Removal of Fluoride Ions (F-1) from Contaminated Drinking Water using MnFe₂O₄ /Banana Peels Composite Synthesized through Chemical Co-Precipitation Method

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ARTICLE INFO	ABSTRACT
	Fluoride (F) contaminated water is of immense health risk. Skeletal as well as dental fluorosis is due to the excessive Fluoride (> 1.5 mg/L) concentration in drinking water. In the present work, MnFe₂O₄ /banana Peels composite a unique adsorbent has been explored for the elimination of fluoride from aqueous system. These nanocomposites were characterized by XRD and FTIR. Retentivity and coercivity value of nanocomposite is determined by Hysteresis loop. The optimized conditions for the removal of 86% fluoride from field water sample was achieved at pH 8 and in 175 min. From the experimental results, it may be inferred that MnFe2O4 /banana peels composite is an adequate adsorbent for the removal of fluoride from water.

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1.   Introduction

Asian countries mainly depends upon the ground water for their water source (Kazi, Brahman, Baig, & Afridi, 2018; Raj & Shaji, 2017). The fluoride content enters into This ground water contain fluoride contents due to the natural sources like leaching of fluoride bearing rocks and minerals (Viswanathan & Meenakshi, 2010).Fluoride due to its ubiquitous property is added to the environment anthropogenically varies its contents in lithosphere from 100 to 1500 g/ton (Maheshwari, 2006). Its dual influences i.e. lower and higher absorption by human being make it of prime importance. Fluoride's specific amount is not only beneficial for human in bone forming, prevention of tooth decay but on the other hand its higher concentration causes fluorosis, brattling of bones, curvature of bones, dwarfishness, mental derangements, cancer, etc. and in extreme cases even death (Viswanathan & Meenakshi, 2008). It is approximated about 450 million people   of 30 countries using water for drinking of more than 1.0 mg/L fluoride contents which is not according to the standards of World Health Organization WHO i.e. slightly above or below 1 mg/L. In lower water intake regions, up to 1.5 mg/L fluoride level is acceptable (Chen et al., 2016). There are various methods which are difficult in operation, highly expensive and time consuming for the removal of fluorides from water such as chemical precipitation, adsorption technique through batch and column process, ion exchange, nanofiltration, electrodialysis, membrane separation, electrocolactose of plants (Dongare et al., 2017) agulation, and reverse osmosis (Aldaco, Irabien, & Luis, 2005), (Turner, Binning, & Stipp, 2005), (Cai et al., 2015), (Tor, Danaoglu, Arslan, & Cengeloglu, 2009), (Onyango, Kojima, Aoyi, Bernardo, & Matsuda, 2004), (Tahaikt et al., 2007), (Lahnid et al., 2008), (Behbahani, Moghaddam, & Arami, 2011), (Schneiter & Middlebrooks, 1983), (Dash, Sahu, Sahu, & Patel, 2015). In this work we use the Manganese Ferrite (MnFe₂O₄) /Banana Peels

Composite for the removal of fluoride. Bananas are internationally known as eatable fruits with yearly cultivated up to one hundred and sixty five million <u>tons</u> in year 2011 (Van Thuan, Quynh, Nguyen, & Bach, 2017). More often, skin of banana includes 6-9% protein and 20-30% fibers. There are 30% and 15 % more free sugar and starch in ripe banana peels than green banana peels. The assistances of banana coverings were recognized for water cleansing to reduce ethyl alcohol, cellulose, (Deshmukh et al. 2017; Kumar et al. 2011)<u>.</u> But the use of banana peels through batch adsorption is a time consuming and costly process because all operating variables remains constant by changing one variable at a time. The present work is aimed at facile synthesizing an efficient and economical composite of Manganese Ferrite ($MnFe_2O_4$) /Banana Peels for the removal of fluoride contents.

