10 mg/L was prepared by the dilution of stock solution, using double distilled water. The pH of prepared solution was measured using pH meter (Thermo scientific Orion Dual Star, pH/ISE meter). The solution was pipetted out in HDPE beakers for analysing fluoride. The total ionic strength adjustment buffer (TISAB III) was pipetted in every solution for quantifying the fluoride ion concentration (Thermo scientific Orion Dual Star, pH/ISE meter). The removal percent (%) of fluoride was calculated using the following equation 2:

$$\text{Removal percentage (\%)} = \frac{C_o - C}{C_o} \text{ X } 100 \qquad (2)$$

where C_o and C was the influent and effluent solute concentration (mg/L) in the solution.

3. Results and Discussion

SEM micrograph, XRD and FTIR of nanoparticles are represented in Figure 3 a, b and c respectively. Particle size was in the range from 15.38 to 32.29 nm with nearly uniform distribution. Observation of clusters in SEM image must be due to heterogeneous agglomeration of particles while drying of samples. XRD spectra for α-Fe_2O_3 nanoparticles were matching with reference number #COD9015065. FTIR data was recorded for the pristine α-Fe_2O_3 nanoparticles as well as the used α-Fe_2O_3 nanoparticles collected from device after fluoride absorption. The vibrations of lattice water stretch and hydroxyl groups are shown at 3425 and 3429 cm^{-1} and OH bending vibration of adsorbed water molecules are shown at 1632 and 1633 cm^{-1}. The characteristic absorption bands of Fe-O bonds occur at 474 and 472 cm^{-1}. Bonding was mainly due to the nanoparticles functional groups. FTIR of residues after filtration has shown presence of fluoride bonding thanks to appearance of bands around 1458 to 1467 $cm^{-1.}$ The BET surface area of iron oxide was 155.67 m^2/g before exposure to the fluoride solution. The bends attained at an adsorbent dosage of 4 and 3 g along with a constant flow are presented in Figure 4 a and b respectively. As the influent concentration increases from 3 to 10 mg/L, the bends become gradually sharper which indicates the decrease in exhaustion period with the increase in influent concentration. Similarly, the volume of water treated decreases as the inlet fluoride concentration increases from 3 to 10 mg/L. The greater influent concentration may have caused in faster mass transfer of fluoride to iron oxide because of the greater concentration among the solution and iron oxide outward. Accordingly, at the high influent concentrations, iron oxide required less time to become saturated, resulting in smaller exhaustion time [7]. Table 1 shows the adsorption capacity comparison of diverse materials reported in the literature, along with the used hematite nanoadsorbent.

Table 1: Comparison of adsorption capacity

Adsorbent	Adsorption Capacity (mg/g)
Hydrous Ferric Oxide [2]	6.71
Iron Oxide [3]	60.8
Modified magnetite [4]	1.86
Aluminum Modified Iron Oxides [8]	0.354
Magnesia-Pullulan Composite [9]	16.6
Hematite	2.5

3D printed microchannel by varying the inner design of the channel could be an alternative method for the traditional column that is being used for fluoride removal [10]. The printed channel device was compact and easy to handle. The number of channels printed in a single device can be varied as per the application and requirement. With the help of 3D printing, the flow rate of contaminated influent can be controlled as per the design for better water resistance inside the channel. These printed channels can be loaded with the synthesized or directly procured nanoparticles for respective application. Increase in the number of channels will provide a higher surface area of contact of nanoparticles towards the adsorbate in comparison to the nanoparticles loaded in single column/channel. From the literature survey, it was observed that the material used for fabricating a small scale column were mainly stainless steel, glass, plexiglass, etc. which are costly, brittle and have traditional designs. While in this research the designed prototype was cost-effective and doesn’t rely on traditional designs instead it can be modified as per the requirement.

4. Conclusion

The efficiency of fluoride removal was examined in 3D printed microchannel loaded with iron oxide nanoparticles. The experimental analysis clearly shown that the adsorption capacity of 2.5 mg/g was attained using the proposed system at lower concentration (3 mg/L).

