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Synthesis and optimization of low-cost and high efficient zirconium-aluminium modified iron oxide nano adsorbent for fluoride removal from drinking water

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Abstract

Zirconium-aluminium modified iron oxide nano adsorbent was synthesized using chemical route using zirconyl nitrate, aluminium nitrate, ferric nitrate and triethanol amine. The precursor materials were calcined at 900°C for 4 h to obtain a carban free nano-adsorbent. XRD of the calcined powder was performed to detect the phase and to estimate the crystallite size. Fluoride removal tests were performed using synthesized fluorinated aqueous solutions of 3 ppm, 5 ppm and 10 ppm. The adsorbent dose was considered 15 mints, 30 mints, 45 mints and 60 mints while adsorbent dose were varied from 0.1 mg to 0.3 mg for every 100 ml fluorinated aqueous solution. FTIR spectroscopy of the nano-adsorbent was studied before and after fluoride removal. Percentage of fluoride removal was checked for at least three cycles using the same adsorbent. Fluoride concentration of treated aqueous solution was studied using UV-Visible spectrometer using standard zirconium alizarin S solution. Maximum % of fluoride removal was observed up to 99.9% for an adsorbent dose 0.3 mg for a contact time of 15 minutes at 3 ppm fluoride concentration. However, the adsorbent dose for highest % of fluoride removal depends highly on the contact time and initial fluoride concentration and they were found to be very selective. The synthesized nano-sdsorbent could be used commercially for effective fluoride removal from fluorinated water for drinking purpose. Copyright © 2017 VBRI Press.

Keywords: Chemical synthesis, nano-adsorbent, fluoride removal, drinking water, removal efficiency.

Introduction

In present decade, pollution of ground water by fluoride (F^-) has been considered as serious problem world-wide [**1**]. In addition to the arsenic and nitrate, fluoride is recognized as a major polluter of water which is used for the consumption of human being according to the world health organization (WHO) [**2**]. Approximately more than 200 million people in the whole world are exposed to drinking water which has fluoride concentration that exceeds the WHO guideline of 1.5 mg/L [**3**]. There are various parts of the world where high fluoride concentrations occur [**4-13**]. Fluoride is widely distributed in the environment [**14**] and normally released into ground-water slowly by dissolution process from fluoride-rocks [**15**]. Minerals such as fluorite, biolites, topaz and their host rocks such as granite, basalt, etc. that can release into the ground water [**16-18**].

Fluoride in drinking water in narrow concentration usually below 1.0 ppm is considered beneficial to decrease the rate of dental caries particularly among the children [**19**]. On the other hand, excess consumption of fluoride results to various diseases as osteoporosis, brittle bone, brain damage, alzheimer syndrome, thyroid disorder [**20-21**], it may interfere DNA synthesis [**22**]. It hampers teeth and bone formation [**23**]. It damages lipids, vitamins, proteins, and mineral metabolism [**24**], leading to gastro intestinal problems. Kidney disease has an increased susceptibility to the cumulative tonic effect of fluoride [**25**]. The traditional method of removing fluoride from drinking water involves the precipitation and coagulation process with iron (III) [**26**], activated alumina [**27**], alum sludge [**28**] and calcium [**29**] have been widely used. However, ion- exchange [**30-34**], reverse osmosis [**35, 36**], electro dialysis [**37**], has also been studied for the removal of fluoride. But the drawbacks of these processes are due to high maintenance cost and secondary pollution and complicated procedure involved in the treatment. In developing countries, Nalgonda process is found to be one of the popular processes vastly used for defluorination of drinking water [**38**]. Among the various methods available for the defluoridation of water, the adsorption process is extensively used with satisfactory results. Different materials such as activated alumina [**38**], amorphous alumina [**39**], activated carbon [**40**], low cost adsorbents like calcite [**41**], tree bark [**42**], clay charcoal [**43, 44**], ground nut husk [**45**], rice husk [**46**], rare earth oxides [**47**] have been used for defluorination of water. The lowest limit of fluoride removal by these adsorbents is higher than 2 mg/L and so are not appropriate for drinking water treatment, especially some of them work better at an intense pH *e.g.*, activated carbon which removes fluoride at pH less than 3.0 [**48**]. The adsorption capacities of these adsorbents are summarized in **Table I** [**49**].

