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Adsorptive removal of fluoride from water samples using Zr–Mn composite material

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ABSTRACT

The toxicity of fluoride to mankind is very high. Thus there has always been need to treat fluoride contaminated water samples for its removal to make it safe for human consumption. A novel and efficient analytical method for the removal of fluoride using Zr–Mn composite material has been developed for water samples. The adsorption was confirmed by the use of various techniques like X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET) and FTIR. The key parameters that influence analyte i.e. fluoride removal were investigated and optimized. Under the optimized conditions of the adsorbent dose 1.2 g/50 mL, pH 7, temp 29 °C and the contact time 145 min, an excellent fluoride removal up to 90% was achieved. The proposed material has successfully been applied to the removal of fluoride in different aqueous solutions having a broad concentration range of fluoride. The effectiveness of the sorption process on the adsorbent (Zr–Mn composite material) was verified by testing it on natural waters loaded with the proposed fluoride. The reproducibility of the method was validated by removing fluoride in various water samples by the proposed method in a different laboratory under the same condition. The simplicity of the proposed fluoride removal material, very high removal efficiency, short time and the use of safe chemicals demonstrate the high potential of the proposed method for routine fluoride removal from water samples. The process of adsorption by Zr–Mn composite material followed Freundlich as well as Langmuir isotherms but is favorable to Freundlich isotherm that provides best fit to the experimental data. The results obtained showed that adsorption on the Zr–Mn composite material could be an effective method for the removal of fluoride.

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1. Introduction

Fluorine is quite a common element that does not naturally occur in elemental form because of its high reactivity. Fluoride is a naturally occurring compound derived from fluorine which is the 13th most abundant element in the earth's crust [1,2]. It exists in the form of fluorides in various minerals such as sellaite (MgF₂), fluorspar (CaF₂), cryolite (Na₃AlF₆) and fluorapatite (Ca₅(PO₄)₃F). Thus fluorides are also found in rocks, soil, plants, animals, humans and fresh as well as ocean water [2,3]. Therefore fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into ground water [2–5]. In addition to water, fluoride is present naturally in almost all foods and beverages but levels vary widely. However, fluoride has both beneficial and harmful effects on human health depending on its level. Among the beneficial effects of fluoride in the human body, strengthening of bones and prevention from tooth decay are significant [5]. Compared to its beneficial effect fluoride is more detrimental. Thus fluoride is a toxic chemical and it is a risk factor for thyroid hormone production in children when the exposure to fluoride occurs during intrauterine

growth period [6]. A report during 2008 in Scientific American on 'second thoughts about fluoride' was a warning to all concerned as it revealed the risk of fluoride causing disorders affecting the teeth, bone, brain and thyroid gland [6,7]. It has also been reported that thyroxine and triiodothyronine in serum decreased with increasing urinary fluoride in cattle. Cattle affected with fluorosis developed hypothyroidism and anemia [6]. In addition, it has been confirmed that there is significant positive relationship between fluoride intake by water and the prevalence of dental fluorosis [2,8–11]. For the general population the intake of fluoride is mainly from drinking water and to a much lesser extent from foodstuffs i.e. drinking water is the major source of daily intake of fluoride [2,12,13].

Water is an essential natural resource for sustaining life and environment that is thought to be available in abundance as a free gift of nature. However, over the past few decades, the ever-increasing population, urbanization, industrialization and unskilled utilization of water resources have led to the degradation of water quality, causing its reduction in per capita availability in various developing countries [13]. Thus there is a substantial shortfall in the availability of potable water in less developed or developing countries, primarily due to water contamination and pollution [14–16]. It has also been reported that about 80% of the diseases in the world are due to poor quality of drinking water, and the fluoride contamination in drinking water is responsible for 65% of endemic fluorosis in the world which affects the teeth, bone and soft tissues [14,17,18]. The beneficial or detrimental

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effects of fluoride in drinking water depend on its concentration and the total amount ingested. It is beneficial especially to young children below eight years of age when present within permissible limits of 1.0–1.5 mg/L for calcification of dental enamel. Excess fluorides in drinking water cause dental fluorosis and/or skeletal fluorosis [9,10,12–14,19,20]. Furthermore, renal failure has also been reported [21]. Therefore many countries have set a maximum allowable concentration of fluoride in drinking waters. Indian standards for drinking water recommend an acceptable fluoride concentration of 1.0 mg/L and an allowable fluoride concentration of 1.5 mg/L in potable waters [22]. However, the U.S. Environmental Protection Agency has set a maximum contaminant level for fluoride of 4.0 mg/L for drinking water for public water systems but has also set a secondary standard of 2.0 mg/L. The U.S. Public Health Service has set the optimal fluoride content in drinking water in the range of 0.7–1.2 mg/L. In 2011, the U.S. Department of Health and Human Services proposed a recommendation of 0.7 mg/L to replace the current range of 0.7–1.2 mg/L [23]. The World Health Organization has set 1.5 mg/L of fluoride as the upper limit in drinking water [20]. Thus high level of fluoride in water is a worldwide problem. According to the United Nations Environmental Program, more than ten million people across twenty five developed and developing countries have been affected by fluorosis [5]. There has been regular report on high fluoride contents in drinking water from India, Pakistan, China, Sri Lanka, West Indies, Spain, Holland, Poland, Italy, Mexico, Thailand, Eritrea (North East Africa), West Africa, Southern Africa, and North and South American countries [4,5,13,14,19,20,24–33]. In China, endemic fluorosis has been reported in all twenty eight provinces, autonomous regions and municipalities except Shanghai [20]. In China alone more than 1.34 million people have suffered from skeletal fluorosis due to high fluoride drinking water and another 30 million are exposed to it [4,20,33,34].

