Synthesis and Characterization of Polyaniline/Fe$_3$O$_4$ Magnetic Nanocomposite as Practical Approach for Fluoride Removal Process

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Authors' contributions

This work was carried out in collaboration between all authors. Author MJ designed the experimental method, performed in collaboration with author RF wrote the protocol, and wrote the first draft of the manuscript. Authors MHS and KF managed the process of the study. Author MHS Supervised of biological studies searches. Author KF Supervised of chemical syntheses. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

In order that removal of excess fluoride from water a novel magnetic nanocomposite has been synthesized. Magnetic nanoparticles were successfully synthesized by chemical co-precipitation method. Afterwards, polyaniline containing magnetic nanoparticles were prepared by in-situ doping polymerization in the presence of HCl. The polyaniline/Fe$_3$O$_4$ magnetic nanocomposite has been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Vibrating sample magnetometer (VSM) was also used for magnetization characterization of polyaniline/Fe$_3$O$_4$ nanocomposite at room temperature. The conductivity and magnetic properties of the polyaniline containing Fe$_3$O$_4$ nanoparticles showed that the samples have a novel conductivity and a superparamagnetic behavior. Subsequently, the ability of the adsorbent to remove fluoride from water was demonstrated in a batch sorption mode. Results reveal that the adsorption is rapid and the adsorbent has high affinity for fluoride, which depends on solution pH and adsorbent dose.

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1. INTRODUCTION

Fluoride has been shown to cause significant effects in human through drinking water. Pursuant to the World Health Organization standards the maximum acceptable concentration of fluoride ions in drinking water are below 1.5ppm. Low concentrations of fluoride are beneficial for bones and teeth [1]. However, long-term utilization of water containing ample amounts of fluoride can lead to fluorosis of the bones and teeth [2]. Because of high toxicity of fluoride to human, there is an immediate need to defluoridation of drinking water to make it safe for human consumption.

The most commonly used methods for the defluoridation of water are ion exchange [3], adsorption [4,5], precipitation [6] and so on. Among these methods, adsorption is the most widely used method for the removal of fluoride from water.

The main point in an adsorption process is to select an adsorbent with high capacity and fast kinetics for contaminant removal from water. As such, several adsorbents such as activated alumina [7], activated carbon [8], polyaniline [9] and polypyrrole [10] have been tested in water defluoridation. Most of these adsorbents show disadvantages like low capacity and large diffusional time scale for transferring an adsorbing species in the internal matrix of the adsorbent. To overcome these restrictions, nano-sized adsorbents has been designed [11]. However, the separation of nano-sized materials from solution is difficult. To dominate this limitation, magnetic nanoparticles have been used in the structure of nano-adsorbents. The magnetic property makes the material easy to retrieve from solution using external magnetic field [12-15].

In order to removal target pollutants from an aqueous solution, magnetic nanoparticles properties can be tailored by using functionalized polymers to impart surface reactivity [13,16]. In recent years, there has been considerable interest in conducting polymers owing to their extensive potential applications in areas such as microelectronics, composite materials, catalysts, and chemical sensing [17-19]. In addition, conducting polymers used as ion exchanger materials have shown new potential applications in water and wastewater treatment [20-22]. One of the conducting polymers that have recently attracted research is polyaniline that shows good efficiency in removal of fluoride from water [9].

According to the above mentioned issues, in this work polyaniline/Fe_3O_4 nanocomposite sorbent was synthesized and used as a novel material for removal of fluoride in water. The factors that influenced on the extraction efficiency of fluoride including contact time, adsorbent dose and pH were investigated and optimized. Finally, the proposed method was successfully applied to the removal of fluoride in water.

2. Experimental

2.1 Materials

Polyaniline was purchased from Sigma–Aldrich, USA and was distilled under reduced pressure prior to use. Ferric Chloride ($FeCl_3$), ferrous chloride ($FeCl_2$) and sodium fluoride (NaF) were also purchased from Sigma–Aldrich, USA. Stock solutions of fluoride were

prepared by dissolving NaF in deionized water. All other solvents used, were of analytical grade and were freshly distilled before use.

