

Defluoridation of Water using an Effective Adsorbent PVA-Alginate/CTAB Bound Nano Magnetite microspheres: Kinetic & Equilibrium study

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Abstract: The objective of present study includes synthesis of polyvinyl alcohol-alginate bound nano magnetite microspheres modified with CTAB (PVA-ANM/CTAB) and assess their application in defluoridation of water by batch sorption method. Characterization of as synthesized PVA-ANM/CTAB microspheres performed by FTIR, XRD and TEM techniques. In batch process fluoride scavenging potential was examined as a function of contact time, concentration, pH, temperature and adsorbent dose. The effects of various co-existing ions were also tested. Equilibrium data are predicted by Langmuir and Freundlich isotherm models. Defluoridation closely followed pseudo-second order kinetic model. Results ascribed that the synthesized adsorbent has potential for treatment of fluoride bearing water, as it revealed $\geq 95\%$ removal and could be regenerated and reused efficiently 4-5 times.

Keywords: Fluoride ions, polyvinyl alcohol-alginate, Defluoridation, nano magnetite, adsorption isotherm,

I. INTRODUCTION:

Fluoride (F) contamination in water resources for human consumption is considered a significant environmental problem in several developing countries of the world. In India, fluoride is the major inorganic pollutant in ground water, several states are affected with excess fluoride in groundwater, endemic fluorosis has been affected approximate one million people, especially Rajasthan, Gujarat, Uttar Pradesh, Andhra Pradesh, Tamilnadu, Madhya Pradesh and Chhattisgarh.[1] Geological, natural factors and anthropogenic sources are main cause of fluoride pollution in water. Fluoride in micro quantity is an essential nutrient for normal mineralization of healthy bones and formation of dental enamels. However, excessive consumption ≥ 4 mg/L of fluoride leads to fluorosis. [2, 3] Various forms of fluorosis arising due to excessive intake of fluoride are briefly discussed in Table1.

Fluoride poisoning can be prevented or minimized by removing excess fluoride. Defluoridation is fundamental to meet environmental regulations for water quality, to reduce the prevalence fluorosis. Extensive research has

been done on various methods viz ion-exchange [4] Donnan dialysis [5] electro dialysis [6] adsorption [7] Precipitation [8] nano filtration [9] catalytic degradation [10] electro coagulation and electro flotation [11] to reduce the excess fluoride under the safe limit.

Table: 1 Effects of fluoride concentration in water on human health

Fluoride Conc. (mg/L)	Effects on human health
< 1.0	Safe limit (WHO)
1.0-3.0	Dental fluorosis(discoloration, mottling and pitting of teeth)
3.0- 4.0	Stiffened and brittle bones and joints
4.0-6.0 and above	Deformities in knee and hip bones and finally paralysis making the person unable to walk/stand in straight posture, crippling fluorosis

Among these methods adsorption process is considered the most effective and advantageous for defluoridation of water due to its efficiency, simplicity, relatively economic and effectiveness [8]. Extensive variety of natural and synthetic adsorbents has been tested and applied such as activated alumina [12] clays/modified clay [13, 14] polymers [15] biomasses[16] activated carbon[8] ash/fly-ash [17] resin [18] multi-valent metal oxides/hydroxides[19,20] nano materials carbonaceous materials[21-23] and bone char [24] etc for the removal of fluoride ions from aqueous solution. Much work has been reported with use of numerous adsorbent and techniques for fluoride removal. Withal a simple, efficient and cost effective technology is not available for widespread use in many affected regions.

In this research work, a novel inexpensive, effective, efficient, simple defluoridation method has been developed which is based on surface modification of nano magnetite co-polymeric adsorbent by surfactant. Alginate (polysaccharide) an abundantly available, biocompatible and hydrophilic biopolymer and

polyvinyl-alcohol (PVA) is nontoxic, biodegradable and biocompatible synthetic hydrophilic polymer, which are inexpensive raw materials formulated with nano magnetite iron oxide particles, modified with cetyl tri methyl amino bromide (CTAB). Use of nano magnetite iron oxide particles with CTAB grafted PVA-alginate co-polymer provides large surface area and high energy with strong sorption ability. A strong magnetic and binding property of adsorbent opens new technology, which is quicker, simpler and more precise than those used traditionally.