2. Experimental Procedure
2.1. Chemicals and Reagents

Manganese(II) chloride tetra hydrate ($MnCl_2$. $4H_2O$, purity $\geq$ 99%), Ferric chloride hexahydrate ($FeCl_3$. $6H_2O$, purity =97%), Ferric sulphate heptahydrate ($FeSO_4.7H_2O$, purity $\geq$ 99%), Sodium hydroxide (NaOH, purity =97%), Acetic Acid (CH_3COOH, purity $\geq$99.7%), Trisodium citrate dihydrate ($Na_3C_6H_5O_7.2H_2O$, purity =99.9%), were purchased from Merck (Germany). Ammonia solution (NH_3, purity $\geq$ 99.98%), Potassium hydroxide (KOH, purity $\geq$ 85%), Sodium fluoride (NaF, purity $\geq$99), Sodium Chloride (NaCl, purity $\geq$99%) were obtained from Sigma-Aldrich (Germany).

2.2. Preparation of Magnetic MnFe₂O₄ Particles

The magnetic nanoparticles were prepared through the chemical co-precipitation method by dissolving 0.1M solutions 4.95g $MnCl_2$.$4H_2O$, 6.758g $FeCl_3.6H_2O$, and 0.2M solution of 13.901g $FeSO_4.7H_2O$ in 250 mL of deionized water under a nitrogen gas flow with constant stirring at 80℃. The precipitating reagent ammonia solution was continuously added until pH reached 10 ~ 11. The precipitates are formed when pH is maintained. These precipitates were separated by using centrifugation machine. These precipitates were centrifuged, washed two to three times with deionized water. Then these are dried into the electrical oven for 24h at 60°C. Solid material was then grinded with pestle mortar into a fine powder form of $MnFe_2O_4$. The fine powder of $MnFe_2O_4$ were annealed by heating in an electrical furnace at 650°C for 240min at the rate of 6°C per min.

2.3. Synthesis of Banana Peels

Banana peels are collected from banana taking from fruit store. Banana peels are washed two or three times to remove impurities by using simple tap water. Then banana peels are dried for two days under sunlight. Furthermore, these are dried in an oven at the temperature of 100°C for 36h. Banana peels were grinded to form a fine powder with the help of simple grinder to form fine powder.

2.4. Preparation of MnFe₂O₄ /Banana Peels Composite

$MnFe_2O_4$ /banana Peels composite was prepared by physically mixing the fine powders 1g of $MnFe_2O_4$ and 1g of fine powder of banana peels and then grinding in pestle mortar at room temperature for 30℃.

2.5. Adsorption Experiments

The adsorption experiment was carried out by controlling variables such as contact time (min), concentration (ppm) and pH. Batch absorption experiments are performed in 15 ml of centrifuge tubes containing 10mg of $MnFe_2O_4$, 5ml deionized water, 2ml buffer solution and 3ml of water sample containing fluorides, 10 mg $MnFe_2O_4$, contact time was (5-240 min) and pH was adjusted (3-11) by adding 0.1M HCl and 0.1M NaOH. Then flasks were shaken at 150rpm in a shaker for 30min. than check it the concentration of fluoride absorbed from fluoride selective electrode by Manganese ferrite nanoparticles. The adsorption capacity (mg/g) of the experimental adsorbent was calculated by using by eq. $Q_e = (C_i - C_f) \times V/m$, Where C is concentration in (mg/L), qe is maximum adsorbed quantity at equilibrium, m is mass of adsorbent in (g) and V is volume of solution.

2.6. Instrumentation

The adsorbent characterization and fluoride ion concentration from aqueous solution was determined by using scanning electron microscope (SEM), X-Ray Diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR), ion selective electrode and hysteresis loop for the softness of material and fluoride sensor for adsorption tests.

3. Results and Discussion
3.1. XRD Analysis

The crystallinity and purity of as synthesized Magnetic manganese ferrite composite were evaluated by powder XRD. All diffraction peaks of XRD pattern is indexed to Face Centered Cubic structure (Fig. 1). The sharpness of diffraction peaks is confirming the Crystallinity of our synthesized material without any impurities.

The X-ray pattern of as prepared manganese ferrite composite depicts the peaks at (111), (220), (311), (222), (400), (422), (511), (440) which are exact corresponding peaks of magnetic manganese ferrite, as confirmed by literature. These peaks are clearly confirming the structure of our as prepared manganese ferrite formation.