The presence of fluoride and other contaminants has also been reported from different parts of India where people suffered from harmful diseases due to industrial discharge of fluorides and thus the water sources have been unsafe for human consumption as well as irrigation and industrial uses [10,12–14,27]. The most seriously affected provinces are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh [10,12–14,19,20,35,36]. The highest concentration observed to date in India is 48 mg/L in Rewari District of Haryana [20,37]. Viswanathan et al. have reported that 50% of the groundwater sources in India have been contaminated by fluoride where more than 90% of rural drinking water supply programs are based on ground water [14]. Therefore, fluoride is the major inorganic pollutant of natural origin found in groundwater [10,12–14,19,27,30,38–54]. There is a narrow margin between the preferred and detrimental doses of fluoride in the human body [33,55]. The defluoridation is carried out when naturally occurring fluoride level exceeds the permissible limits as it is the only option to control fluoride related diseases. Therefore, the removal of fluoride from drinking water when it exceeds the recommended limit is extremely important for the public's interest. Meenakshi and

Maheshwari have presented a review on the sources, ill effects and techniques available for fluoride removal [13]. Mohapatra et al. have also published a review that provides precise information on efforts made by various researchers in the field of fluoride removal for drinking water [56]. For defluoridation of water various methods have been used such as membrane separation processes [57,58], adsorption [12,59–65], ion-exchange [66,67], precipitation–coagulation [68,69], nano-filtration [70,71], reverse osmosis [58,72,73], electrolytic defluoridation [74–76], electrodialysis [77,78] and Donnan dialysis [79–81]. However, in the recent review, the fluoride removal techniques have been broadly categorized in two sections such as membrane and adsorption techniques [56]. Considering factors like cost effectiveness, flexibility and simplicity of design, ease of operation and maintenance, the conventional adsorption technique has been found to be superior technique for fluoride removal [4,82]. As the efficiency of adsorption technique depends upon the nature of adsorbents used so, in recent past, considerable efforts have been directed toward the study of fluoride removal using various types of adsorbents like natural, synthetic and biomass materials which include activated alumina/aluminum based materials [40,62,66,68,83–85], fly ash [86], alum sludge [62,87], algal biosorbent [41], chitosan beads [12,47,49–51,53,88], red mud [65], synthetic compounds/amberlite resin/zeolite [63,89,90], calcite [91], hydrated cement [92], hydrotalcite and layered double hydroxides [93,94], clays and soils [3,4,19,42,45,46,61,95], carbon based materials [82,96–98], synthetic hydroxyapatite [9,50,53,54], quick lime [99], etc. Fluoride removal from aqueous solutions using various reversed zeolites, modified zeolites and ion exchange resins based on cross-linked polystyrene as well as layered double oxides has also been of great interest as adsorbents [56]. Lately, we have published a critical review on the efficiency of different materials for fluoride removal from aqueous media [38]. We observed that activated alumina has widely been used because of its efficiency and low cost but its main disadvantage is its residual aluminum, soluble aluminum fluoride complexes, generation of sludge and having a narrow pH range of 5.0–6.0 [4,13,84]. In continuation of our interest on developing analytical method for fluoride removal, the present study reports the novel Zr–Mn hybrid oxide i.e. composite adsorbent material to remove fluoride from aqueous solutions where the batch experiments including sorption isotherms were also studied. Studies were carried out in synthetic fluoride solutions with the objective of establishing optimum parameters for adsorption.

2. Materials and methods

2.1. Materials and adsorbent preparation

NaF, NaOH, HCl, and all other chemicals and reagents used were of analytical reagent grade. Sodium fluoride with purity > 99%, $\text{Zr}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were purchased from E. Merck Ltd. India. All chemicals were used without further purification.

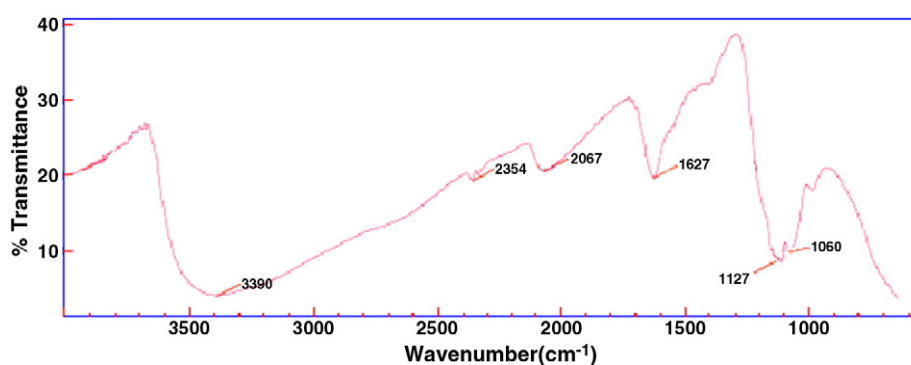


Fig. 1. FTIR spectra of the powdered Zr–Mn oxide adsorbent before fluoride adsorption.