2.2 Preparation of Fe$_3$O$_4$ Nanoparticles

Fe$_3$O$_4$ NPs were synthesized by chemical co-precipitation method [23] as follows: 800mL of deionized water was placed in a three-necked flask. Then, FeCl$_3$.6H$_2$O and FeCl$_2$.4H$_2$O with 2:1 molar ratio was added into the deionized water. The mixture was stirred under nitrogen atmosphere for 45 min. By addition of 1.5 M NH$_4$OH solution, the pH of the solution reached to 8 and the reaction was allowed to run for 2 h. Finally, the resulting black sediment was separated by an external magnet (Fig. 1), and washed by deionized water and then ethanol severally times.

Fig. 1. Fe$_3$O$_4$ NPs separated by a magnet

2.3 Preparation of Polyaniline/Fe$_3$O$_4$ Nanocomposites

In a typical preparation of polyaniline/Fe$_3$O$_4$ nanocomposite, 11.30mL aniline was dissolved in 150mL distilled water containing 20mL hydrochloric acid, and then the desired quantity of Fe$_3$O$_4$ NPs were added to the solution and stirred. 27.5g of Ammonium peroxydisulfate dissolved in 1.5M HCl solution and slowly added to the reaction mixture. During the synthesis, the mixtures were vigorous stirred for 16 hours and the temperature was kept at 0ºC. The precipitated powder was centrifuged and washed with distilled water. Then powders dried in an oven at 100ºC for 24h.

2.4 Characterization of Polyaniline/Fe$_3$O$_4$ Nanocomposite

The X-ray diffraction patterns of polyaniline/Fe$_3$O$_4$ were recorded by Philips PW-180. The XRD data were matched with standard JCPDS data files. Scanning electron microscopy (SEM) images were recorded by a Philips XL-30 microscope operating at an accelerating voltage of 30 kV. Fourier transform infrared (FTIR) spectra were recorded by a Nexus 670

FT-IR spectrometer using KBr pellet. Magnetic properties of the sample determined by a Lake Shore 7307 vibrating sample magnetometer (VSM).

2.5 Removal of Fluoride by Polyaniline/Fe$_3$O$_4$ Nanocomposite

The removal experiments were carried out by batch method. A known quantity of polyaniline/Fe$_3$O$_4$ nanocomposite and desired concentration of fluoride solutions were taken in a 100mL flask. The pH of the solution was adjusted by using dilute NaOH or HCl solution. The final volume was made up to 50mL with distilled water. All the experiments were carried out in a horizontal shaker at 50spm. Primary studies showed that 120 min was necessary to attain equilibration. After equilibration period, the polyaniline/Fe$_3$O$_4$ nanocomposites were separated by an external magnet then the resulting solution was filtered. The resulting solution was analyzed for remaining fluoride. The experimental parameters studied are contact time (10–150 min), pH effect (3–11), adsorbent dose (0.05–0.25g/l).

The fluoride concentration was measured with a specific ion electrode (ISE25F) by using total ionic strength adjustment buffer (TISAB) solution (58g of NaCl, 57mL of CH$_3$COOH and approximately 150mL of 6M NaOH in a volume of 1000mL) to maintain pH 5.3 and to eliminate the interference of complexion ions. The fluoride samples and the standard solutions were diluted to 1:1 with TISAB [24]. Fluoride concentration and pH were determined by an ion meter (PHM 250, Ion Analyzer, France). The amount of fluoride removal was calculated by subtracting the fluoride remaining in the solution from initially taken.

Each removal experiment was conducted thrice to obtain reproducible results with an error of less than 5%. The original fluoride solution (control) was used in all the analysis that further reduces considerably the absolute error associated with the fluoride analyzer to <4%.