The novelty of study is the adsorbed fluoride ions may be desorbed by acceptable method and adsorbent could be regenerated for further experiments. Plausible mechanism of fluoride ions uptake also discussed. The reported adsorbent combines the advantages of magnetite nano particle as well as surfactant modified co-polymeric PVA-Alginate hydrogel with magnetic separability and high affinity toward fluoride ions, which provides distinctive merits including easy separation, high adsorption capacity and quick isolation from sample solutions using an external magnetic field.

The **objectives** of this study include:

- Synthesis of co-polymeric microspheres of CTAB modified PVA-alginate.
- In-situ magnetization of microspheres
- Characterization of adsorbent by FTIR, XRD and TEM analysis.
- Batch sorption and kinetic studies to assess their fluoride removal capacity.
- Study of co-ions effects, which can compete with F ions in natural water,.
- Originate acceptable method to regenerate the adsorbent for reuse
- Plausible mechanism of defluoridation also discussed

II. EXPERIMENTAL:

2.1. Materials:- Ferric chloride anhydrous, ferrous chloride tetrahydrated, sodium fluoride with purity >98% were purchased from Central Drug House, New-Delhi, India. CTAB, sodium alginate, polyvinyl alcohol were purchased from Loba Chemie, Mumbai, India of analytical grades.

2.2. Preparation of PVA-ANM/CTAB microspheres:- The adsorbent were prepared in three steps, in first step a viscous gel of PVA was prepared at 90°C in doubled distilled water and was mixed thoroughly with gel of sodium alginate and CTAB to get 1:1:1/9 ratios, stirred for three hours for homogeneity at constant speed of 150 rpm and kept aside to obtain a bubble free solution. In second step microspheres were prepared by drop wise addition of the above mixture in cross linker (0.5M CaCl₂). The microspheres so produced were allowed to harden by leaving them in solution for 24 h then washed several times with distilled water. In third step for insitu magnetization, these microspheres were equilibrated in an aqueous mixture of ferrous chloride tetrahydrate and

ferric chloride in 1:3 ratios for 24 hours. The microspheres were then added into alkaline solution and kept for 2 h so that Fe²⁺/Fe³⁺ ions get precipitated into nano Fe₃O₄ within CTAB/PVA-Alginate matrix. These PVA-ANM/CTAB adsorbent were then completely washed 3-4 times and stored for adsorption experiments.

2.3. Characterization of Adsorbents:-

Characterization of adsorbent PVA-ANM/CTAB was performed by XRD, FTIR & TEM analysis.

2.4. Batch Sorption Experiments:-

A stock solution of 1000 mg/L fluoride was prepared by dissolving 2.21 g of sodium fluoride salt (NaF) in 1 L of triple distilled water and the operating solutions were freshly prepared by diluting the stock solution.

Adsorption experiments were conducted by batch method by varying shaking time, pH, concentration of adsorbate, amount of adsorbent and temperature. For adsorption experiments, the adsorbent microspheres 0.2 g and 20 mL fluoride solution of 10 mg/L concentration at pH range 5-6 and temperature 25°C (±2) was stirred in an orbital shaking incubator with temperature control (SONAR-159) for 90 min.

The fluoride ions analysis (before and after equilibrium adsorption) was carried out using fluoride sensitive electrode, ion analyzer (model Elico-LI 126)

Sorption degree and amount of F adsorption at time t, q_t (mg/g) of the sorbent (sorption capacity) were calculated according to Eq. 1 and 2, respectively:

$$\text{Sorption degree} = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

$$\text{Sorption Capacity}(q_e) = \frac{C_i - C_e}{C_i} \times \frac{V}{m} \quad (2)$$

where C_i and C_e are the initial and equilibrium concentration (mg/L) of fluoride ions solution, respectively. V (L) is volume of the adsorbate solution, subjected to sorption and m (g) is weight of adsorbent. The adsorption data were analyzed by intra particle diffusion, pseudo-first and pseudo second order kinetic models. The effect of complementary anions (Cl⁻, SO₄²⁻, PO₄³⁻ and NO₃⁻) on F ions adsorption was also studied.