It has been established that activated alumina shows maximum adsorption capacity in the pH range between 5 and 7 [**50**]. Synthetic Fe-oxide is also found be a good adsorbent for removal of fluoride from contaminated water [**51-54**], but its Langmuir adsorption capacity is low, about16.5 mg/g [**55**]. It has been reported by various researchers that the fluoride adsorption capacity of Fe_2O_3 can be increased by chemical modification of its surfaces. Due to small ionic size and high electro negativity, fluoride ion is classified as hard base. So it has a strong affinity towards hard acid centre such as electro positive multivalent metal ions like Al^{3+}, Ca^{2+}, Zr^{4+}, La^{3+}, Ce^{4+}, etc. Impregnation of positively charged ions like those mentioned above, on to the adsorbent surface which attracts F^- and improves fluoride adsorption capacity. These metallic cations serve as a bridge between adsorbed fluoride and Fe_2O_3 surface. The mechanism involved of such type of adsorption can be represented as follows:

$$=\mathrm{Me{-}OH_2^+} + \mathrm{F^-} \longrightarrow =\mathrm{Me{-}F} + \mathrm{H_2O}$$

$$=\mathrm{Me{-}OH} + \mathrm{F^-} \longrightarrow =\mathrm{Me{-}F} + \mathrm{OH^-}$$

(=Me – represents the multivalent metallic cation surfaces)

It has been observed that adsorption capacity of iron oxide is increased when it is incorporated with different metal ions such as Aluminium (III) [**56**], Zirconium (IV) [**57**], Tin (IV) [**58**], Chromium (III) [**51**] and Titanium (IV) [**59**] ions. The synthetic process and adsorption capacity of these bimetallic oxide adsorbents are summarized in **Table II.**

New chemical bonds formed between the two metal ions through an oxygen atom increases the concentration of hydroxyl groups onto the adsorbent surface and the adsorption capacity of the adsorbents increases. However, their adsorption capacity is not high enough and the adsorbents needs frequent regeneration [**59**].

Most of adsorbents used for fluoride removal, reported in open literatures are micron sized particles. In recent years, nano materials have got great interest and been extensively used as sorbents because of its enhanced high surface to volume ratio, high pore volume, etc [**27**]. Because of comparatively large surface area, the nanomaterials are used as a useful tool to enhance the adsorption capacity of fluoride from drinking water. However smaller particle size hinders the isolation of nano sized adsorbents from water. Magnetic nano-adsorbents may overcome their short coming of non - magnetic nano materials.

Table I. Comparative analysis of various techniques for fluoride removal.

Sample No	Initial fluoride concentration (mg/L)	Fluoride concentration after treatment (mg/L)			
		Activated alumina	Activated saw dust	Nalgonda	Reverse Osmosis
1	4.2	1.13 (73.10)	1.42(66.19)	1.32 (68.57)	0.32 (92.38)
2	7.8	1.96 (74.87)	2.32 (70.26)	2.24 (71.29)	0.63 (91.93)
3	8.6	2.23 (74.07)	2.56 (70.23)	2.47 (71.30)	078 (90.93)
4	9.3	2.11 (77.31)	2.42 (73.98)	2.31 (71.16)	0.88 (90.54)
5	8.2	2.17 (73.54)	2.43 (70.37)	2.34 (71.46)	0.77 (90.61)
6	6.8	1.81 (73.38)	2.16 (68.24)	1.95 (71.32)	0.56 (91.76)

Values in parentheses show the percent fluoride removal.

Table II. Bimetallic oxide adsorbents syntheses and their adsorption capacities reported in the literature.

Adsorbents	Amount of fluoride adsorbed (mg/g)	Synthetic Method	Structure	Ref.
Fe - Al	17.7	NH_3, H_2O into $FeCl_3 + AlCl_3$ (1:1)	Crystalline Fe - O - Al	[**56**]
Fe - Zr	8.2	NaOH into $FeCl_3 + ZrOCl_2$ (9:1)	Crystalline Fe - O - Zr	[**57**]
Fe - Sn	10.5	NaOH into $FeCl_3 + NaSnO_3$	Amorphous Fe - O - Sn	[**58**]
Fe - Cr	16.3	NH_3, H_2O into $FeCl_3 + CrCl_3$ (1:1)	Amorphous Fe - O - Cr	[**51**]
Fe - Ti	47.0	NH_3, H_2O into $FeSO_4$ + $Ti(SO_4)_2$ (2:1)	Amorphous Fe - O - Ti	[**59**]

Synthesis of iron doped titanium oxide nano-adsorbent and its adsorption characteristics for fluoride in drinking water were reported by Chen et.al. [**60**]. Iron (III) – aluminium (III), iron (III) – zirconium (IV), iron(III)–tin(IV) bimetal mixed oxide for fluoride removal and their adsorption kinetics were systematically studied by Ghosh et al. [**51,56-58**]. Mg-doped nano ferrihydrite was synthesized by Mohapatra et al. [**61**] who, have shown a highest of 90.7 % fluoride removal capacity at 0.98% doping concentration of Mg (II). However, to increase the fluoride removal efficiency Fe based trimetallic oxides such as Fe-Al-Ce tri-metallic oxide [**62-64**] and Fe-Al-Cr ternary oxides [**65**] which are of micron – size, have been reported recently. The major drawbacks of most of the studies involved either high cost of materials with complicated synthetic procedure consuming long time and high energy while some of the adsorbents exhibit very low removal capacities.