All lattice parameter values such as, cell unit volume 'a' and X- Ray density of sample was calculated by using this formula
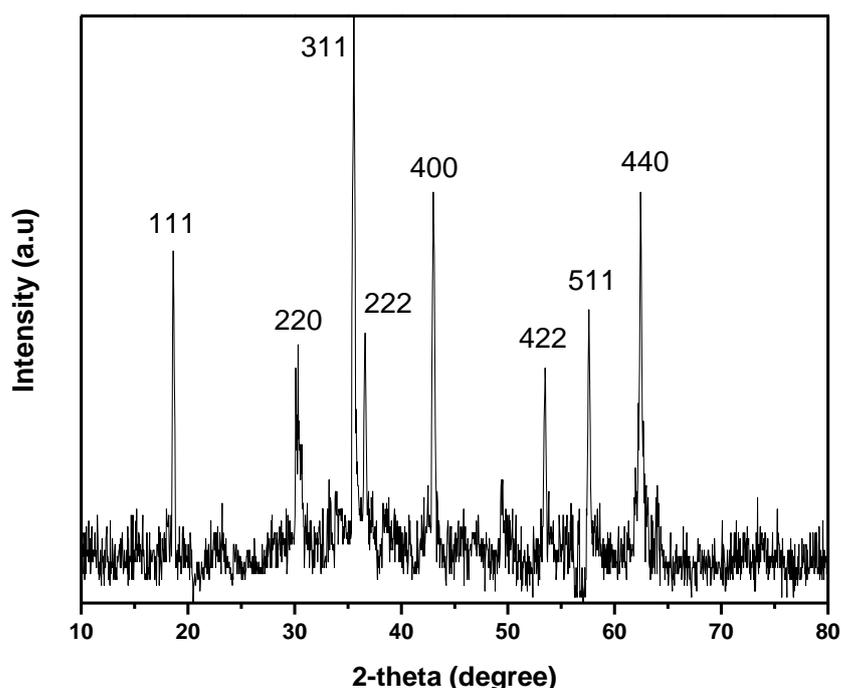
$$Sin^2\theta = \frac{\lambda^2}{3a^2}(h^2 + k^2 + l^2) \tag{1}$$

Where λ is the wavelength, h,k,l are the miller indices and a is the lattice constant. i.e. a= 8.25 Å

$$V=a^3 \tag{2}$$
$$dx = 8 M/N_A V \tag{3}$$

Here M is Molar mass, N_A is Avogadro number, V is unit cell volume and 8 is number of molecules per unit cell.


Figure 1: XRD patterns for single phase MnFe$_2$O$_4$ ferrite synthesized by co-precipitation method

The arrangement/geometry of atoms and unit cell size is measured by angular positions and relative intensities of diffracting peaks.

3.2. FTIR Analysis

FTIR spectrum of both Simple $MnFe_2O_4$ were taken which reveals the similarity of spectrum of both $MnFe_2O_4$ and Our as prepared materials, which confirms that our prepared nanocomposite is formed properly as confirmed by its representing characteristics peaks.