2.5. Desorption Studies:

After the sorption experiments, the sorbent was collected by filtration and washed with distilled water drying the fluoride-loaded PVA-ANM/CTAB at room temperature. The adsorbed fluoride was then desorbed using 0.1 M CH₃COOH, NaCl, NaOH and Na₂SO₄ solutions, respectively.

III. RESULTS AND DISCUSSION

3.1. Characterization of Adsorbent

➤ **FTIR analysis:-** Fourier transforms infrared (FTIR) spectra of bare (a) and fluoride loaded PVA-ANM/CTAB adsorbent (b) recorded by Perkin-Elmer FTIR spectrometer to examine adsorption mechanism. Vibrancy signals of bare and F loaded adsorbent are

different, as shown in Fig. 2. FTIR spectra shows the characteristic peaks at 3408 cm^{-1} is an exclusive of bonded hydroxyl group ($-\text{OH}$). The peak near 2900 cm^{-1} assigned to stretching vibration of CH_2 group. The adsorption peak at 1760 cm^{-1} assigned the stretching band of free carbonyl double bond from the carboxyl functional group. In addition band at 1458.5 and 1592.6 cm^{-1} are assigned to symmetric and asymmetric stretching peaks of carboxylate anions of cross-linked alginate [20] carboxylic group of cross linked alginate dissociated into $-\text{COO}^-$ groups that can be related with tri-valent cations through electrostatic interaction. The characteristic peak at 517.5 cm^{-1} relates to Fe-O group and is indicative of loading of nano iron oxide particles on PVA-Alginate matrix [26] Strong asymmetric stretching band at 1638 cm^{-1} attributed to C=O stretching, band 1240 cm^{-1} attributed to C-O vibration indicate presence of many oxygen containing functional groups on adsorbent and band 1590 cm^{-1} attributed to trimethyl amino group ($-\text{N}^+\equiv$) vibration. FTIR spectrum after F^- ions adsorption on PVA-ANM/CTAB reveals many variations, as depicted in Fig. 2(b). The band at 3408 and 1060 cm^{-1} detected on adsorbent, slight shift to lower wave numbers 3390 and 1045 cm^{-1} suggests alcoholic $-\text{OH}$ performs a vital role in adsorption process. Besides the peak at 1638 and 1458.5 cm^{-1} shifting to lower frequency 1625 and 1469 cm^{-1} can be attributed to association of hydroxyl-ate with adsorbate F^- ions. Slight changes in shape and intensity of absorbance of shifting of the C-O , $-\text{COO}^-$ and $-\text{OH}$ group was observed. These changes mentioned above may be attributed due to positively charged surface of the adsorbent arise from the existence of various groups on CTAB modified PVA-ANM microspheres can provide adsorption sites for electrostatic interaction with F^- ions. Slight shift of characteristic peak (Fe-O) from 518 to 529 cm^{-1} may be due to electrostatic binding of some F^- ions onto cationic sites of nano-magnetite iron-oxide surfaces ($\gamma\text{Fe}_3\text{O}_4$) [19].

