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RESEARCH ARTICLE

DEFLUORIDATION OF WATER USING MUSA ORNATA HUSK NANO HYDROXYAPATITE-ALGINATE BIOCOMPOSITE.

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Abstract

In this research work, a new biocomposite namely MOH@n-HAp/Alg biocomposite was developed by the musa ornata husk on nano-hydroxyapatite (n-HAp)/ alginate (Alg) biocomposite for defluoridation in batch mode. The synthesized biocomposite possess an enhanced defluoridation capacity (DC). The structural changes of the adsorbent, before and after fluoride sorption were studied using FTIR, XRD and SEM with EDAX techniques. There are various physico-chemical parameters such as contact time, pH, co-existing anions, initial fluoride concentration and temperature were optimized for maximum fluoride removal. The equilibrium data was well modeled by Freundlich, Temkin, D-R and Langmuir isotherms. The present systems follows Freundlich isotherm model. The thermodynamic parameters revealed the nature of adsorption are feasible, spontaneous and endothermic nature of fluoride sorption. The efficiency of the adsorbent material was examined with polluted water samples using the standard procedure.

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Introduction:-

Fluoride has been considered as an essential mineral in our body. A very trace amount of fluoride is beneficial for the maintenance of healthy bones and teeth in human body (M.R. Boldaji et al, 2009). The permissible limit of fluoride level in drinking water is in between 0.5 and 1.5mg/L, which is established by the WHO, may give rise to the prevalence of dental fluorosis and skeletal damage in both children and adults(Y.C.Lu et al, 2002) and its accumulation for a long period of time can alter the DNA structure (M. Maharamanlighu et al, 2002, T.J. Song, 1978). Several methods like adsorption (V.Sivasankar et al, 2010, A.Sivakamy et al, 2001) precipitation (A.K.Chaturredi et al, 1990) ion exchange(N. Azhar et al, 2000) electro-dialysis (M.Castel et al, 2000, Z.Amor et al, 2001) and electrochemical methods(Al E. Shen et al, 2003) were developed to remove the fluoride from water. The choice of a treatment technique usually depends on the concentration of the fluoride ions, chemical species in the water source, operation costs, waste management and technical versatility. Limitations in terms of cost, production of significant amounts of waste and difficulties in end-use applications of some of the current treatment techniques have prompted the search for environmentally benign reliable and low cost alternation. Adsorption is an economical efficient and applicable technology for fluoride removal from drinking water (S.O. Lesmana et al, 2009). Biosorption is the one of the environmental friendly techniques which minimize the operation cost and make the adsorption technology more eco-friendly and feasible. In this scenario, scientists have paid increased attention on the development of bioadsorbents using the chitosan, chitin, tamarind fruit shell, neem leaf, aliginate, cellulose etc for the removal of toxic ions from the aqueous solution (Varma, A.J et al, (2004), Viswanathan et al, 2009 a,

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Jayakumar et al, 2009, Sairam Sundaram et al, 2009, Googerdchian et al, 2012, Yu, X et al, 2013, Pandi, K et al, 2014, V.Sivasankar et al, 2010, Rajan Kr et al, 2015). The nano biocomposites have unique properties for the valuable applications in removal of fluoride from the environment. Very small size of nano-particles creates a large surface are in relation to their volume, which makes them highly reactive, compared to non-nano forms of the same sorbents.The ultimate aim of the present work is to develop low cost, eco-friendly and functionalized wasted biomaterials for fluoride removal. Based on the above aspiration, the authors have synthesized nano-hydroxyapatite-Alginate biocomposite for defluoridation of water in batch mode studies. The sorption studies were carried out to optimize various equilibrating conditions like pH, contact time, different initial fluoride concentration, interfering anions and temperature. The equilibrium data was filled with various isotherms and kinetic models. The thermodynamic parameters viz., ΔG°, ΔH° and ΔS° have also been calculated and interpreted. The suitability of the developed MOH@n-HAp/Alg biocomposite was tested with a water sample collected from a nearby fluoride endemic village.

Materials and Methods:-

Materials Sodium alginate, ammonium di hydrogen ortho phosphate, calcium chloride di hydrate, ammonia solution and sodium fluoride and all other were used AR grade.