In this paper, a novel ternary oxide, Zirconium-Aluminium modified Iron oxide nano adsorbent was prepared by novel chemical process aiming for the optimization of low cost and high efficiency of fluoride removal capacity from drinking water. To check the reusability of the adsorbent material, desorption study was also performed and hence sustainability of fluoride removal process.

Experimental

Materials required

All chemicals were of analytical grade and used without further purification The Chemicals required were $Al(NO_3)_3$ $9H_2O$ (E. Marck India Ltd. 98.5%), $Fe(NO_3)_3$ $9H_2O$(E. Merck India Ltd. 98.0%), $ZrO(NO_3)_3$ xH_2O (Sigma Aldrich 99.0%), Triethanolamine (TEA) (Sigma Aldrich 99.0%) and HNO_3 (Sigma Aldrich70%), NaF (Sigma Aldrich 99.0%),

Methods

Preparation of $Al(NO_3)_3$, $Zr(NO_3)_4$ and $Fe(NO_3)_3$

Standard aqueous solutions (1 M) of $Al(NO_3)_3$, $Zr(NO_3)_4$ and $Fe(NO_3)_3$ were prepared from $Al(NO_3)_3$ $9H_2O$, $Fe(NO_3)_3$ $9H_2O$, $ZrO(NO_3)_3$, xH_2O respectively using 0.2 M HNO_3 solution in 1 L volumetric flask of each at room temperature.

Preparation of Fe – Al – Zr mixed oxide

Standard aqueous solution of $Al(NO_3)_3$, $Zr(NO_3)_4$ and $Fe(NO_3)_3$ were mixed in 1:1:1 ratio with appropriate amount of TEA (the total metal ion to TEA mole ratio was maintained at 1:3) and then heated on a hot plate at a temperature 200°C. The evaporation of nitrate ions provided an oxidizing atmosphere for the conversion of hydroxyl groups of TEA to carboxylic acids. The solution was heated until it forms fluffy black mass. The obtained black mass was then calcined for 4 h at a temperature 900°C and brown- red nano powder was obtained. The detailed synthetic procedure is mentioned in the flow chart in **Fig. 1.**

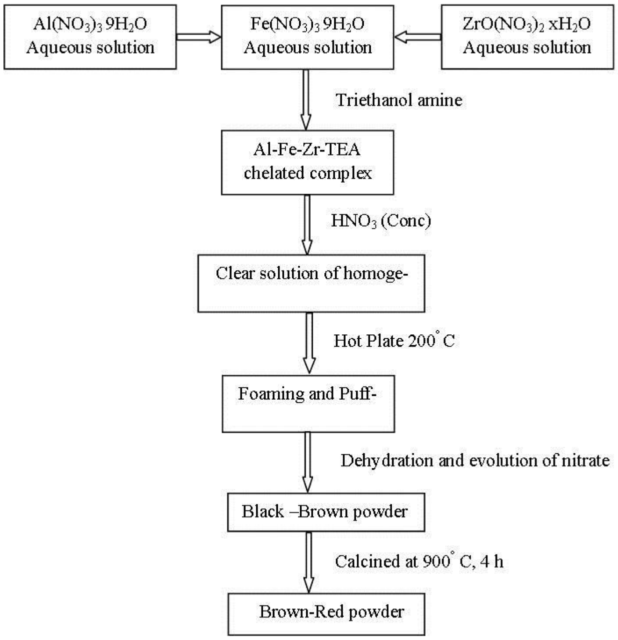

Fig. 1. Flow chart diagram for the preparation of Fe – Al – Zr mixed oxide.

Preparation of standard fluoride solution

A standard stock solution of 1000 mg/L fluoride was prepared by dissolving appropriate amount of Sodium Fluoride (Merck India) with purity 99% in double distilled water and all the solution for fluoride removal experiments as well as analyses were made by proper dilution of standard stock solution.