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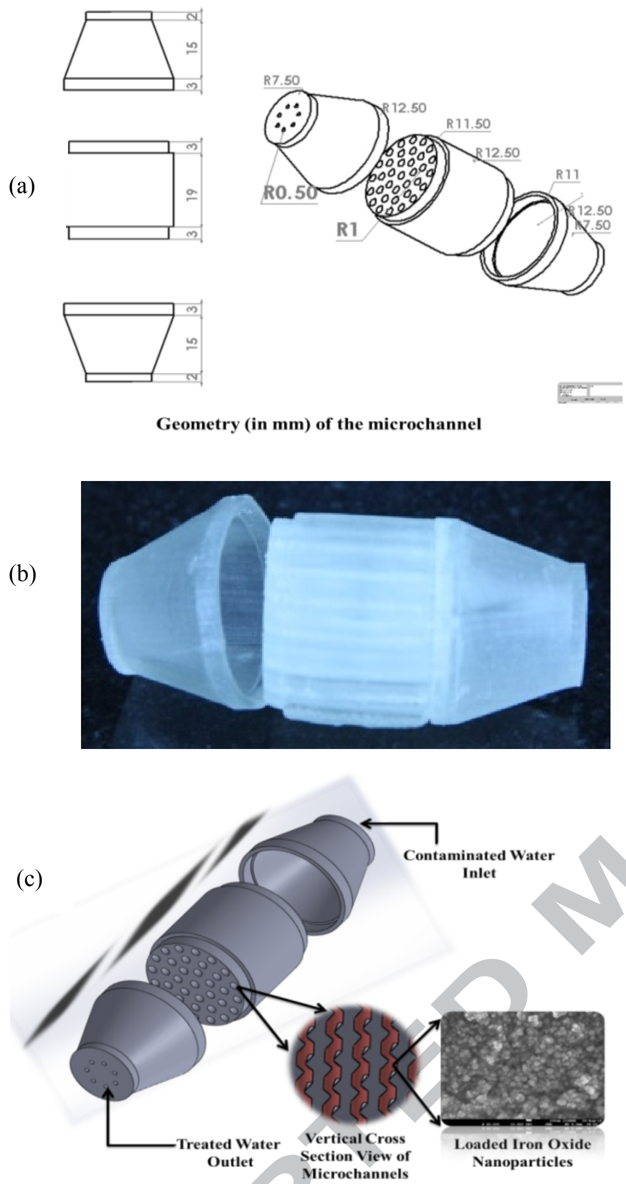


Fig. 1. (a) Geometry representation (in mm) (b) Actual 3D image and (c) Sectional view of loaded nanoparticles of the microchannel device