3. RESULTS AND DISCUSSION

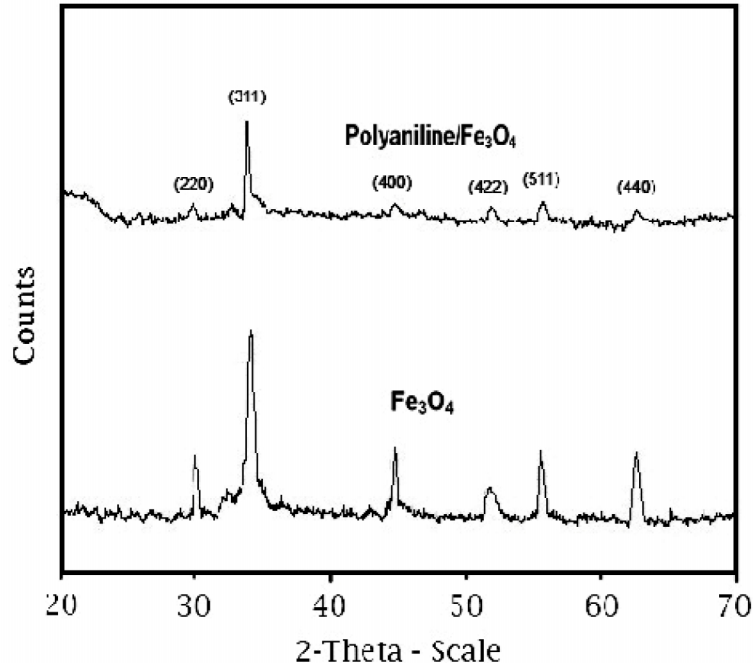### 3.1 Characterization of Polyaniline/Fe$_3$O$_4$ Nanocomposite

Fig. 2 shows the XRD patterns of Fe$_3$O$_4$ nanoparticles and polyaniline/Fe$_3$O$_4$ nanocomposite. The diffraction peaks of Fe$_3$O$_4$ in 2θ = 32.2º, 35.5º, 43.2º, 53.5º, 57.1º, 62.9º, and the diffraction peak appears corresponding inverse spinel type Fe$_3$O$_4$ (220), (311), (400), (422), (511) and (440) crystal plane [23]. XRD patterns of the sample by comparing the two, shows that the main components of composite Fe$_3$O$_4$ nanoparticles, relatively few polyaniline content.

In addition, in this figure, any kind of characteristic peaks of impurities was observed. The crystallite size Dc of prepared particle, according to the FWHM of the (311) plane refraction peak, was estimated using the Debye-Scherrer formula through equation:

$$D_c = \frac{k\lambda}{\beta \cos\theta}$$

Where K is the shape factor, λ is the X-ray wavelength (0.154 nm), β is the line broadening at half the maximum intensity (FWHM) in radian, and θ is the Bragg angle [25,26]. D (in nm)

is the mean size of the ordered (crystalline) domains that may be smaller or equal to the grain size. According to XRD data, average size of Fe_3O_4 is around 33nm.


**Fig. 2. XRD patterns of Fe_3O_4 NPs and polyaniline/Fe_3O_4 nanocomposite**

The FT-IR spectrum is used to characterize the molecular structures of polyaniline/Fe_3O_4 nanocomposite. The characteristic peaks of Polyaniline/Fe_3O_4 nanocomposite and also polyaniline sample (without Fe_3O_4 NPs) is showed at Fig. 3., Polyaniline/Fe3O4 nanocomposite have characteristic peaks at around 3234 cm^{-1} (N–H stretching), 1582cm^{-1}, 1300cm^{-1} (C–N stretching of secondary aromatic amine), 1140cm^{-1}, and 822cm^{-1} (out of plane deformation of C–H in the 1, 4-disubstituted benzene ring) [27,28].

Fig. 4 shows typical magnetization curves as a function of applied field at room temperature. No pronounced hysteresis loop, which indicates that both the coercivity and the retentivity of the nanocomposite are zero, is consistent with superparamagnetic behavior and a saturated magnetization of the polyaniline/Fe_3O_4 nanocomposite (Ms=4emu/g for the samples containing 10 wt% Fe_3O_4 NPs and Ms= 9 emu/g for the samples containing 20 wt% Fe_3O_4 NPs).