Characterizations

The powder was characterized by X-Ray Diffraction (XRD) (Model PW1710 and PW1810, Philips Research laboratories) using CuKα ($\lambda = 1.5406$ Å) radiation over a 2θ (Bragg's angle) range of 20°-80°. Nitrogen adsorption–desorption isotherms of the synthesized materials were obtained by using a surface area and porosity analyzer (Quantachrome NovaWin – Data Acquisition and Reduction instrument) to determine Brunauer-Emmett-Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore size. Before adsorption measurements, all samples were out gassed using nitrogen flow at 200°C for 18 h. A Fourier Transform Infra-Red Spectrometer (Perkin Elmer Spectrum Version 10.4.00) was used to acquire the IR spectrum of the sample. KBr (Merck Spectra grade, Merck India Private Limited) was used to make the samples for FTIR analysis. Elemental composition was determined by Energy Dispersive X-ray (EDX) analysis in vacuum, in the specimen chamber of an EDX coupled with Scanning Electron Microscope (SEM) (Model JFM 5800 Jeol, Tokyo, Japan). Scanning electron micrographs were recorder using SEM. The study detected the chemical bonds of the composite material. The surface morphology of the adsorbent was also observed by scanning electron microscope.

Removal of fluoride by nano-sized alumina & zirconium based iron oxide

Desired concentrations of fluoride solutions were taken in plastic bottles. All experiments were done in a shaker (Paragon RPM-0249 TXT-7203, India) at 200 RPM. After shaking, the suspensions were settled and centrifuged by a centrifuge (REMI R-8C, India). Fluoride concentrations in the solutions (before and after treatment) were measured using a UV–VIS spectrophotometer at 427 nm with a Zirconium-Alizarin-S complex reagent. The Zirconium-Alizarin-S dye was prepared by mixing Alizarin-S dye with zirconium solution in a mixture of H_2SO_4 and HCl [**66**]. Decolorization of Zirconium-Alizarin-S dye occurred on reaction with fluoride ions forming colorless zirconium fluoride (ZrF_6^{2-}). This reaction was used spectrophotometrically for determining fluoride ion concentration. During analysis, 2 mL of reagent solution was added to 1 mL of fluoride solution (2:1 volume ratio).

Desorption study

Desorption studies were performed in fluoride adsorbed adsorbent. Initially, the fluoride-adsorbed adsorbent was generated by adsorbing 25 mg/L fluoride solution on 8 g/L nano sized alumina & iron oxide based zirconium oxide at pH 6.5. After attaining the equilibration condition, the residue was filtered off and the filtrate was measured for fluoride content. Then this adsorbed fluoride was subjected for desorption studies by adding 50 ml 0.1 (M) HCl (for every 2.5 g of fluoride adsorbed adsorbent) followed by neutralization using 0.1 (M) NaOH solution and subsequent conditioning of the neutral suspension for 30 min at 100 rpm.

Results and discussion

XRD study

The XRD study of the sample which was calcined at 900°C for 4 h was performed as shown in **Fig. 2**. The diffraction pattern of the sample has extremely broad line width, might be due to the smaller size. The XRD picture shows that the crystallite has some amorphous nature which was purposefully done to get high surface area to enhance the adsorption process. The most interesting information observed from the XRD peaks was that the ZrO_2 remained in two different phases. According to XRD pattern, two phases of ZrO_2 was formed namely the t-ZrO_2 and m-ZrO_2 phases. Nevertheless, the existence of the t-ZrO_2 phase in the sample is at a very small level. This fact could be well explained by Schmid et al. [**67**]. The monoclinic phase of ZrO_2 is shown by two peaks at diffraction angles of 28.21° and 31.45°, from crystal planes of (-111) and (111) respectively. The peak intensity for t-ZrO_2 is lower on increasing the calcination temperature because of thermal treatment of the amorphous zirconia gels at various temperatures above 400-600°C, the crystallization was occurred via a thermodynamically metastable tetragonal phase, whilst at temperatures above 600°C, the tetragonal to monoclinic phase transformation occurred. The peak intensity from the m-ZrO_2 was becoming sharper with the increase of the calcination temperature.