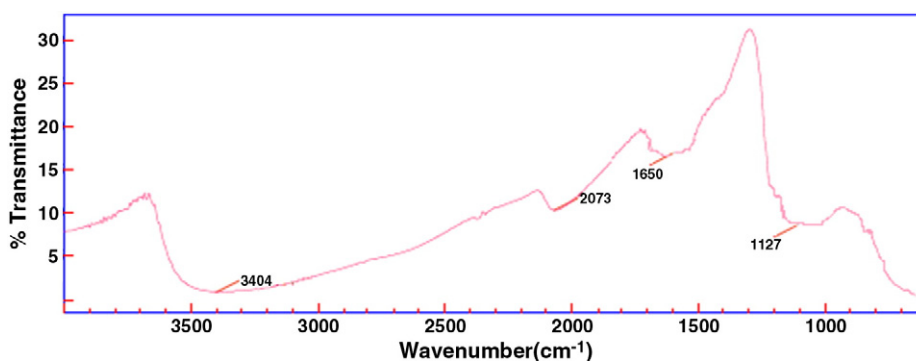


Fig. 2. FTIR spectra of the powdered Zr-Mn oxide adsorbent after fluoride adsorption.

1000 mg/L fluoride stock solution was prepared by dissolving appropriate amount of NaF in 1 L of distilled deionized water from a Milli-Q water system. Synthetic fluoride solutions were prepared by adding appropriate amounts of sodium fluoride to distilled water. All the solutions for removal experiment and analysis were prepared by appropriate dilution from the freshly prepared stock solution. 4.62 g of $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ dissolved in 100 mL distilled water was added to 3.02 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ dissolved in 100 mL distilled water. The pH of the above solution was adjusted to 7.4–7.8 by dropwise addition of 4 M NaOH solution under vigorous stirring leading to precipitation. The precipitate was obtained by filtration and washed with distilled deionized water. The precipitate thus obtained was dried with slow increase in temperature at the rate of 2 °C/min from 80 to 600 °C for 6 h. Finally, the dried composite adsorbent was allowed to cool at room temperature in the furnace and then crushed into fine powder below 200 meshes, and used for adsorption experiments.

2.2. Characterization of adsorbent

Infrared spectroscopy has extensively been used for the characterization of transition-metal cation modified zeolites. The developed Zr-Mn adsorbent calcined at 400 °C for better adsorption to increase its porosity by driving off volatile gasses. The adsorbent after fluoride sorption at 10 mg/L was also obtained. They were blended separately with KBr (0.005 g sample and 0.1 g KBr) and pressed into disks to form pellets for FTIR analysis. FTIR spectra of the Zr-Mn adsorbent and the adsorbent after fluoride sorption were recorded on an FTIR spectrophotometer (Agilent 660, USA) under ambient conditions in the wave number ranging from 600 to 4000 cm^{-1} .

The X-ray diffraction (XRD) analysis of the Zr-Mn composite adsorbent material was carried out by the powder XRD technique with the help of Bruker D8 ADVANCE X-ray diffractometer, Germany. Cu K α radiation was used at the scanning range of $2\theta = 10\text{--}80^\circ$ with a speed of 0.5 s/step and a scan step of 0.02°. The Zr-Mn adsorbent was analyzed at 80 °C.

Brunauer, Emmett and Teller (BET) being the most common method, was used to describe specific surface area using BET equation shown below [100].

$$\frac{1}{W((P_0/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0} \right)$$

In BET method, the plot of $1/[W(P/P_0) - 1]$ versus P/P_0 gives a straight line where W = weight of gas adsorbed, P/P_0 = relative pressure, W_m = weight of adsorbate as monolayer and C = BET constant. The specific surface area of the adsorbent was recorded at liquid nitrogen temperature (77 K) with the help of BET surface area analyzer, model Nova 2000e, Quantachrome Instruments Limited, USA, and using 'multipoint BET method'. In this method 0.20 g of the powdered sample (taken before and after fluoride adsorption) was placed in the sample cell and allowed to degas at one of the degassing stations for 3 h at 250 °C in a vacuum degassing mode (cf. Section 3.1.3).