Synthesis of *musa ornata* husk nano hydroxyapatite-Alginate biocomposite (MOH@n-HAp/Alg):-

Banana flower botanically known as musa ornata belongs to the family of musaceae and plantae kingdom. Banana flower husks were collected and thoroughly washed with double distilled water, further dried in the air. The dried husks were powdered sieved into the fractions measuring from BSS52. The MOH@n-HAp/Alg biocomposite was prepared by 2%(w/v) concentration of sodium alginate was dissolved in double distilled water and the dried powder was mixed with in the ratio of 1:1 at 40ºC and continuously stirred for 2 hours. Then 20 ml of 1M $NH_4H_2PO_4$ solution was added and stirred for one hour at 40°C. The pH of the medium was adjusted to using 25% of ammonia solution. Therefore, 20 ml of 1M $CaCl_2.2H_2O$ solution was added to the above mixture at the same temperature and stirred for one hour. The formed biocomposite was kept aside for 24 hours and the filtered washed with plenty amount of distilled water and dried at 80ºC for 24 hrs in an oven. The dried biocomposite crushed into fine powder and then used for fluoride sorption studies.

Fluoride adsorption experiments:-

The synthesized material (MOH@n-HAp/Alg) biocomposite were used as adsorbents for the removal of fluoride from the aqueous solution by the batch equilibrium method in duplicate. Experiments were conducted by adding 0.1g of biocomposite sorbent into 100mL of 5mg/L sodium fluoride solution with a constant speed of 200rpm at room temperature. At a range of time intervals, the sorbent was separated and the concentration of fluoride was determined. The solution of 0.1M HCl and 0.1M NaOH was used for pH adjustment. In isotherm studies, 100mL of different initial fluoride concentration(3,5,7,9,11 and 13mg/L) was stirred with 0.1g of biocomposite adsorbent dosage in a thermostat shaker in the temperature range of 301, 311 and 321K at neutral pH. The sorbent was separated and the fluoride concentration was analyzed. The defluoridation capacity(DC) can be calculated by

Defluoridation capacity = C_i-C_e XV/m

Percentage of removal = C_i-C_e/C_i X 100

Where C_i and C_e were initial and final fluoride concentration in mg/L, 'm' is the mass of the sorbent (g) and V is the volume of solution(L).

Analytical Methods:-

The fluoride determination was done by photometric method at 570nm using the UV-Visible spectrophotometer. The pH measurements were done with the pH meter of the Susma pH meter. All other water quality parameters were investigated using standard methods (APHA, 2005).

Characterization Studies:-

Fourier Transform Infrared (FTIR) spectra of the composite were carried out on Shimadzu IR Affinity 1 model to confirm the functional groups present in it. Surface morphology of the composite was examined with scanning electron microscope(SEM) with Vega3 Tescan model fitted with an energy dispersive X-ray analyzer (EDAX) which allows a qualitative detection and the localization of elements present in the composites (EDAX-Bruker nano GMBH, Germany). SEM images enable a direct observation of the surface of the before and after fluoride-sorbed composite. X-ray diffraction (XRD) measurements were obtained using XRD 3003TT, GE, Inspection Technology model to determine the crystalline phases present in the sorbents. The pH at zero point of charge (pH_{zpc}) of the sorbents was determined by the pH drift method (Lopez-Ramon et al, 1999).