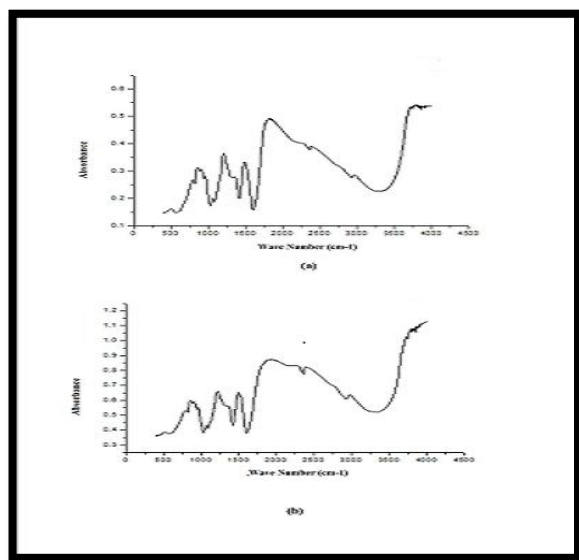


Fig. 2 FTIR spectra of Bare (a) and (b) F^- ions loaded PVA-ANM/CTAB adsorbent

➤ XRD analysis

Powder XRD was carried out to identify nanocrystalline structure of iron-oxide and amorphous nature of adsorbent PVA-ANM/CTAB using Brucker D8 advanced X-ray diffractometer (20° to 80° (2θ)) using $\text{Cu}_K\alpha$ radiation with wavelength of $1.5406\text{ \AA}$, Fig 3 showed five characteristics peaks ($2\theta = 26.93, 31.89, 38.87, 41.23$ & 45.55). The position and relative intensity of all diffraction peaks match well with those from the JCPDS file number 89-5984 for nano magnetite Fe_3O_4 . The particle sizes can be quantitatively evaluated from XRD data using the Debye-Scherrer Eq. 3 as follows:

$$D = \frac{K\gamma}{\beta \cos \theta} \quad (3)$$

where D is the crystal thickness, K is Scherrer constant 0.89 , the wave length of X-ray is 0.15406 nm , β is the peak width of half maximum and θ is the Braxton Bragg angle of the XRD peak ($1, 1, 1$).

The calculated average crystallization size was found to be 31.86 nm . Iron nano magnetite particles are obtained consistent with the following reactions:-

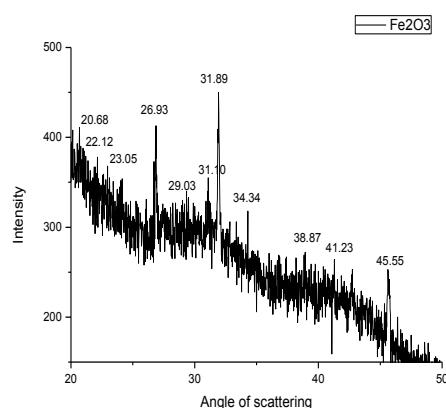
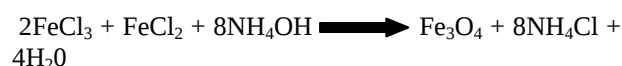


Fig 3 XRD pattern of adsorbent

➤ TEM analysis

The average particle size, morphology and size distribution of iron-oxide nanoparticles were examined using TECNAI-G-20 TEM at voltage of 200 KV . The solvent dispersion of particles was drop cast onto a carbon coated copper grid. TEM images of nanoparticles Fe_3O_4 , Fig. 4 shows almost spherical iron-oxide particles with an average size of 2 to 9 nm . It should be noted however, the majority of particles were scattered, a few of them showing aggregates indicates stabilization of the nanoparticles.

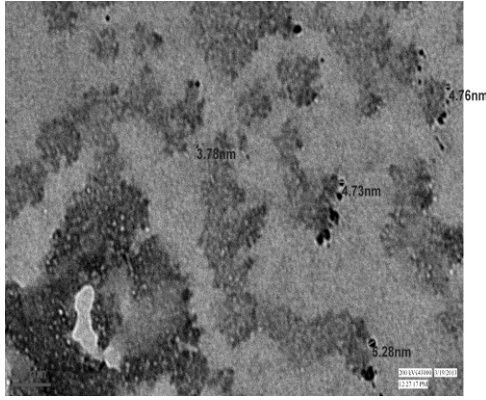


Fig 4 TEM image of adsorbent

3.2. Analysis of Batch Adsorption Data

3.2.1. Adsorption Isotherm Models

Most widely accepted adsorption isotherm models Langmuir and Freundlich models were applied for the analysis of F adsorption onto PVA-ANM/CTAB adsorbent.

➤ Langmuir Adsorption Isotherm

The linearized equation of Langmuir is represented by Eq. 4 as follows:-

$$\frac{C_e}{q_e} = K_L \frac{1}{q_m} + \frac{C_e}{q_m} \quad (4)$$

where q_m is the adsorption capacity of adsorbent (mg/g) and K_L is Langmuir adsorption constant related to energy (L/mg). Fundamental characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant called separation factor R_L , is defined by Eq. 5

$$R_L = \frac{1}{K_L q_m C_i} \quad (5)$$

Table 2: Value of R_L indicates the shape of the isotherm as shown in table

Separation Factor (R_L)	Types of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

➤ Freundlich Adsorption Isotherm

Freundlich isotherm model can be applied for non ideal adsorption on heterogeneous surfaces and multilayer adsorption. Linear form of the Freundlich isotherm model is given by Eq. 6.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Freundlich constant K_F and sorption intensity $1/n$ may be evaluated by the linear plot of $\ln q_e$ vs. $\ln C_e$ as shown in Fig. 5(B). Langmuir and Freundlich constants values are given in Table 3. In present sorption systems R_L and n value obtained 0.078 and 2.0 (>1) that indicates favorable adsorption of F ions on adsorbent.