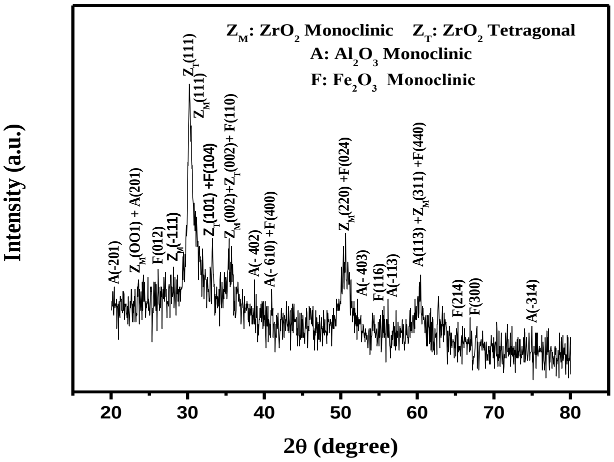

Fig. 2. X-Ray Diffractogram of nano zirconium-zluminium-iron mixed oxide.

Al_2O_3 and Fe_2O_3 crystallized in monoclinic phase [JCPDS, File. No. 11-0517 and 16-0653 respectively]. The major peaks for monoclinic Al_2O_3 appears at 2θ value 60.55° which corresponds to (113) plane. This peak comes along with peaks corresponding to (440) plane of monoclinic Fe_2O_3 and (311) plane of monoclinic ZrO_2. The most important peaks for monoclinic Fe_2O_3 appear at 2θ values 33.36°, 35.41°, 50.30° and 60.55° which correspond to (140), (110), (024) and (440) planes respectively. There are some peaks for the mixed oxides formed in the reaction which are appeared as spikes [**68**]. The average crystallite size obtained from the X-ray diffraction pattern was calculated using Scherr's equation [**69**]. By analyzing the XRD spectrum, the average size of the crystallite was calculated to be 21.99 nm.

Microstructure

SEM study

The SEM images as shown in **Fig. 3(a)** and **Fig. 3 (b)** of the mixed oxides taken before and after fluoride adsorption at fluoride free condition confirmed that the adsorbent was composed of irregular grains with wide range of grain size distribution. The mixed oxide grains dispersed well and there were some agglomerations. The image also confirmed the presence of porous structure. Smaller particle size and porous structure offered a good adsorption capability for fluoride ions. The result from SEM analysis was also confirmed from the XRD analysis.

EDS study

The energy dispersive spectrum (EDS) as shown in **Fig. 3 (c)** represents the elemental composition of the material. The EDS spectrum clearly indicated the presence of O, Zr, Fe and Al as elements in the material. The approximate atomic weight percentage ratio for

O:Al:Fe:Zr is 7:1:1:1. The total positive charge of the unit mixed oxide is +10 *i.e*, five O atoms required for charge balance. Here the extra oxygen atom is for carbonate impurity which can be confirmed form EDS study (also discussed in IR study). The EDS study of the adsorbent after adsorption experiments at fluoride free condition confirmed the absence of any fluoride.

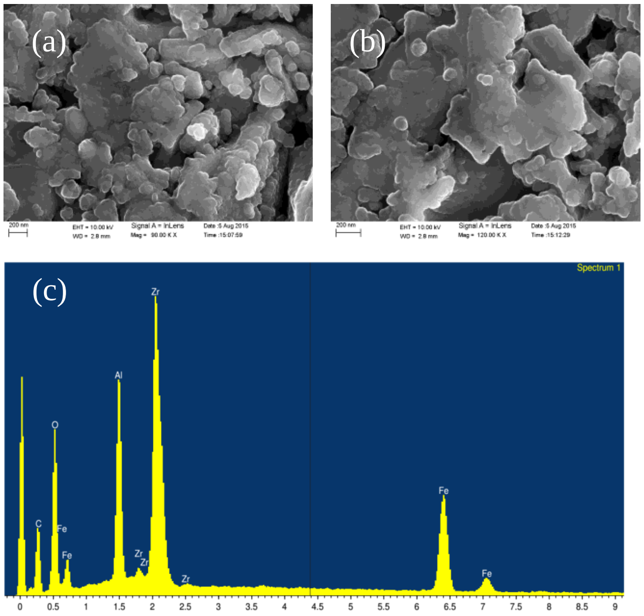

Fig. 3. SEM images of nano zirconium-aluminium-iron mixed oxide (a) before and (b) after adsorption study at fluoride free condition and (c) EDS study of nano zirconium-aluminium-iron mixed oxide.