Scanning electron microscopy (SEM) was employed for particles size measurement, shape evaluation and aniline in-situ polymerization with Fe_3O_4 magnetic nanoparticles confirmation. The SEM also indicates that the polyaniline/Fe_3O_4 nanocomposites possess a nearly spherical shape with a smooth surface, via a diameter of approximately 50 nm (Fig. 5).
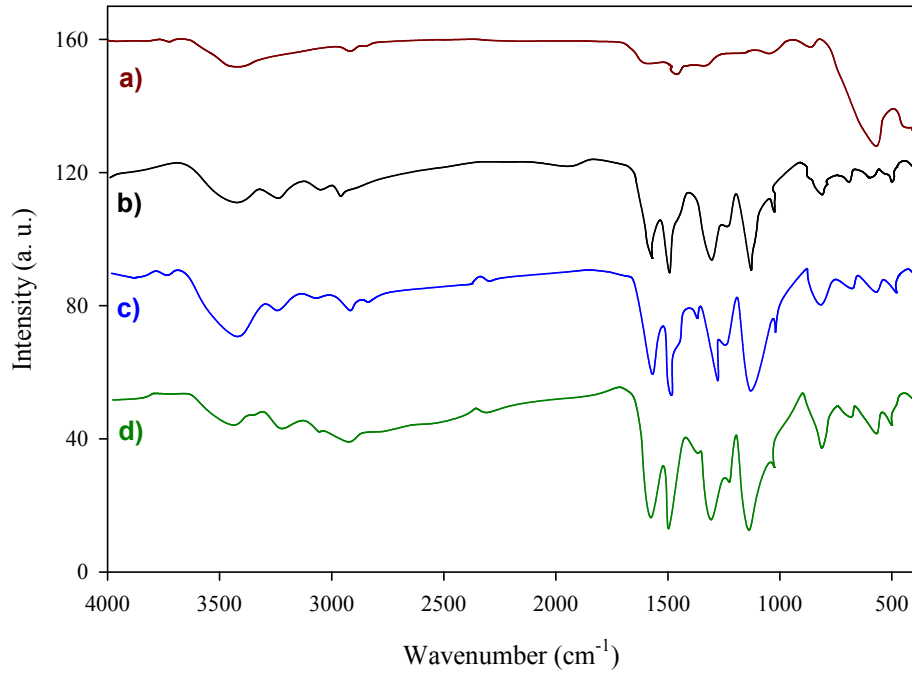
Fig. 3. FTIR spectra of polyaniline containing: (a) Fe$_3$O$_4$ nanopartilces, (b) 0 wt%, (c) 10wt% and (d) 20wt% Fe$_3$O$_4$ NPs
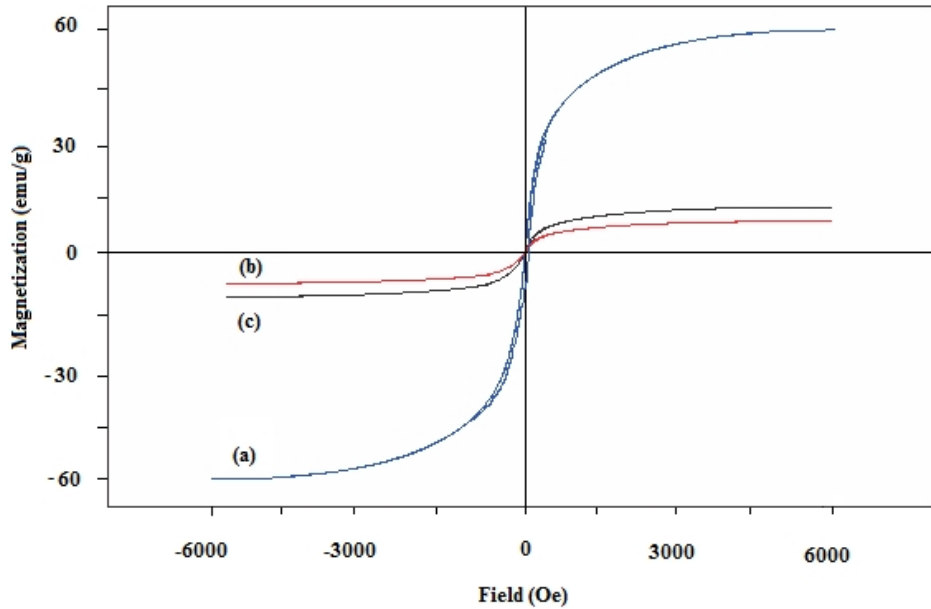
Fig. 4. Magnetization vs. applied magnetic field for: (a) Fe$_3$O$_4$ NPs and (b) 10wt% and (c) 20wt% Fe$_3$O$_4$ NPs in polyaniline
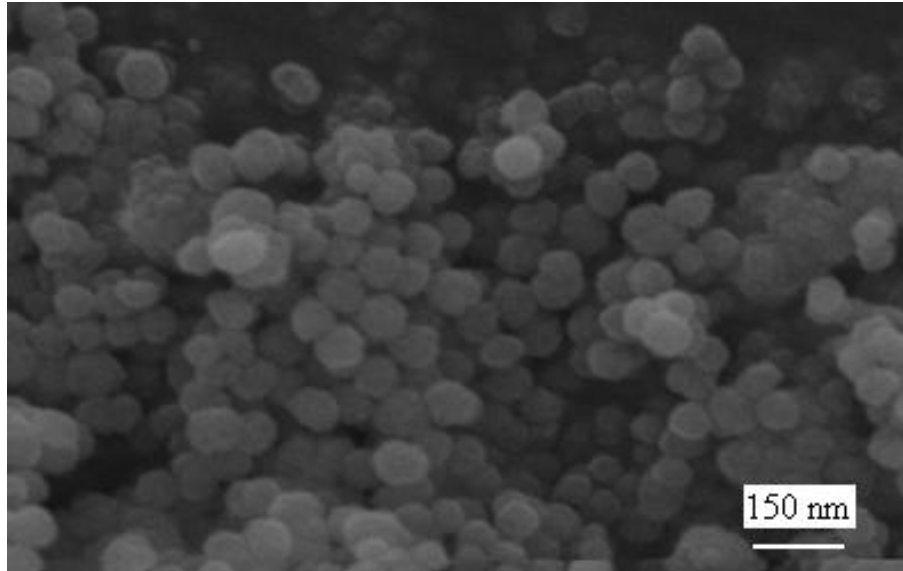
Fig. 5. SEM image of Polyaniline/Fe$_3$O$_4$ nanocomposites