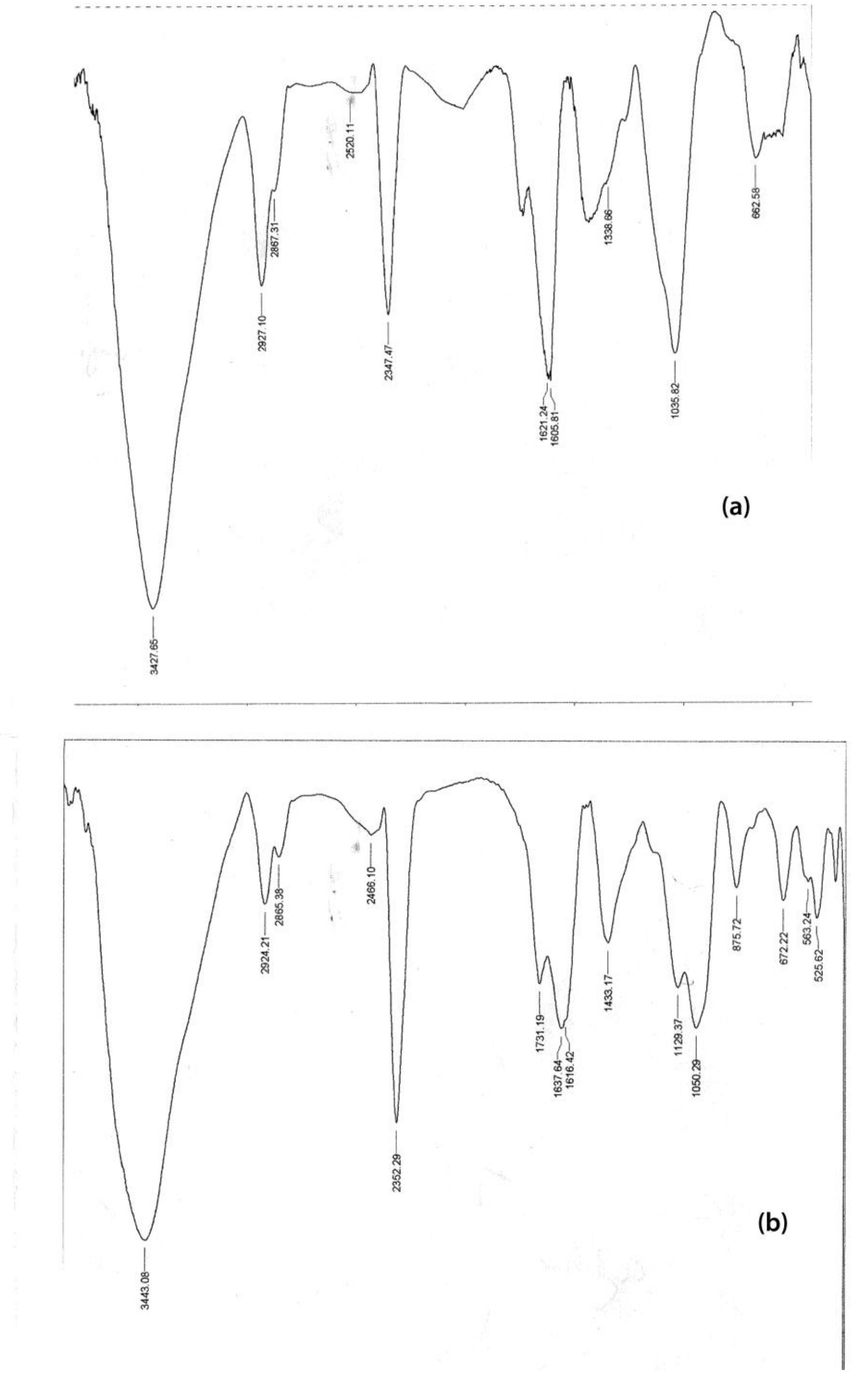
Computations were made using Microcal Origin software. The best fit is discussed using error bar plot, regression correlation co-efficient(r^2) and standard deviation.

Results and discussion:-

Characterization of the composite:-

FTIR analysis:-

Figure 1:- FTIR spectra of (a) MOH@n-HAp/Alg and (b) fluoride sorbed MOH@n-HAp/Alg biocomposite



FT-IR spectrum is a useful tool to identify the functional groups present in a molecule, as each specific chemical bond often has a unique energy absorption band and can obtain structure band information and study of strength and fraction of hydrogen bonding. Fig 1(a and b) are spectra of synthesized MOH@n-HAp/Alg biocomposite and fluoride sorbed MOH@n-HAp/Alg composite respectively. The strong absorption band observed at 525, 563, 672 and 875cm^{-1} which are attributed to the stretching and bending of PO$_4^{3-}$ of MOH@n-HAp/Alg(M.G. Ma et al, 2006). In addition, alginate also has a strong band at 1050cm^{-1}(H.H, Jin et al, 2008). Thus the observed broad band at 1050 cm^{-1} is attributed to the overlap of C-O-C stretching of Alg and PO$_4^{3-}$ stretching of n-Hap(Kalimuthupandi et al, 2015). The absorption band at 1637, 1731, 2352, and 2924cm^{-1} shows the stretching vibration of C=C, C=O, C≡C and C-H group respectively. The band 2865 and 2924 cm^{-1} is attributed to the O–H band in alcoholic group. The intensity of the band 3443cm^{-1} in the fluoride sorbed MOH@n-HAp/Alg biocomposite was decreased due to the exchangeable hydroxyl anion present in the composite was replaced by fluoride ions.