FT-IR analysis

FT-IR spectra **[Fig. 4 (a)]** showed that the band observed at 3437 cm^{-1} was due to the vibration of structural OH groups, hydrogen bonded with intermolecular water molecules or OH groups in adjacent layers [**70**]. The peak at 1382cm^{-1} was due to the -OH stretching mode of water molecule [**71**]. The peaks at 1642.5 cm^{-1} might be due to the bending mode of water molecules. After adsorption, the shifting of OH and the small decrease in intensity indicated the presence of OH in the fluoride adsorption. The peaks detected in the region within 1100 cm^{-1} and 1010 cm^{-1} might be due to the stretching mode of Al–O bonds [**72**]. In the spectra, a peak due to stretching vibrations of Fe–O bond was observed at 531 cm^{-1} [**73**]. It was reported that the peaks observed in the range of 1200–400 cm^{-1} were the characteristic vibrations of mixed metals by Liu et al. [**74**]. The absorption band at 2348.5 cm^{-1} was common in the spectra which were presumed to be for the carbonate impurity [**75**]. The peak observed at 527.87 cm^{-1} was assigned to the metal-oxygen bonding (Zr - O) which also noticed a shifting at 531.58 cm^{-1} as well as change in intensity in case of ZrOF [**76**]. Analysis of the spectrum of the materials thus provides evidence towards the involvement of hydroxyl groups as possible coordinating sites for binding with fluoride in the solution.

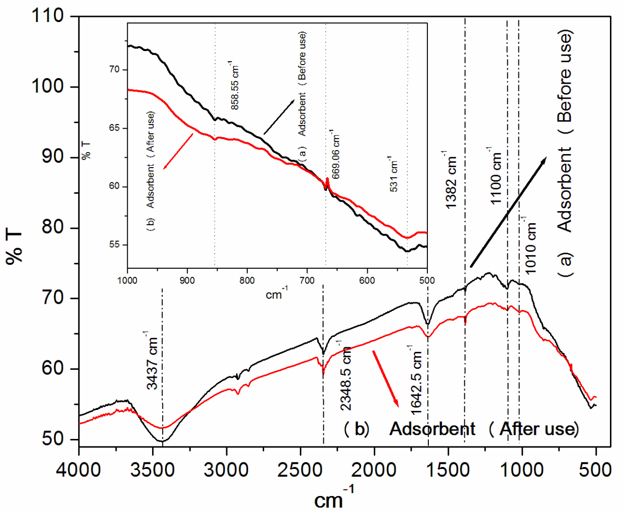

Fig. 4. FT-IR spectra of the composite material (a) before adsorption and (b) after adsorption.

Surface area, pore volume and pore size distribution (PSD)

The surface characteristics such as the specific surface area, pore volume and PSD of the adsorbent prepared in this study were determined by a Quantachrome NovaWin – Data Acquisition and Reduction instrument. The multipoint Brunauer, Emmett, and Teller (BET) surface area was measured using the nitrogen adsorption/ desorption isotherm. N_2 gas was used as an adsorbent for isotherm data acquisition at 77.3 K. Before measurement, the samples were degassed at 200°C for 18 h to remove any adsorbed water or trapped gases in the samples. The total pore volume was measured from the amount of N_2 adsorbed at the relative pressure below 0.89613. The PSD was calculated from desorption isotherm by the Barrett, Joyner, and Halenda (BJH) method. The material was found to be porous and the total pore volume calculated was 4.150 $x10^{-02}$ cc/g. However Deng et al. have synthesized cerium impregnated fibrous protein having pore volume 0.0046 cc/g [**77**]. The pores are smaller than 20 nm in diameter at P/P_0 = 0.89613. From the BJH desorption isotherm the surface area, pore volume and pore diameter were found to be 23.873 m²/g, 0.028 cc/g, and 4.060 nm respectively.

Effect of adsorbent dose and initial fluoride concentration vs time for % of fluoride removal

The percent of fluoride removed was investigated as a function of contact time, adsorbent dose and concentration of the fluoride aqueous solution as summarized in **Table III**. The % fluoride removed with the variation of shaking time (min) taking the adsorbent dose 0.1 g/100 ml, 0.2 g/100 ml and 0.3 g/100 ml were plotted in **Fig. 5 (a), (b)** and (c) respectively. **Fig. 5 (a)** showed that on increasing the shaking time from 15 min to 30 min the % fluoride removal increased from 26% and 8% to 98.8% and 96% respectively for 3 and 5 ppm whereas in case of 10 ppm the change is from 97.6% to 99.9%. However on further increasing the shaking time to

45 min there is a decreasing trend of % fluoride removal except for the fluoride concentration 5 ppm. In case of **Fig. 5 (b)** and **(c)** for the adsorbent dose 0.2g/100 ml and 0.3 g/100 ml respectively, the % fluoride removal did not follow a regular trend.