2.3. Batch sorption experiments

To examine the adsorption isotherm of fluoride removal, batch sorption experiments were conducted. The adsorption experiments were carried out in 250 mL polypropylene flasks containing 50 mL of fluoride solution of different concentrations (vide infra) and 1.2 g

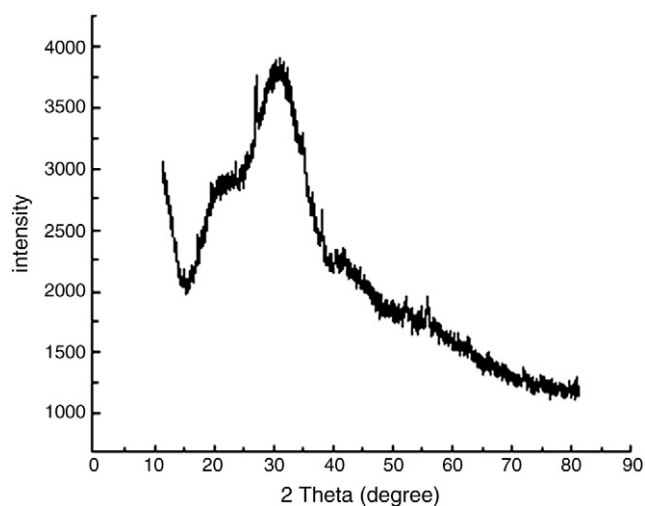


Fig. 3. XRD patterns of the powdered Zr-Mn oxide adsorbent before fluoride adsorption.

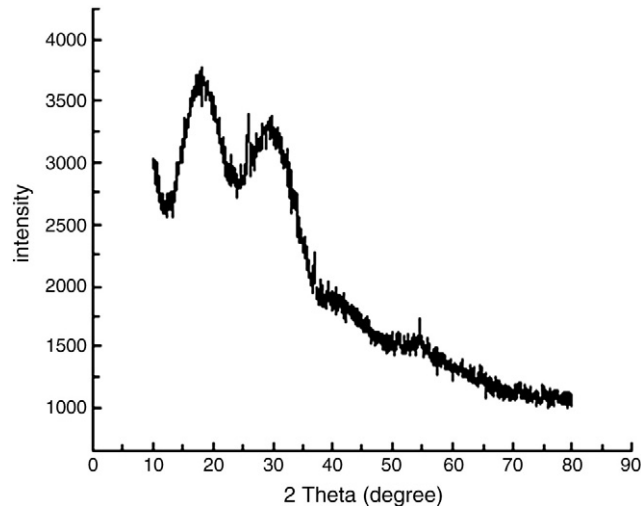


Fig. 4. XRD patterns of the powdered Zr-Mn oxide adsorbent after fluoride adsorption.

Table 1

The specific surface area of the nano-adsorbent Zr–Mn determined before and after fluoride adsorption.

Adsorbent	Surface area (m ² /g)	DA pore size (Å)
Before fluoride adsorption	234.973	12.20
After fluoride adsorption	247.280	11.40

adsorbent, and the flasks were shaken at 150 rpm in a shaker at 29 °C for 145 min except where the effect of the contact time was studied. Fluoride solution at different concentrations was prepared while pH (1–10) of the working solution is controlled by adding sufficient HCl/NaOH solution. At the initial fluoride concentration of 10 mg/L, the adsorption experiment was carried out at the solution pH 7. After the sorption experiments, the adsorbent was separated from the solution by filtration using Whatman filter paper no. 42. The residual fluoride concentration in solution was measured by a fluoride meter equipped with Orion fluoride ion selective electrode (Thermo Scientific Orion, USA).

3. Results and discussion

3.1. Characterization of the Zr–Mn adsorbent

3.1.1. FTIR studies of adsorbent

The FTIR spectra of the Zr–Mn adsorbent before and after adsorption of fluoride are depicted in Figs. 1 and 2 respectively. For the adsorbent, the broad band at 3390 cm^{−1} and the peak at 1627 cm^{−1} are assigned to the stretching and bending vibration of adsorbed water and the peak at 1127 cm^{−1} due to the bending vibration of hydroxyl group of metal oxides (M–OH) [101–106]. Fig. 2 clearly shows that after fluoride adsorption, the band at 3390 cm^{−1} was shifted to 3404 cm^{−1}. The broad band at 3390 cm^{−1} was attributed to the stretching vibration of both the hydroxyl group on adsorbent i.e. metal oxides and adsorbed water. After the fluoride adsorption, the peak did not disappear but its shape changed. There is a reduction in the intensity of –OH bands at 3450–3390 cm^{−1} with some displacement to higher frequencies in fluoride treated adsorbent which may be due to fluoride adsorption/exchange. It was observed that the intensity of peaks at 1627 and 1127 cm^{−1} decreased which indicated that the surface hydroxyl groups on the adsorbent almost disappeared. Thus the results showed the involvement of surface hydroxyl group in defluoridation of water.