FTIR spectrum of simple manganese ferrite is taken and its characterization peaks are observed at 3377 cm^{-1} , 1980 cm^{-1}, 1378 cm^{-1} due to Mn-O-Fe stretching, 661cm^{-1} due to Fe-O and Mn-O bonds (Fig. 2).
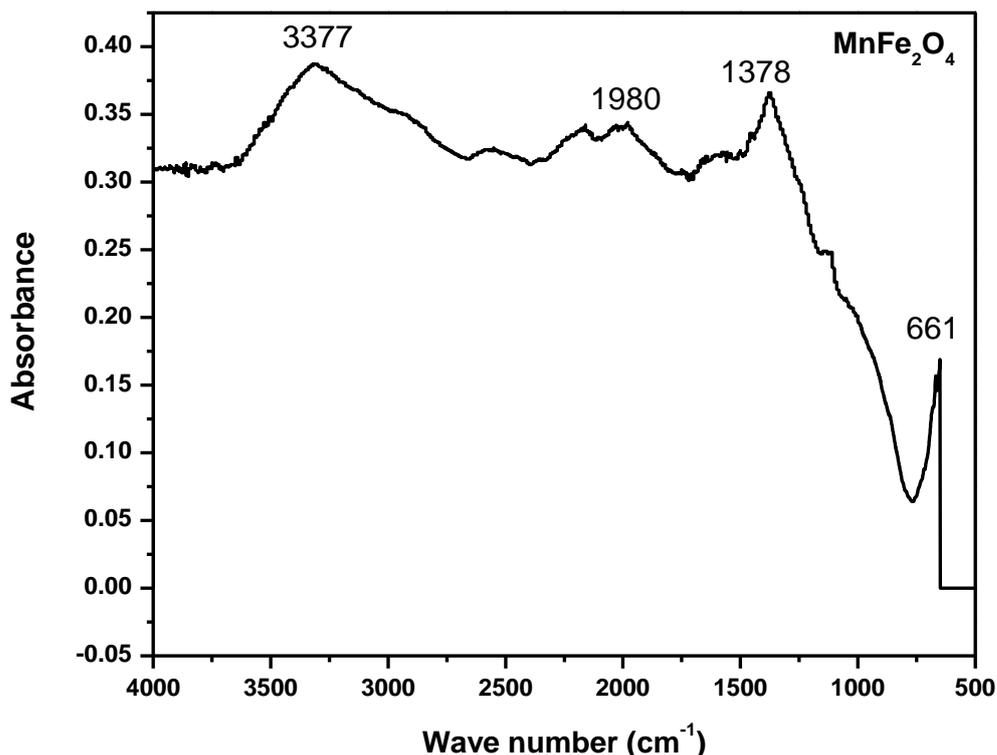
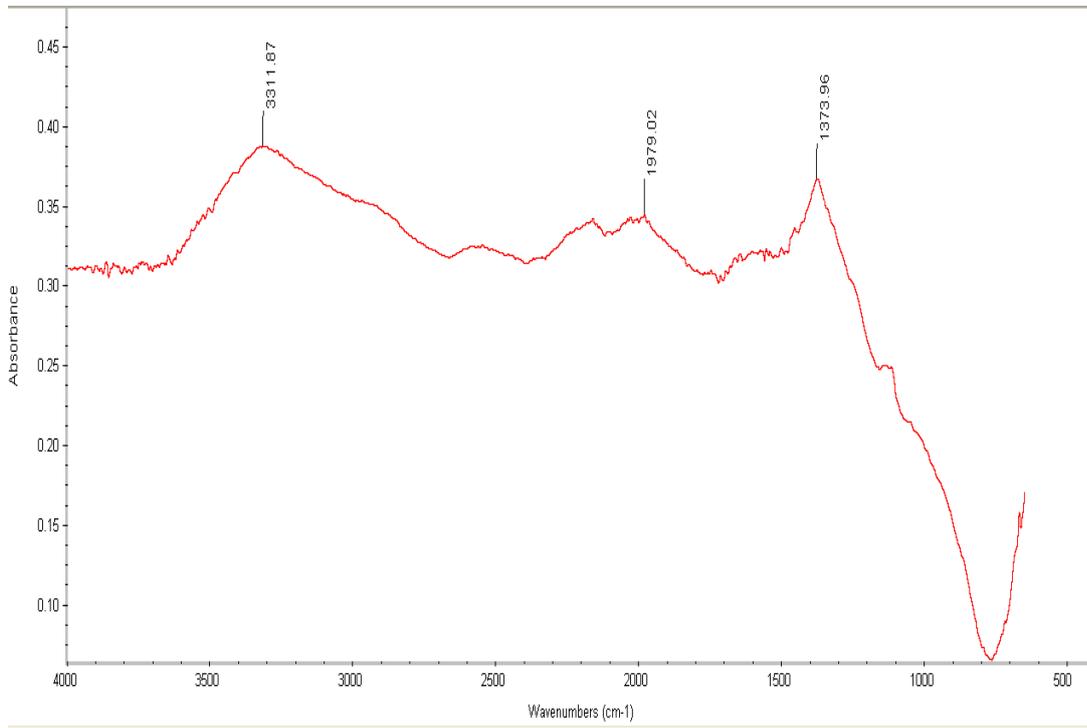**Figure 2: FTIR Spectrum of Simple Manganese ferrite**

FTIR spectrum of as prepared manganese ferrite composite is shown in Fig. 3. The spectrum shows four characteristic absorption bands which clearly indicate the formation of manganese ferrite. The peak at 660 and 66 cm^{-1} are an evidence for the presence of Fe-O and Mn-O bonds. The absorption band at 1378 cm^{-1} represents the Mn-O-Fe stretching whereas the peak at 1980 cm^{-1} is an indication of double bond character of metal-oxygen bond which may be attributed to Fe=O double bond in the manganese ferrite. The broad absorption band at 3377 cm^{-1} may be attributed to O-H stretching mode of certain water moieties associated with the manganese ferrite.