3.2 Effect of Contact Time

The removal of fluoride from water with time is shown in Fig. 6. It can be seen from the figure that the removal of fluoride increases with increase in time and after 10min the rate of removal is very fast, i. e. within 10–90 min, most of the fluoride is removed and reaches a maximum at 150min and thereafter remains constant. The optimum time to attain the equilibrium is 120min. The sudden rise in removal of fluoride indicates that the adsorption of fluoride probably takes place due to the diffusion taking place into the pores on the surface of the adsorbent.
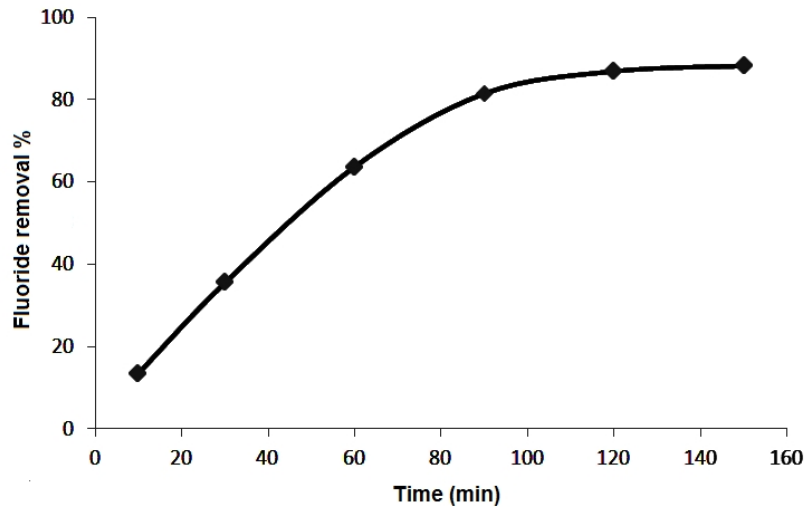