3.1.2. XRD patterns of the Zr–Mn adsorbent

The XRD patterns of the Zr–Mn adsorbent before and after adsorption of fluoride are depicted in Figs. 3 and 4, respectively. The XRD study reveals that the structure of adsorbent showed significant changes after the fluoride was adsorbed. The diffraction peak of adsorbent was found at 29.55°, which is the characteristic peak of ZrO₂ (Fig. 3). Due to the presence of MnO₂ in much less amount in

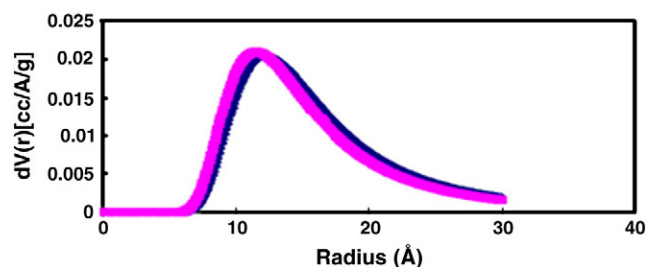


Fig. 6. Dubinin–Astakhov plots for pore radius where blue curve is before fluoride adsorption and pink curve is after fluoride adsorption.

the adsorbent, its phase was hardly detected. It may also be due to formation of Zr–Mn solid solution where the Mn species entered the lattices of ZrO₂. The diffraction peak of the adsorbent after adsorption of fluoride was found at 20° (Fig. 4), which indicates the adsorption of fluoride [107]. However, after the fluoride adsorption, the characteristic structure is reconstructed which suggests that the uptake of fluoride ions by the adsorbent is partly by chemical adsorption.

3.1.3. BET analysis

The specific surface area of the nano-adsorbent Zr–Mn was carried out before and after fluoride adsorption and the results are presented in Table 1. Through BET analysis, the surface area before fluoride adsorption was found to be 234.973 m²/g. It suggested the development of porous structure in the adsorbent. At one of the degassing stations 0.20 g of the powder sample was placed in the sample cell and allowed to degas for 3 h at 250 °C in a vacuum degassing mode. Specific surface area of entire solid solution has been estimated using multipoint BET equation in the P/P₀ range of 0.05–0.35 (Fig. 5) which comes out in the range of 234.9–247.2 m²/g [100]. The pore size distribution and pore characteristics were analyzed based on Dubinin–Astakhov (DA) equation [108] where the corresponding plot is shown in Fig. 6. DA pore radius came out in the range of 12.20–11.40 Å (Fig. 6) which is well corroborated with the surface area value; as the surface area increases the pore radius decreases accordingly and was found in the present investigation (Table 1). The increase in surface area supports the view that a major structural change has occurred during the adsorption of the fluoride ions [9].

3.2. Effect of pH

The pH of the solution is an important variable which affects the adsorption phenomena of fluoride at the solid–water interface. Hence the effects of solution pH were studied in the range of 1 to 10. The effect of pH on the percentage removal of fluoride ion was conducted at the adsorbent dose 1.2 g/50 mL, temp 29 °C and the contact time 145 min and the results are presented in Fig. 7. As shown in Fig. 7, the

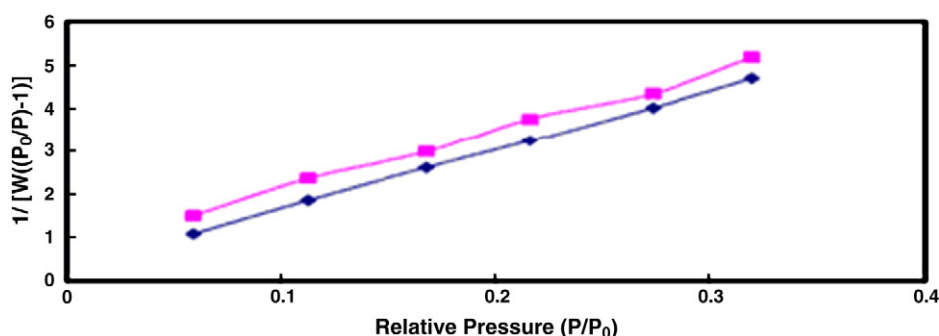


Fig. 5. Brunauer, Emmett and Teller surface area plots where blue line is before fluoride adsorption and pink line is after fluoride adsorption.

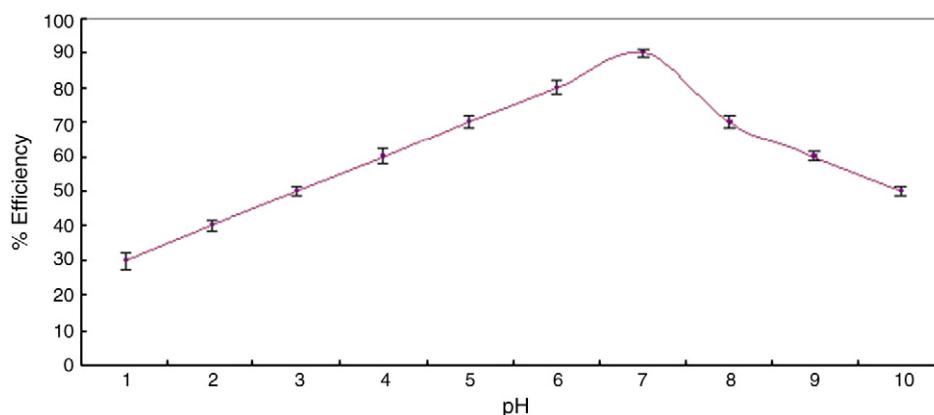


Fig. 7. Effect of pH on the percentage removal of fluoride ion at adsorbent dose 1.2 g/50 mL, temp 29 °C and time of contact 145 min.