The stretching vibrations values given below in spectrum clearly depicts the synthesis of as prepared manganese ferrite with banana peels for the removal of fluoride ions from real water samples.

Table 1
Representing functional groups stretching values

| Sr. No.	Functional group	Absorption frequency
1	O-H stretching	3377 cm^{-1}
2	Mn-O-Fe stretching	1378 cm^{-1}
3	Fe=O bond	1980 cm^{-1}
4	Fe-O	661 cm^{-1}

Figure 3: FTIR Spectrum of MnFe₂O₄ Composite

Spectrum of our prepared manganese ferrite composite given below, whose similarity with that of simple manganese ferrite spectrum shows that our prepared MnFe₂O₄ Composite accurately had synthesized.

3.3. Magnetic Measurements

Magnetic measurements were carried out of our as prepared material with vibrating sample magnetometer and its hysteresis loop was obtained. These measurements were carried out for investigating the magnetic properties of that as prepared material. The hysteresis loop is exhibiting the soft magnetic nature of our material, as very small area occupied by closed curve is basically related to soft magnetic materials properties (Fig. 4). These properties are dependent upon sintering temperature, metal ions in ferrite structure and preparation methods.
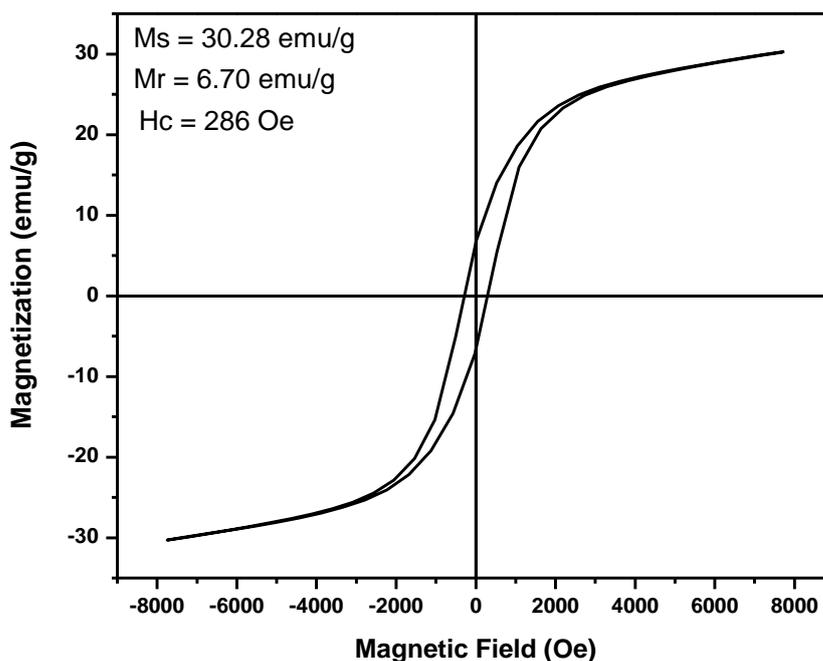
Figure 4: Hysteresis loop of Single phase MnFe2O4 ferrite synthesized by Co-precipitation method

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Magnetic moment value of the sample was calculated by magnetization saturation data by given formula (Raghuvanshi, Satalkar, Tapkir, Ghodke, & Kane, 2014). The calculated data is in full agreement to the saturation magnetization as both the parameters are directly related to each other.

$$nB\ (\mu B) = M \times Ms\ /\ 5585 \tag{4}$$

where n_B is magnetization moment, M is the molecular weight of sample, Ms is saturation magnetization and Hc is coercivity of manganese ferrite.

3.4. Adsorption Study

For exploring the adsorption performance and for ensuring the reliability, accuracy and reproducibility of our material, adsorption experiments were carried out.