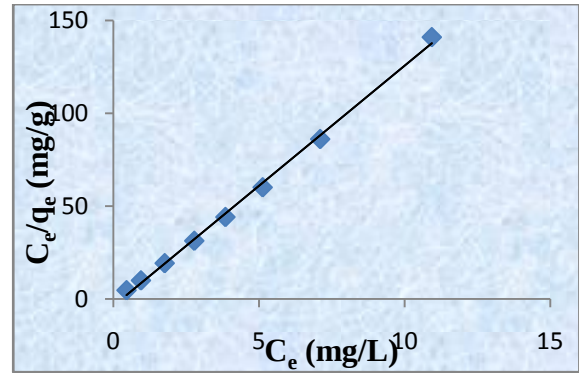


Fig 5(A) Langmuir Adsorption Isotherm

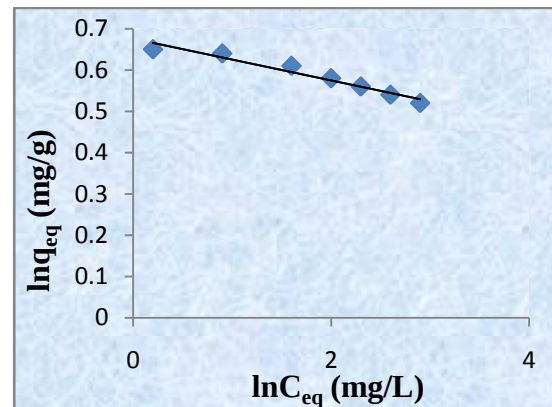


Fig 5(B) Freundlich Adsorption Isotherm

Table 3:- Isotherm Constants for F ions adsorption onto PVA-ANM/CTAB

Isotherm Models	Constants	Values
Langmuir Isotherm Model	K_a (L/mg)	0.27
	q_m (g/L)	12.93
	R_L	0.078
	R^2	0.997
Freundlich Isotherm Model	K_F (mg/g)	0.675
	n	2.0
	R^2	0.952

3.2.2. Kinetic study of adsorption

Adsorption kinetic studies are provides solute uptake rate, mechanism and valuable information of reactions pathway. Kinetics sorption of a material onto sorbent follows three steps viz pore, diffusion, film diffusion and intraparticle transport. For solid-liquid sorption process the solute transfer is usually characterized by either external mass transfer or intraparticle transport or both. Overall rate of adsorption will be regulated by slowest step viz pore or film diffusion.

Three most commonly suggested kinetic models are applied for analysis of system viz. Lagergren pseudo-first order kinetics, Ho-McKay pseudo-first order kinetics and Weber-Morris intraparticle diffusion model which are expressed by Eq.7, 8 and 9 respectively:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{(2.303)} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} t \quad (8)$$

$$\log q_{eq} = K_p t^{1/2} + c \quad (9)$$

Where K_{ad} is pseudo-first orders rate constant, k_2 (g/mg min) is rate constant of pseudo-second order and K_p (gm/g/min) is intraparticle diffusion constant of adsorption, values are shown in Table 4. The system closely followed pseudo-second order kinetics.