XRD analysis:-

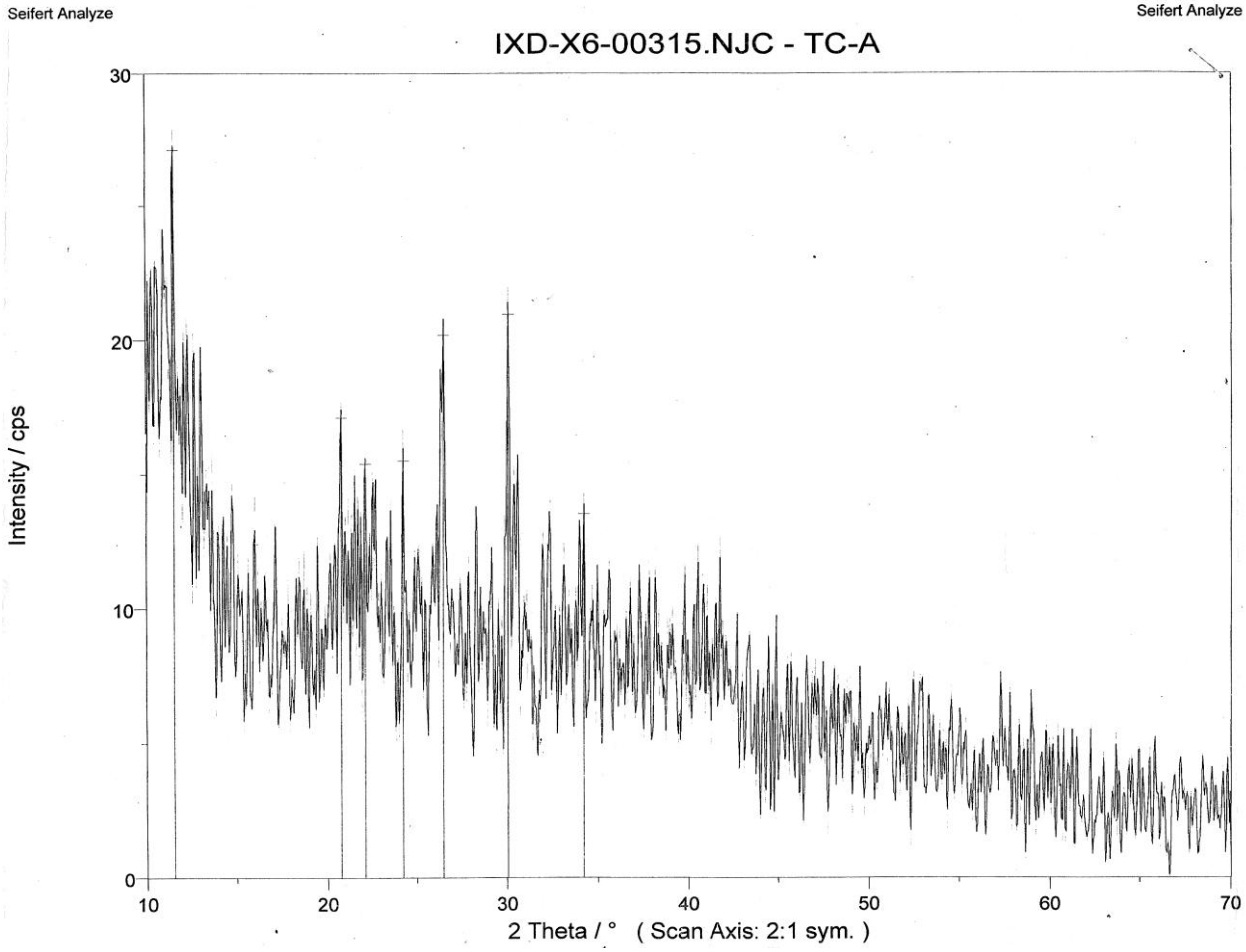


Figure 2:- XRD curves of MOH@n-HAp/Alg biocomposite

The X-ray powder patterns of composites are shown in the figure 2. The average particle size was calculated using Debye Scherer's formula