Fig. 6. Plot of percent removal of fluoride as a function of equilibrium time (min) at adsorbent dose 0.25g/l, fluoride concentration 25 mg/l and pH 6.5

3.3 Effect of Adsorbent Dose

The relation of the polyaniline/Fe_3O_4 nanocomposite dose on fluoride removal is shown in Fig. 7. It is shown dose-dependent between fluoride removal (percentage) and polyaniline/Fe_3O_4 nanocomposite dose. Nanocomposites fluoride removal efficiency was increased with increasing amount of adsorbent because of the increasing of contact surface. Volume fluoride removal changes from 30% at the dose of 0.05g to 80% at the dose 0.25g of polyaniline/Fe_3O_4 nanocomposite.
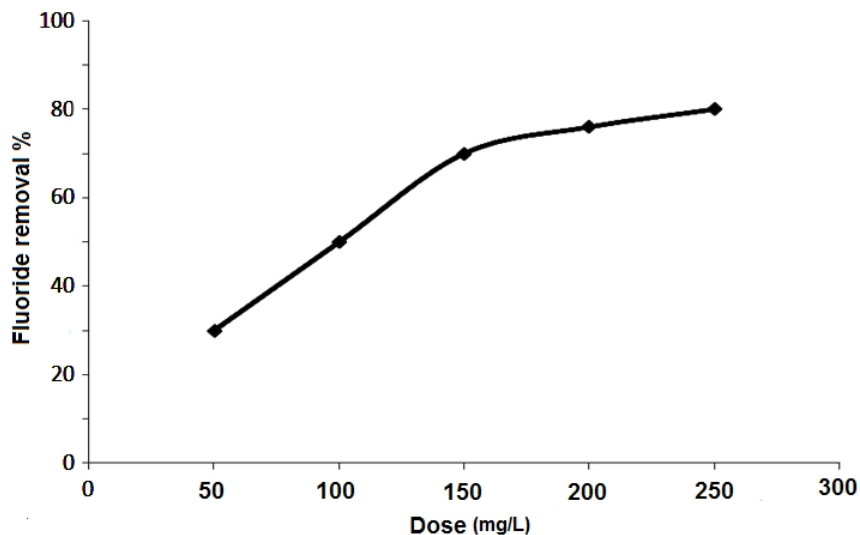
Fig. 7. Effect of adsorbent dosage on the removal of fluoride

3.4 Effect of pH

Fluoride adsorption behavior of the polyaniline/Fe_3O_4 nanocomposites were investigated under different pH conditions. The fluoride isolation had direct relationship with solution pH from 3 to 6, but above pH 6, there is a slight decrease in fluoride uptake. Fig. 8 the reason low fluoride uptake, In the low pH rang, was due to reduced availability of free fluoride ions in solution, while in high pH, the slight reduction may resulted from competitive interaction with hydroxyl ions and interaction between some deprotonated active sites and fluoride. However, results suggest that the polyaniline/Fe_3O_4 nanocomposite is more effective in the near neutral pH range.

3.5 Effect of Competing Anions

The impact of various anions including chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}) on fluoride removal by polyaniline/Fe_3O_4 nanocomposite was investigated at 25mg L^{-1} of initial fluoride concentration. The concentration of competing anions was varied from 25 to 100mg L^{-1} (Fig. 9). Anions present in the fluoride solutions are likely to limit the fluoride removal efficiency. In the presence of sulphate and phosphate percent removal of fluoride was ~50-60%, while in case of other anions (chloride and nitrate) percent removal of fluoride was ~70-75%. It was observed that fluoride adsorption was more influenced by the presence of sulphate and phosphate ions. This can be explained by the fact that fluoride,