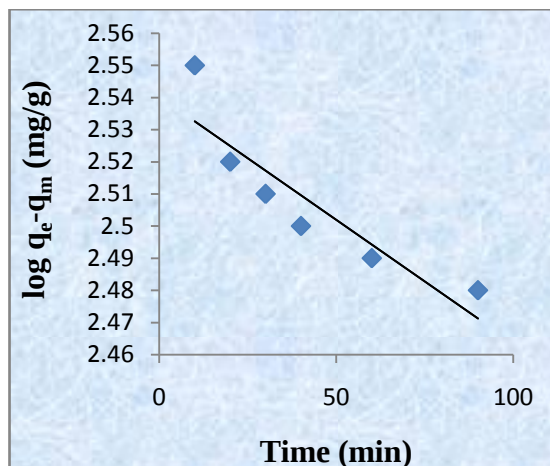


Fig 6: (A) Pseudo-first order model

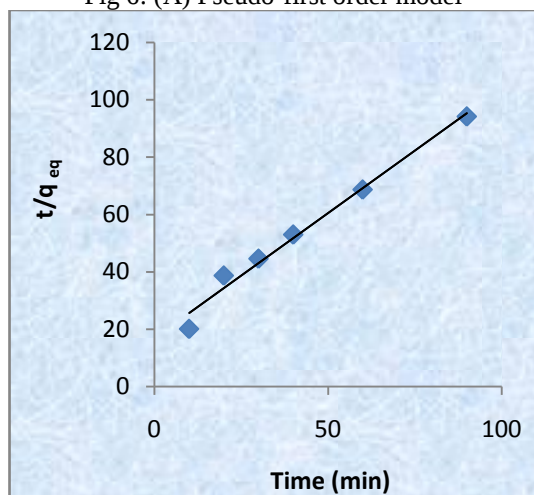


Fig 6: (B) Pseudo-second order model

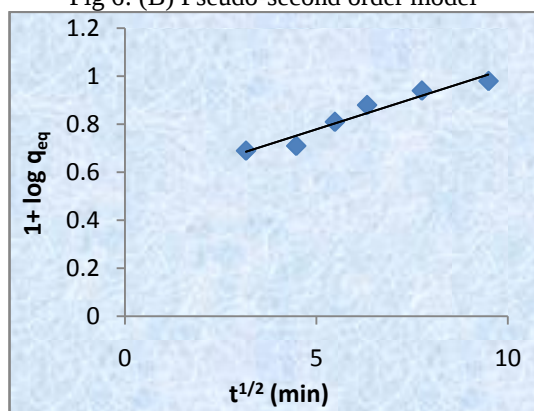


Fig 6: (C) intraparticle diffusion model

Table 4: Value of Kinetic Constants of F ions adsorption onto PVA-ANM/CTAB

Kinetic Model	Parameter	Value
Intra particle diffusion	K_p (g. mg/min ^{1/2})	0.524
	R^2	0.941
Pseudo first order	K_a (min ⁻¹)	2.540
	R^2	0.816
Pseudo second order	k^2 (g/min)	1.149
	q_m (g/mg)	16.94
	h (mg/g. min)	0.870
	R^2	0.983

3.3. Factor Affecting F Ions Sorption

- **Effect of pH** Maximum adsorption of F ions ($\geq 94\%$) observed at pH 5, due to protonation surface become positive and removal efficiency of sorbent will get significant enlargement.
- **Effect of Adsorbent dose** Maximum sorption occurred at adsorbent dose of 0.20 g
- **Effect of Agitation time** Agitation time is most significant factor, removal of F ions was studied in the range between 10 to 180 min. The maximum removal obtained at 90 min.
- **Effect of Concentration:-** Removal of F was studied at initial F concentration ranging between 05 and 50 mg/L, maximum removal received at 10 mg/L.
- **Effect of Temperature:-** Effect of temperature on uptake of F ions was investigated at various temperature ranges between 15 to 55 °C, maximum removal obtained at 25°C (± 2).
- **Effect of complementary ions:-** Effects of Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} anions on F adsorption studied at concentrations ranging from 25 to 100 mg/L. F ions adsorption reduction was obtained in order of anions $PO_4^{3-} > SO_4^{2-} > NO_3^- > Cl^-$ as shown in Fig 7.