Adsorption removal studies for removing fluoride by both simple manganese ferrite and our magnetic manganese ferrite composite were investigated and compared the capabilities of our materials.

3.4.1. Factors Affecting Adsorption

The following two parameters i.e., time and pH were carried out for adsorption studies.

3.4.1.1. Effect of Contact Time

The data obtained from different contact time experiments by both materials i.e., Mn_2FeO_4 and Mn_2FeO_4/banana peels were plotted in Fig. 5. From fig, it can be clearly observed that adsorption removal efficiency increased with contact time till 175 min, then equilibrium constant value was achieved. This was probably due to the abundant adsorption sites of our Composite material at initial states (Wang et al., 2022), as the interaction sites becomes occupied with passage of time, adsorption of fluoride becomes lower by adsorbent (Wang et al., 2022). When the equilibrium is achieved, all sites become fully saturated. The optimum time for equilibrium is 175 min. as it is much more efficient in adsorption removal of fluoride ion as compared to simple manganese ferrite.

The fluoride specific amount of uptake (qt), was determined by given formula i.e.

$$Q_t = V\ (Co - Ct)\ /\ W \tag{5}$$

And the percentage removal efficiency of fluoride was calculated by

$$\%\ adsorption = 100 \times (Co - Ct)\ /\ Co \tag{6}$$

Where Co (mg/ L) is initial concentration, Ct (mg/L) is concentration at time t. V is volume (L) of solution and W (g) is mass of adsorbent.

After treatment with manganese ferrite for 175 min, total amount of adsorbate after time t (qt), onto adsorbent is maximum in case of our composite i.e., 8.9 value is being calculated. As qt is total amount of fluoride ions uptake after time t. The results obtained by this study in Table 2 as given below.

Table 2
Effect of Contact Time on removal of fluoride

$MnFe_2O_4$								
Time (min)	5	10	15	30	60	175	180	240
qe (mg/g)	2.9	3.9	4.1	8.3	8.6	8.7	5.7	4.9
$MnFe_2O_4$/Banana peels								
qe (mg/g)	3.4	4.2	5.9	8.6	8.7	8.9	6.1	5.2
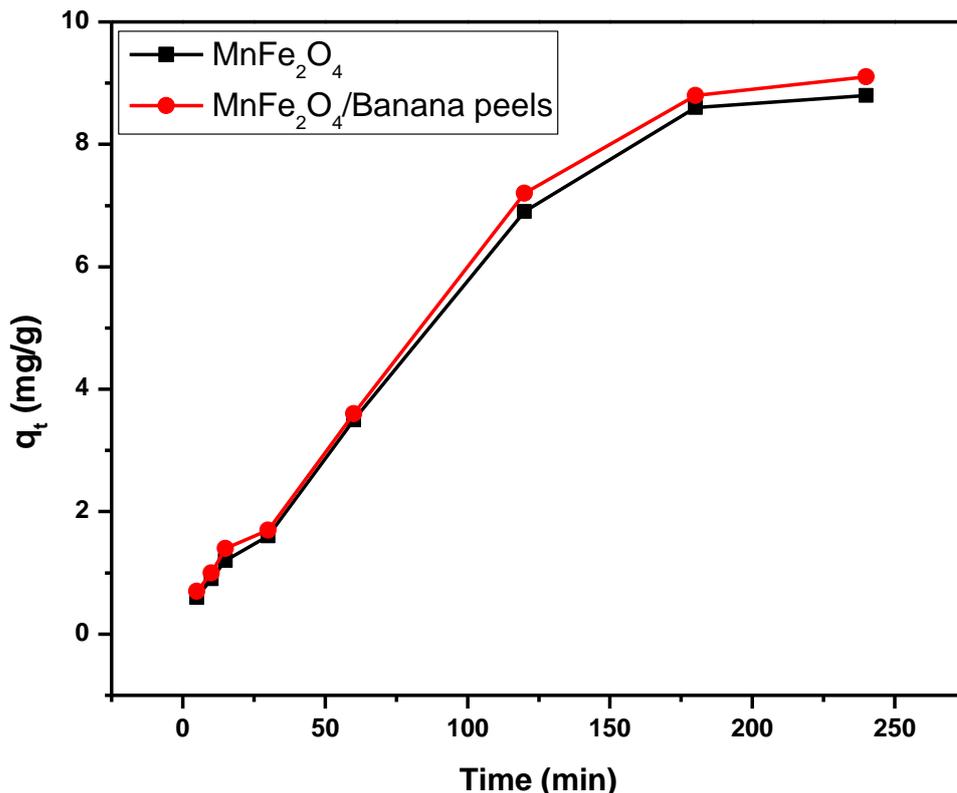
Figure 5: Effect of Contact time on fluoride removal