The variation of % fluoride removed with varying adsorbent dose (in g/100 ml) in 15 min, 30 min, 45 min and 60 min were plotted in **Fig. 6 (a), (b), (c)** and **(d)** respectively. For 15 min shaking time with the change of adsorbent dose from 0.1 g to 0.2 g, the % of fluoride removal changes from 26% to 99.8% for 3 ppm solution and that for 5 ppm solution 8.1% to 99.8% fluoride removal took place. Similar trend was found for **Fig. 6 (b)** and **(d)** *i.e.* for 30 min and 60 min shaking time. In all these cases when the adsorbent dose was 0.3 g was found to be not suitable for better fluoride removal. In case of **Fig.6 (c)** for 45 min shaking time, it did not follow same trend.

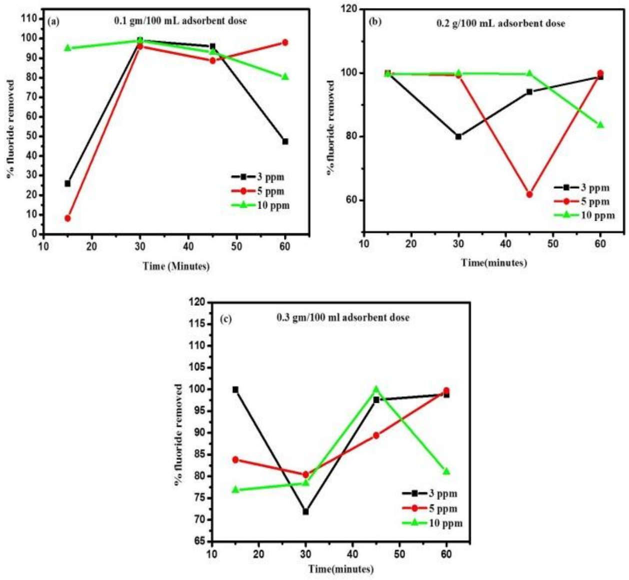

Fig. 5. %fluoride removal vs time when adsorbent dose (a) 0.1 g/100 mL, (b) 0.2 g/100 mL and (c) 0.3 g/100 mL.

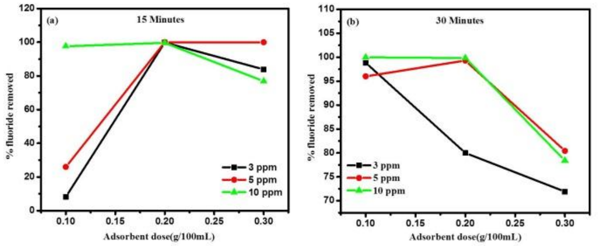

Fig. 6. %fluoride removal vs adsorbent dose when time (a) 15 min, (b) 30 min, (c) 45 min and (d) 60 min.

The variation of % fluoride removed with respect to time for 3.0 ppm, 5.0 ppm and 10.0 ppm fluoride concentrations were plotted in **Fig. 7 (a), (b),** and **(c)** respectively. For 3 ppm and 5 ppm solution it was found that with increasing time from 15 min to 30 min it undergo decrease in % fluoride removal for 0.2g and 0.3g adsorbent dose, whereas with further increasing time form 30 min to 45 min to 60 min it increased continuously for 3 ppm solution and a decreasing trend for 5 ppm solution. However 0.1 g adsorbent dose for both these two different solutions as in **Fig. 7 (a)** and **(b)** did not follow same trend. From **Fig. 7 (c),** we could see an adsorption maximum for all these three adsorption doses at 45 min shaking time.

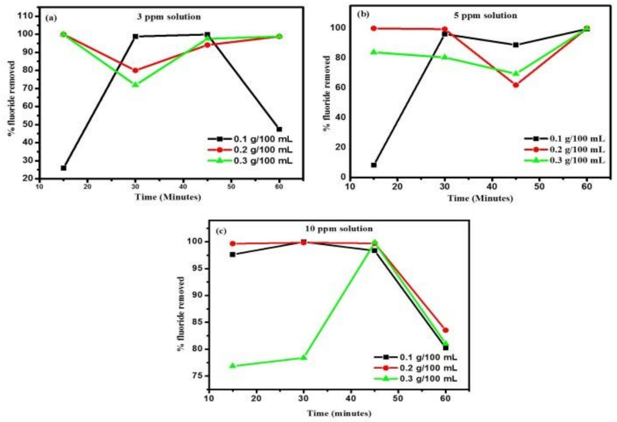

Fig. 7. %fluoride removal vs time when fluoride concentration (a) 3.0 ppm, (b) 5.0 ppm (c) 10.0 ppm.