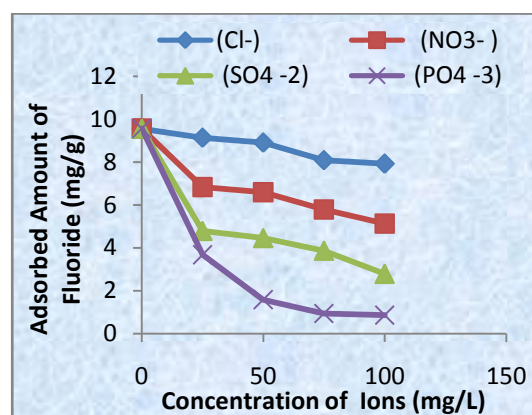


Fig. 7: Effect of complementary ions on F ions adsorption onto PVA-ANM/CTAB

3.4. Uptake Mechanism:- Most plausible sorption mechanism expressed by given schematic illustration Fig. 8 as follows:

- Cross-linked polyvinyl alcohol-alginate contains oxalate ($--O-$), carboxylate ($---COO-$) and hydroxyl ($--OH-$) groups.
- Whence co-polymeric matrix of PVA-Alginate modified with cetyltrimethyl ammonium bromide (CTAB), the hydrophobic groups of CTAB attached with carboxylate (a), hydroxyl (b) and oxalate (c) groups respectively.
- Fluoride ions attached through cationic ammonium group () of CTAB by electrostatic interaction.
- In addition with electron deficient nano magnetic iron-oxide particles within PVA-A/CTAB co-polymeric matrix may be co-ordinate by fluoride ions (d).

3.5. Desorption Study:- An adsorbent will be significant in waste-water treatment when it has good sorption capability with regeneration and reusability in adsorption/desorption cycles. Desorption studies conducted by different concentration of NaOH ranging from 0.025 to 0.30M with 1.0g, F ions loaded microspheres at 25 °C . Maximum desorption $\geq 98\%$, obtained with 0.1 M NaOH solution. Desorption efficiency was calculated using Eq. 10:-

$$\text{Desorption} = \frac{\text{Amount of F desorbed}}{\text{Amount of F adsorbed}} \times 100 \quad (10)$$

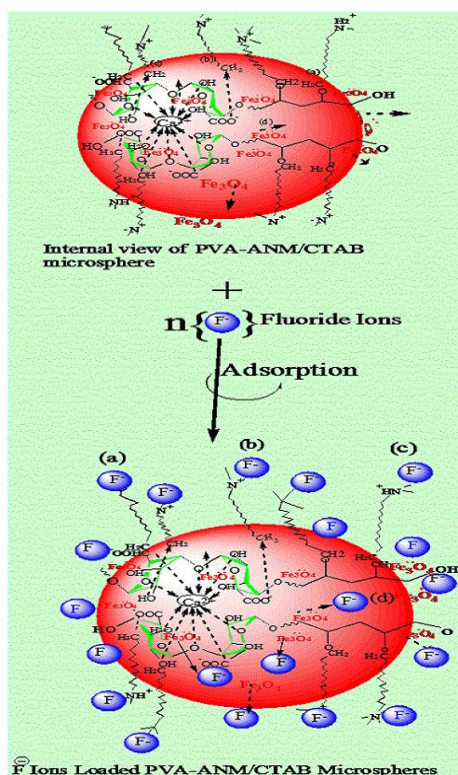


Fig: 8 Mechanism of F Ions Sorption onto PVA-ANM/CTAB Microspheres

IV. CONCLUSION

In conclusion, a novel adsorbent PVA-ANM/CTAB microsphere has been synthesized by in-situ magnetization and its efficiency evaluated for F ions removal by batch sorption system. Maximum removal of F ions ($\geq 95\%$) was noticed at pH 5-6 and 25°C in 90 min, which was higher than that mostly, reported adsorbent. Experimental data fitted well to Langmuir and Freundlich isotherm model. Pseudo second order reaction rate model described the kinetic data best for present system and it is physi-sorption. Investigated adsorbent has been found to be very effective, efficient, ecofriendly and economical for defluoridation of water and proves great potential for F ions uptake and also exhibited its efficiency in multiple cycles of usage. Moreover, the residual concentration of F ions using PVA-ANM/CTAB as adsorbent could reach 0.245 mg/L with an initial concentration of 10 mg/L, which met the standard of WHO norms for drinking water quality. Results suggested that adsorbent with strong and specific affinity to F ions could be excellent for fluoride contaminated water remediation.

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