removal efficiency of adsorbent increased with increasing pH 1 to 7. It is well established that the surface is highly protonated in acidic medium and therefore maximum fluoride removal in acidic medium is attributed to the gradual increase in attractive forces between positively charged surface and negatively charged fluoride ions. At pH 7, the removal efficiency was found at 90% which may be due to ligand exchange interactions between F^- and OH^- groups. However, after pH 7, the adsorption efficacy of adsorbent is decreased because the increased hydroxyl ions in solution caused competition of OH^- ions for adsorption sites with F^- . This may also be explained in terms of the change in surface negative charge of the adsorbent.

3.3. Effect of initial fluoride ion concentration and contact time

The effect of initial fluoride ion concentration on the adsorption capacity of adsorbent was studied by varying the initial fluoride ion concentration in the range of 10.0–45.0 mg/L at pH 7, temp 29 °C. It was observed that the adsorption capacity increased as initial fluoride ion concentration increased to a specified level and then leveled off (not shown here). It may be due to the presence of more fluoride ion than the adsorption capacity of the adsorbent and similar results have been reported in the literature [5,12,88].

The effects of the contact time on the defluoridation capacity of adsorbent were studied by varying the contact time from 2 to 145 min under the adsorbent dose 1.2 g/50 mL, pH 7 and temp 29 °C and the results in terms of percentage efficiency are presented in Fig. 8. It was observed that the adsorption capacity i.e. the removal of fluoride ions increased with increase in contact time. A close inspection of the adsorption pattern (Fig. 8) revealed that initially

during the first 60 min of the contact time the adsorption was much faster where maximum fluoride removal took place. This was followed by a slow adsorption phase till 145 min probably tending toward attainment of the equilibrium but no subsequent experiments were carried beyond 145 min. Similar results have been reported in the literature [5,9,12,19].

3.4. Effect of adsorbent dosage

To study the effect of the increased adsorption dosage on the percentage removal of fluoride the amount of adsorbent i.e. Zr–Mn composite material dose was varied between 0.1 and 1.2 g/50 mL. The result in terms of percentage removal of fluoride with different sorbent dosages is presented in Fig. 9. The results obtained clearly showed that the percentage removal of fluoride increased with increase in adsorbent dosage. The fluoride removal efficiency increased with adsorption dose because of the increase in the number of active sites as the dosage increases [12]. In other words, the continuous increase is due to increase in surface area as more active sites were available for adsorption with increased dosages. The results show that maximum fluoride adsorption i.e. 90% fluoride removal efficiency took place at maximum adsorbent dose of 1.2 g/50 mL which is a very good defluoridation efficiency. Thus based on the present study 1.2 g/50 mL of the adsorbent was selected for further experiments as the optimum dosage.

3.5. Adsorption isotherm method

The adsorption isotherms have been quite useful in expressing the feasibility of an adsorbent for an adsorbate [4,5,9,12]. The two

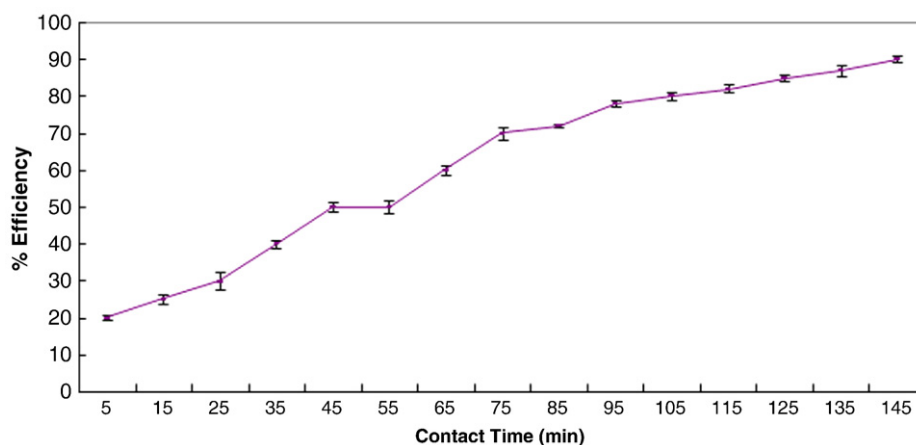


Fig. 8. Effect of contact time on the removal of fluoride ion under the adsorbent dose 1.2 g/50 mL at pH 7 and temp 29 °C.