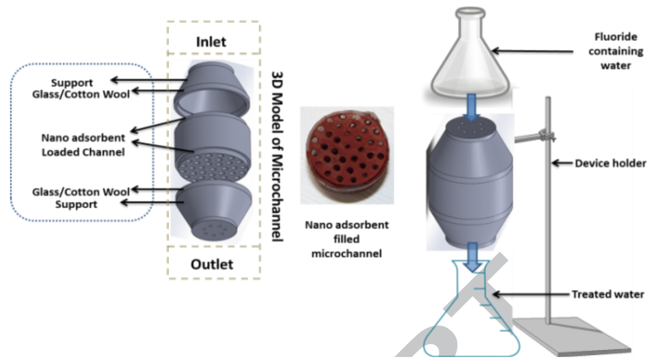


Fig. 2. Process flow system setup for the removal of fluoride from water

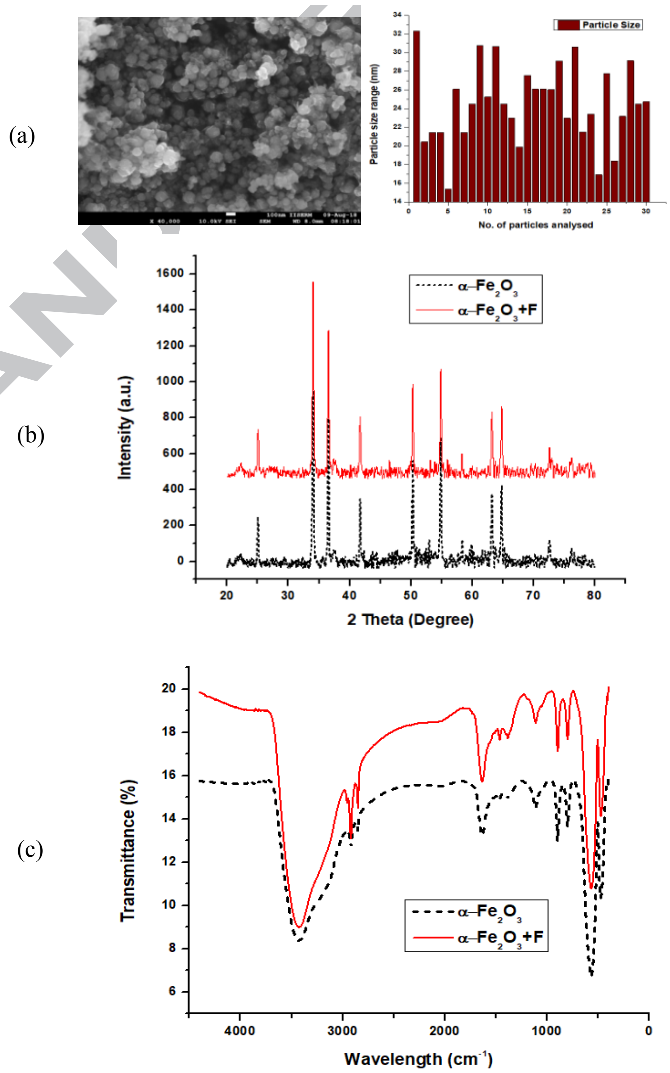
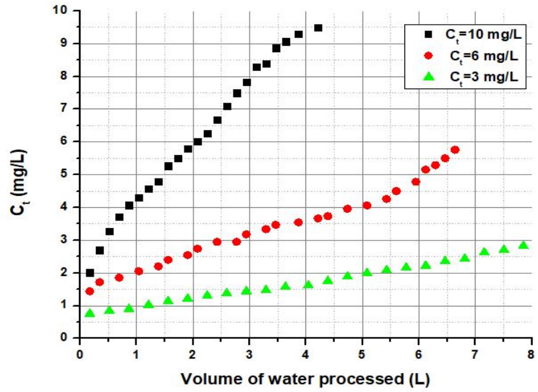


Fig. 3. (a) FESEM image and particle size of nanoparticles (b) XRD and (c) FTIR characterization of iron oxide before and after fluoride adsorption

(a)



(b)

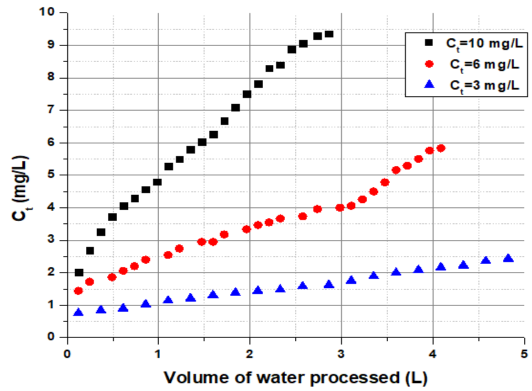


Fig. 4. (a) and (b) shows experimental bends representing adsorption of fluoride onto iron oxide at varying fluoride concentrations (3, 6 and 10 mg/L) for adsorbent dosage= 4.0 g and 3.0 g respectively at temperature = 25 ^{o}C)

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- 3D printed microchannels were fabricated and loaded with synthesized hematite (α-Fe_2O_3) nanoadsorbent.
- The synthesized α-Fe_2O_3 nanoadsorbent was tested for the removal of fluoride from water.
- Fluoride removal efficiency of the microchannels was analysed.