3.4.1.2. Effect of pH on Adsorption Capacity (q_e)

Effect of pH on adsorption of fluoride ions on both $MnFe_2O_4$ and $MnFe_2O_4$ Composite was investigated by keeping different pH of same solutions. It reveals the dependence of pH on adsorption capacity of our as prepared material. The adsorption is high at low pH values and low at high pH. This high uptake at low pH was ascribed to high hydrogen ions concentration at lower pH which causes the increase in positive charges at the sorbent surfaces leading to increase amount of fluoride removal. Similar results were observed by Sahira et al in 2012, while they were removing the same fluoride ions from water by using Zirconyl - impregnated activated carbon which were prepared by lapsi seed stone. They also noted the same thing that pH had great influence on surface charge of adsorbents as it increased the interaction of fluoride ions with adsorbent (Joshi, Adhikari, & Pradhananga, 2012).

At higher pH (> 8), due to presence of higher concentration of hydroxide ions, they hindered the diffusion of fluoride ions which leads to low uptake of the fluoride ions. That hindrance is caused due to repulsive forces occurring between the negative charges of fluoride ions and hydroxide ions.

$$q_e = \frac{C_i - C_f}{m} * V \qquad\qquad (7)$$

Where C is concentration, qe is maximum adsorbed quantity at equilibrium, m is mass of adsorbent and V is volume of solution.

Batch experiments results confirmed our biomaterial is given better results at pH 8, i.e.8.9 than that of Simple ferrites at the same pH as can be seen by Fig. 6. At room temperature (initial concentration C_i = 10 mg/L, shaking time = 2h, T = 25 °C, pH = 7 ± 0.1, m = 10 mg and V = 10 mL).

Table 4
Effect of pH on adsorption removal

$MnFe_2O_4$

pH	3	4	5	6	7	8	9	10	11
Qe (mg/g)	2.9	3.9	4.1	8.3	8.6	8.7	5.7	4.9	3.8

$MnFe_2O_4$/Banana peels

Qe (mg/g)	3.4	4.2	5.9	8.6	8.7	8.9	6.1	5.2	3.9
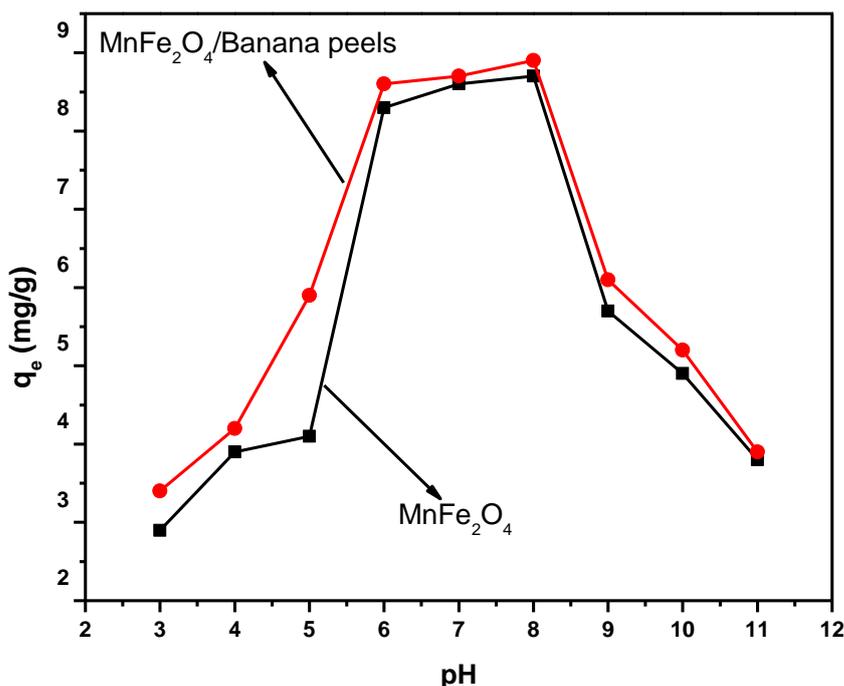
**Figure 6: Effect of pH on adsorption removal**