Table III. Adsorbent dose, initial fluoride concentration, time and % of fluoride removal.

Time (min)	3 mg/L		5 mg/L		10 mg/L	
	% of fluoride removal	Adsorbent Dose (g)	% of fluoride removal	Adsorbent Dose (g)	% of fluoride removal	Adsorbent Dose (g)
15	26.0	0.1	08.1	0.1	97.6	0.1
	99.8	0.2	99.8	0.2	99.6	0.2
	99.9	0.3	83.8	0.3	76.8	0.3
30	98.8	0.1	96.0	0.1	99.9	0.1
	80.0	0.2	99.2	0.2	99.8	0.2
	71.9	0.3	80.4	0.3	78.4	0.3
45	99.9	0.1	88.7	0.1	98.3	0.1
	94.1	0.2	61.8	0.2	99.7	0.2
	97.6	0.3	69.4	0.3	99.8	0.3
60	47.4	0.1	99.4	0.1	80.2	0.1
	98.8	0.2	99.9	0.2	83.5	0.2
	98.8	0.3	99.6	0.3	81.0	0.3

The effects of adsorbent dosages on the removal of fluoride from drinking water were studied at neutral pH. So for a certain concentration and certain time as adsorbent dose was increased, the % of fluoride removal was also increased up to a certain limit and thereafter % of fluoride removal started decreasing. This unusual and irregular behavior could be explained by two opposing facts. It is expected that with the increasing fluoride concentration or the adsorbent dose and time, the % fluoride removed should increase; on the other hand due to the adsorption of fluoride, the active surface area decreases due to diffusion of adsorbed particles into the pores of the adsorbent [**78**], a second factor arises when the F^- ions are adsorbed on the pore, it repels the adsorbed fluoride on the surface and releases the adsorbed fluorides [**79**] and this trend is generally followed in the samples which are porous in nature as previously observed by Deng et al. [**76**]. Thus we can conclude that the relationship between the initial fluoride concentration and the rate of adsorption will not be linear, when pore diffusion limits the adsorption process. This is nicely in agreement with the study conducted by Ghorai et al. [**70**]. Thus the %fluoride removed depends on the extent to which any of these factors predominates. As a result it is very difficult to correlate the sorption capacities of this type of materials because it depends on experimental conductions like pH, temperature, initial concentration, effect of co-ions, contact time, etc [**80**].

We found from our studies that for 0.1 g/100 mL adsorbent dose, the maximum adsorption was observed at 30 min for 10 ppm fluoride solution with 99% removal which was much better result than the result obtained by Shrivastava et al. [**81**] who have shown 45% fluoride removal using alumina as adsorbent when all other conditions were maintained same. According to the studies of Zhao et al. [**82**] fluoride removal capacity of $Fe_3O_4@Al(OH)_3$ magnetic nano particles the maximum removal was observed at 90 min with 75% removal where as our study showed the removal of 99.84% at 30 min when the adsorbent was taken 0.3g/100 ml. From the studies of Swain et al. [**83**] we could see that meso-structured ZrP could remove nearly 96% of fluoride with a dose of 3.0 g L^{-1} where our composition provides 99% removal at 45 min. Mohapatra et al. have found that the adsorption of fluoride on Mg-doped nano ferrihydrate was showing 90.7% fluoride removal in 3 h [**61**] whereas our study showed a removal of 95% on an average at 30 min time.

Conclusion

In present study, novel and highly efficient adsorbents for fluoride have been developed by modifying iron oxide by zirconium and aluminum oxides prepared by chemical route. The formation temperature was set just 900^{o}C for 4 h heating in static air. From the above analysis of the adsorption capacities, and XRD, FTIR, SEM and EDS study of the adsorbents, it can be inferred that the Fe-Al-Zr mixed oxide adsorbent was not a simple mixture of Al-oxide, Zr-oxide and Fe-oxide, and that a synergistic interaction between Fe and Al and Zr occurred during the synthesis. High adsorption of fluoride occurs (99.97%) at an adsorbent dose of 0.1 g/100 mL adsorption dose in 30 min. This material is highly efficient nano-adsorbent in its type. As the whole work was done in neutral pH, it can be easily applied in practical purpose.

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Author's contributions

Conceived the plan: D. Dhak; Performed the expeirments: S. Chakraborty, M. K. Adak, S. Sen; Data analysis: D. Dhak, S. Chakraborty; Wrote the paper:D. Dhak, S. Chakraborty, M. K. Adak . Authors have no competing financial interests.

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