sulphate and phosphate ions are all inner-sphere complex-forming species and therefore competed for the same active sites of adsorption [29].
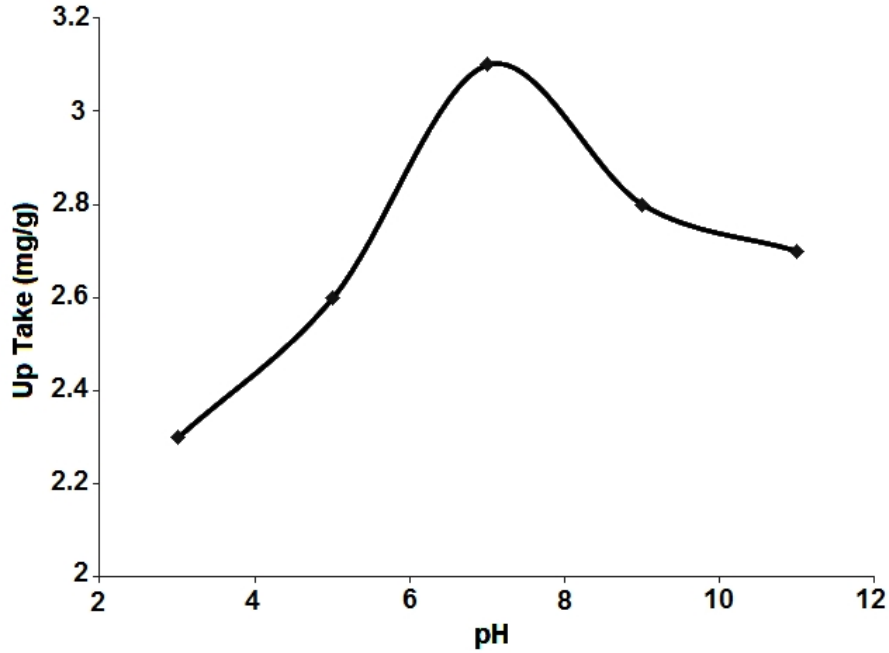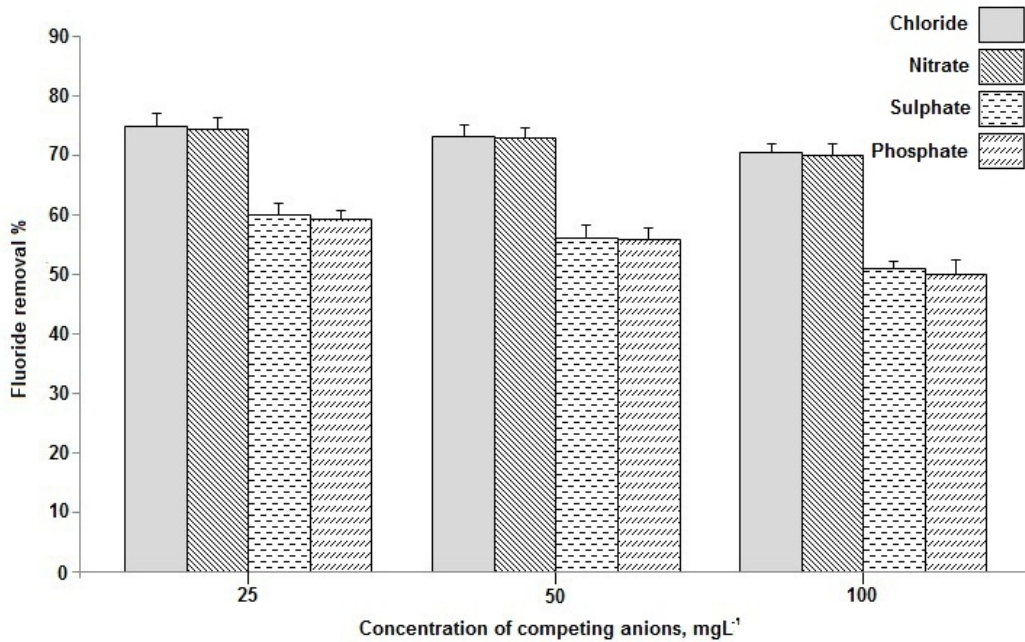

Fig. 8. Effect of pH on the removal of fluoride

Fig. 9. Effect of different concentrations of competing anions on fluoride sorption on polyaniline/Fe$_3$O$_4$ (contact time=150 min, sorbent dose= 250mg L^{-1})