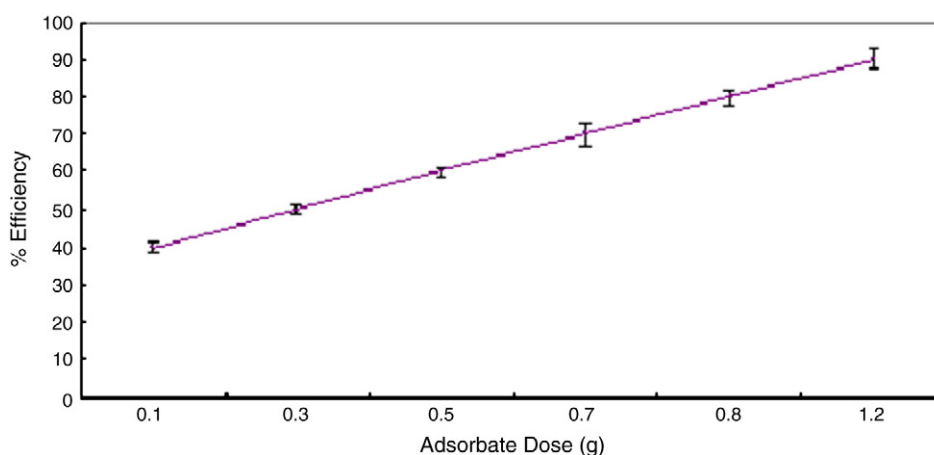


Fig. 9. Effect of adsorbent dose on the removal of fluoride ion at pH 7, temp 29 °C and time of contact 145 min.

frequently used isotherms that are used to describe the adsorption characteristics of adsorbent and the linear forms of isotherms are Freundlich and Langmuir models. They provide the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. The nature of the fluoride adsorption isotherm was investigated under optimized conditions taking 1.2 g adsorbent in 250 mL polypropylene flasks containing 50 mL of fluoride solution of different initial concentrations at pH 7, temp 29 °C and contact time 145 min. The data thus obtained for the removal of fluoride in adsorption method were allied with Freundlich and Langmuir isotherm models. The defluoridation capacity of Zr–Mn composite material was calculated using Eq. (1) where Q_m is the amount adsorbed (mg/g), C_o is the initial fluoride concentration in solution (mg/L), C_e is the equilibrium concentration in solution (mg/L), V is the solution volume (L) and M_s is the mass of the adsorbent (g).

$$Q_m = (C_o - C_e)V/M_s \quad (1)$$

Freundlich adsorption model is purely an experimental model whereas the Langmuir model has certain assumptions. Freundlich model is generally expressed as in Eq. (2). Eq. (2) can be converted in the linear form of the Freundlich adsorption isotherm as in Eq. (3) where Q_e is the total amount of fluoride ion adsorbed/total weight of adsorbents (mg/g). K_f and $1/n$ are Freundlich isotherm constants while C_e is the fluoride concentration at equilibrium. If $1/n > 1$ then bond energy

decreases with surface density, if it is < 1 then bond energy increases with surface density and if $1/n = 1$ then all sites at the surface are equivalent.

$$Q_e = K_f C_e^{1/n} \quad (2)$$

$$\log Q_e = \log K_f + 1/n \log C_e \quad (3)$$

As shown in Fig. 10, the plot of $\log Q_e$ versus $\log C_e$ at different initial concentrations is linear which confirmed the applicability of the Freundlich model for the removal of fluoride ions [4,5,12,109,110].

Langmuir isotherm model assumes that the valence active site on the surface of the adsorbent is capable of adsorbing one molecule and all the sites for adsorption have the same attraction for the molecules of adsorbate and there is no interference or effect of the adsorbed molecule at the adjacent site. With these assumptions Langmuir isotherm is expressed as in Eq. (4) where Q_e is the adsorbed amount of fluoride per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate in liquid phase (mg/L), and Q_o and b are Langmuir constants [4,5,12,110,111]. In the linear form Langmuir isotherm is expressed as in Eq. (5) [111].

$$Q_e = Q_o b C_e / (1 + b C_e) \quad (4)$$

$$1/Q_e = 1/Q_o + 1/b Q_o C_e \quad (5)$$

As shown in Fig. 11, the plot $1/Q_e$ versus $1/C_e$ gave a straight line with a slope of $1/b Q_o$ and the intercept $1/Q_o$ which shows that adsorption also follows Langmuir isotherm.

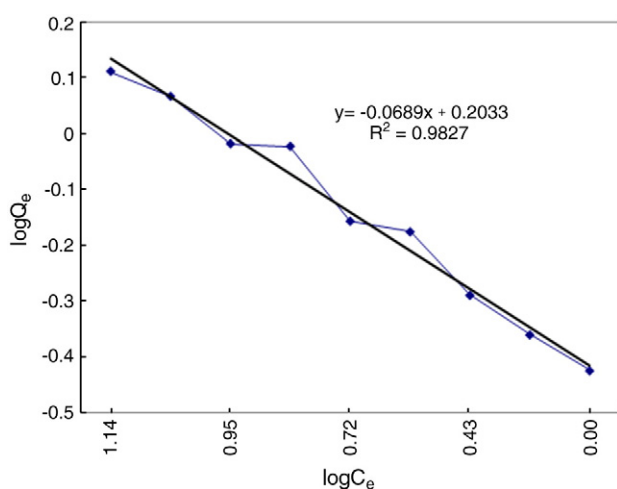


Fig. 10. Linear model of Freundlich isotherm for the removal of fluoride at 50 mL volume, pH 7, temp 29 °C, contact time 145 min and varied initial concentration of adsorbate.