3.4.2. Real Time Application

It is important to determine the adsorption mechanism which is essential for determining its residence time. The mechanism of adsorption removal from aqueous system by porous adsorbents require four basic steps i.e.

1. Migration of ions from aqueous system to boundary layer or film surrounding adsorbents.
2. Diffusion of ions to exterior layer of adsorbents known as external diffusion.
3. Transport of ions from exterior to interior surface through pore diffusion mechanism.
4. Uptake of ions by available sites.

The slowest step defines the uptake rate and rate determining step. Here in given Fig. 7, value of C determines the boundary layer thickness of adsorbent. It provides the understanding of ions either those had been got adsorbed or remained in solution. Higher value of c exhibits higher adsorption.

Table 5
Real water sample analysis at room temperature (initial concentration Ci = 10 mg/L, T = 25 ºC, pH = 7 ± 0.1, m = 10 mg and V = 10 mL)

Time (min)	5	10	15	30	60	120	180	240
Ct (mg/L)	10	9.4	8.1	6.3	4.2	2.1	1.2	0.9
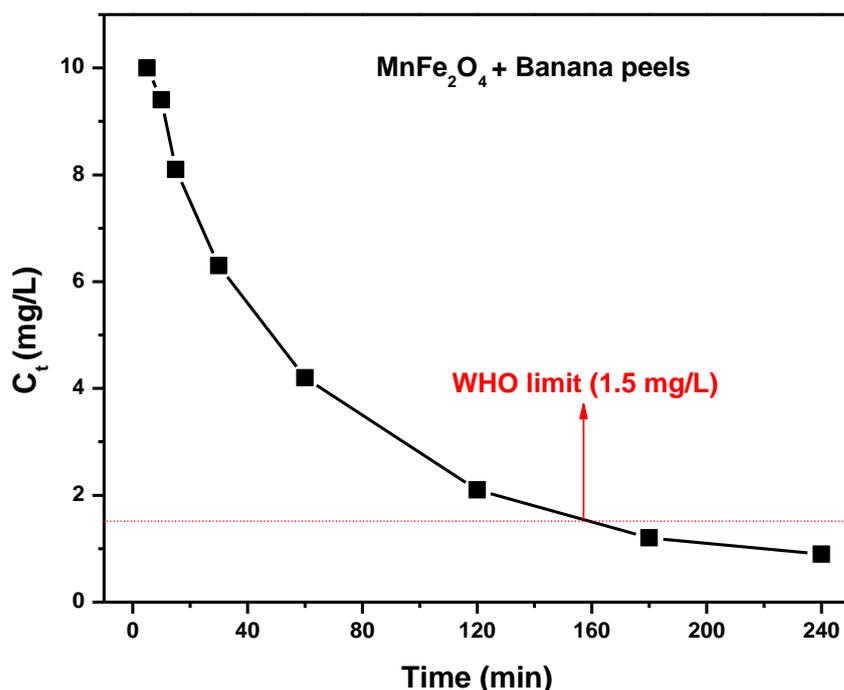
Figure 7: Effect of time on adsorption tendency of adsorbent

Conclusion

The magnetic material was successfully synthesized and that was confirmed by FTIR studies which indicated the existence of the anchored functional groups.it was found to be effective removal up to 86 %. The optimum contact time and pH were found to be 175 min and 8 respectively.

Fluoride ions cause oxidant effect which is responsible for several diseases like thyroid problems, neurological problems cardiovascular problems reproductive issues and bone cancer. Manganese ferrite/Banana peel composite is very good fluoride ion adsorber. From our research it is identified that maximum amount of fluoride ions is adsorbed easily by our material. This material had potential application for fluoride removal and is biodegradable, economic and environmentally friendly. It can be beneficial at industrial scale if prepared at bulk scale.

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