3.6 Desorption

To develop a cost effective adsorbent for fluoride removal, it is important that the adsorbed fluoride should be easily desorbed for reusability of the media. Desorption of fluoride from loaded nanocomposite was conducted under different pHs and the results are shown in Fig. 10. In the acidic pH range, small amount of fluoride was eluted from the media while in the alkaline pH range a significant elution was observed. Specifically, 85% of the adsorbed fluoride was released at pH 12. The adsorption capacity of the regenerated adsorbent from a 25mg L^{-1} of fluoride solution was found to be ~2.63mg g^{-1}. This value is the same as the amount obtained in the first adsorption cycle. The results indicate the recyclability of the material for further use.
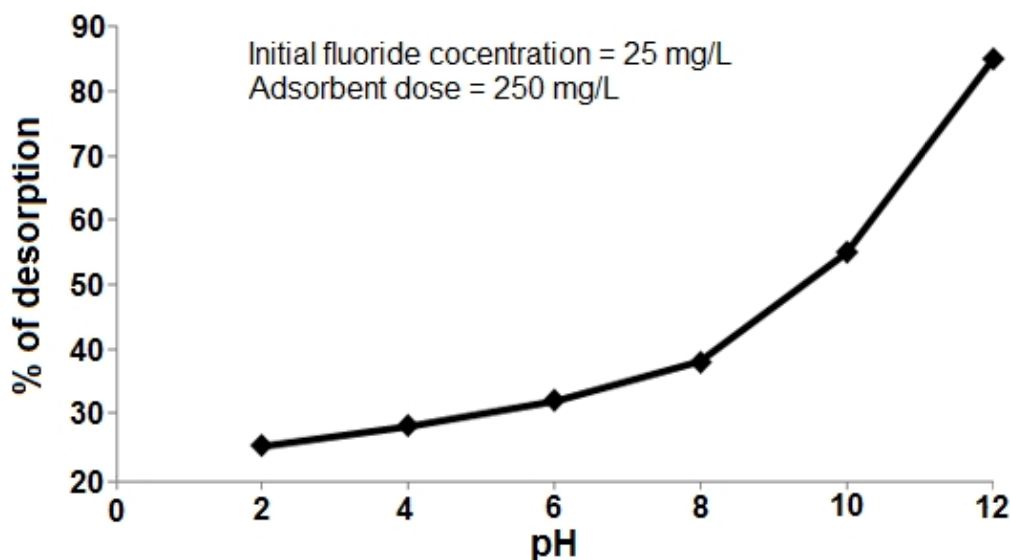

Fig. 10. Desorption of fluoride adsorbed polyaniline/Fe$_3$O$_4$ nanocomposite under different pH values

4. CONCLUSIONS

According to the Necessity of remove excess fluoride from water, a novel fluoride adsorbent has been synthesized. Polyaniline-coated magnetic nanoparticle synthesized by in-situ doping polymerization in the presence of HCl. XRD and FTIR was used to characterize the chemical structure of the polyaniline/Fe$_3$O$_4$ nanocomposite and by SEM was observed a uniform morphology this structure. Also, the magnetic properties of polyaniline/Fe$_3$O$_4$ determined by VSM. The fluoride uptake was very fast, and depended on contact time, adsorbent dose and pH. The extent of fluoride removal changes from 30% at the dose of 0.05g to 80% at the dose 0.25g of polyaniline/Fe$_3$O$_4$ nanocomposite. The increasing amount of the polyaniline/Fe$_3$O$_4$ nanocomposites significantly influenced the extent of fluoride adsorption due to the increase in the number of active sites available for adsorption. Different pH conditions were investigated, and observed that fluoride uptake increases with an increase in solution pH from 3 to 6. Fluoride sorption was more affected by the presence of sulphate and phosphate anions. The results of the present study suggest that polyaniline/Fe$_3$O$_4$ nanocomposite can be used for the removal of excess fluoride from water.

CONSENT

All authors declare that 'written informed consent was obtained from the patient (or other approved parties) for publication of this case report and accompanying images.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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