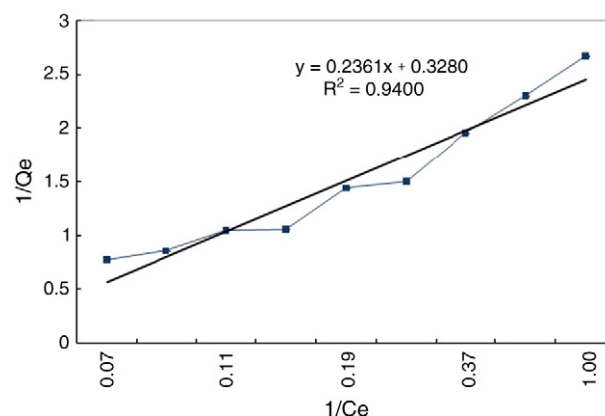


Fig. 11. Linear model of Langmuir isotherm for the removal of fluoride at 50 mL volume, pH 7, temp 29 °C, contact time 145 min and varied initial concentration of adsorbate.

Table 2

The values of Freundlich and Langmuir isotherm constants.

Langmuir isotherm			Freundlich isotherm		
$1/Q_o = 0.328$	$1/b = 0.72$	$R^2 = 0.9400$	$K_f = 1.59$	$1/n = 0.069$	$R^2 = 0.9827$
$Q_o = 3.05$	$b = 1.39$			$n = 14.5$	

The values of Freundlich and Langmuir isotherm constants were calculated from the intercept and slope of the respective plots i.e. Figs. 10 and 11, and are shown in Table 2. The values of the coefficient of determination, R^2 , shown in Table 2 are quite close to unity and hence the process of removal of fluoride followed Freundlich isotherm as well as Langmuir isotherm. The magnitude of $1/n$ is in between 0 and 1 for Freundlich isotherm and thus the value of n is 14.5, i.e. very high which demonstrates that Zr–Mn composite material follows Freundlich isotherm more closely than Langmuir isotherm [12,63]. This is also supported by the high value of the coefficient of determination (R^2) i.e. 0.9827 which indicates that the fluoride absorption process is quite favorable using Zr–Mn composite material as adsorbent where Freundlich isotherm provides the best fit to the experimental data.

3.6. Fluoride removal from fluoride loaded waters

The removal of fluoride from natural water samples (NWS) was carried out in 250 mL polypropylene flasks containing 1.2 g adsorbent per 50 mL natural water that was loaded with fluoride concentrations in the range of 10–30 mg/L. The optimized conditions of pH 7, temp 29 °C and the contact time 145 min were used and the results obtained on residual fluoride levels (1.30–5.40 mg/L) are presented in Fig. 12. Fig. 12 shows that the removal of fluoride in different water samples ranged from 82 to 87% which proved that the removal of fluoride using Zr–Mn composite material has a promising application for water treatment. The removal of loaded fluoride from natural water samples is relatively low (82–87%) in comparison to those obtained using distilled water samples which was 90%. Slightly low removal may be attributed to the presence of complex matrix in natural water samples.

4. Conclusions

Zr–Mn composite material as an adsorbent for fluoride removal from water was successfully prepared via co-precipitation method. The adsorption of fluoride was dependent on pH, initial fluoride concentration, adsorbent dose as well as contact time which were optimized. Removal of fluoride efficiency increased with increase in contact time and adsorbent dose. From FTIR study it has been verified that hydroxyl groups on the adsorbent were responsible for the

fluoride sorption which could be due to the anion exchange and electrostatic interaction in the sorption process. The process of adsorption by adsorbent followed Freundlich as well as Langmuir isotherms. However, the fluoride absorption process is quite favorable using Zr–Mn composite material as adsorbent where Freundlich isotherm provides the best fit to the experimental data. In the removal of fluoride, the reported Zr–Mn adsorbent has a promising application for water treatment.

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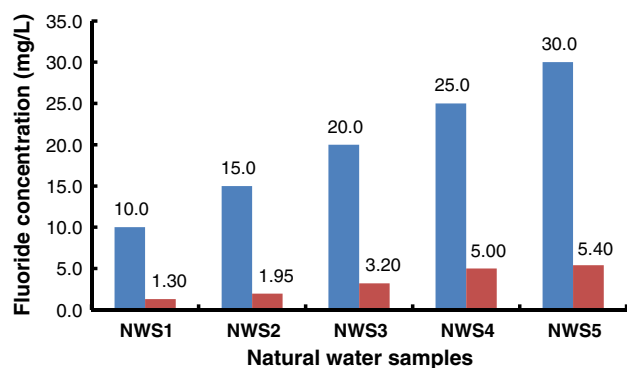


Fig. 12. Removal of fluoride from natural water samples (NWS) loaded with 10.0–30.0 mg/L fluoride using optimum conditions 1.2 g/50 mL adsorbent, pH 7, temp 29 °C and contact time 145 min where residual fluoride is 1.30–5.40 mg/L, respectively.

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