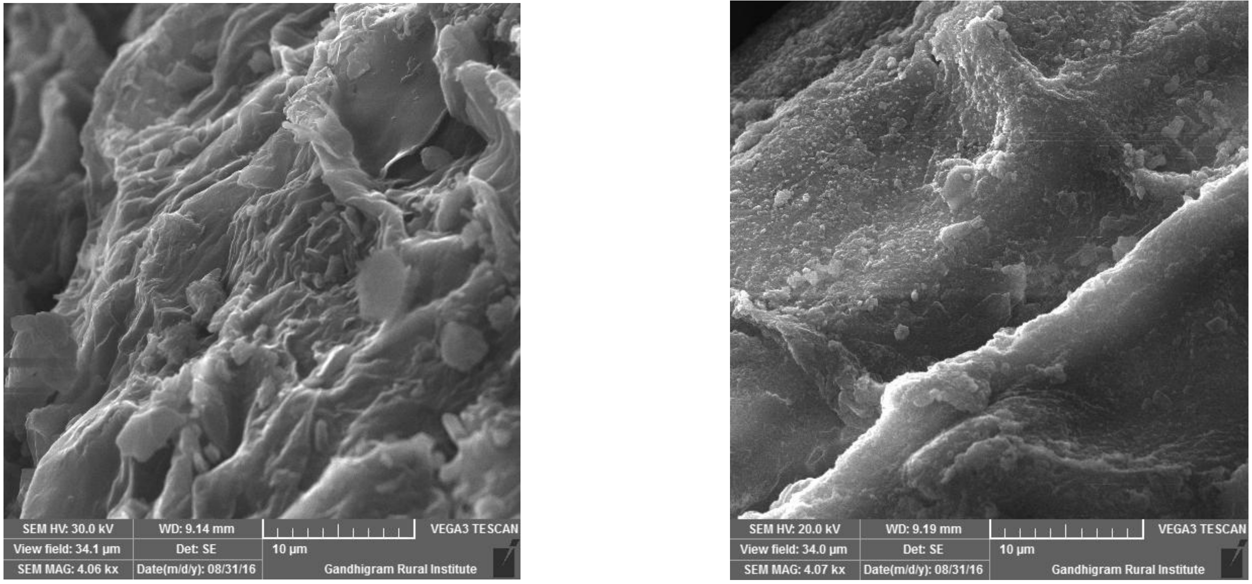
$d= k\lambda/\beta\cos\theta$

'β' is the full width at half maximum(FWHM), 'θ' is the diffraction angle, 'λ' is the wavelength, 'd' is the particle size and 'k' is the Scherrer constant.

The average particle size of biocomposite from XRD was found to be 4.09nm. The composite peaks are in between 20º and 30°. Similarly (Shihabudeen et al, 2006, Eskandarpour et al, 2008 and sivakumar et al, 2012) observed the poorly crystalline nature of sorbents in their study for the removal of fluoride in aqueous solution.

SEM and EDAX analysis:-

The structural surface of the sorbent was studied with a scanning electron microscope(SEM) and the element composition before and after fluoride sorption was examined by energy dispersive X-ray analysis(EDAX). SEM images of MOH@n-HAp/Alg and fluoride sorbed MOH@n-HAp/Alg biocomposites are presented in Figure 3(a and b) respectively.



(b)

Figure 3:- SEM images of (a) MOH@n-HAp/Alg and (b) fluoride sorbed MOH@n-HAp/Alg biocomposite.

The particles had irregular surface with a porous lock, containing large number of wavy and highly broken edges. These images are clearly shown the difference in surface morphologies of these composites. After reaction with fluoride, the composite porous was partly destroyed and this might be attributed to deposition of fluoride over the pores of biocomposite surface. This is further supported by EDAX analysis, which provides the direct conformation for the sorption of fluoride ions onto MOH@n-HAp/Alg biocomposite. In figure 4(a and b) is the EDAX spectra before and after analysis of composites confirm the presence of respective ions are present in the composite. The fluoride peak in the biocomposite confirmed the fluoride treated composite.

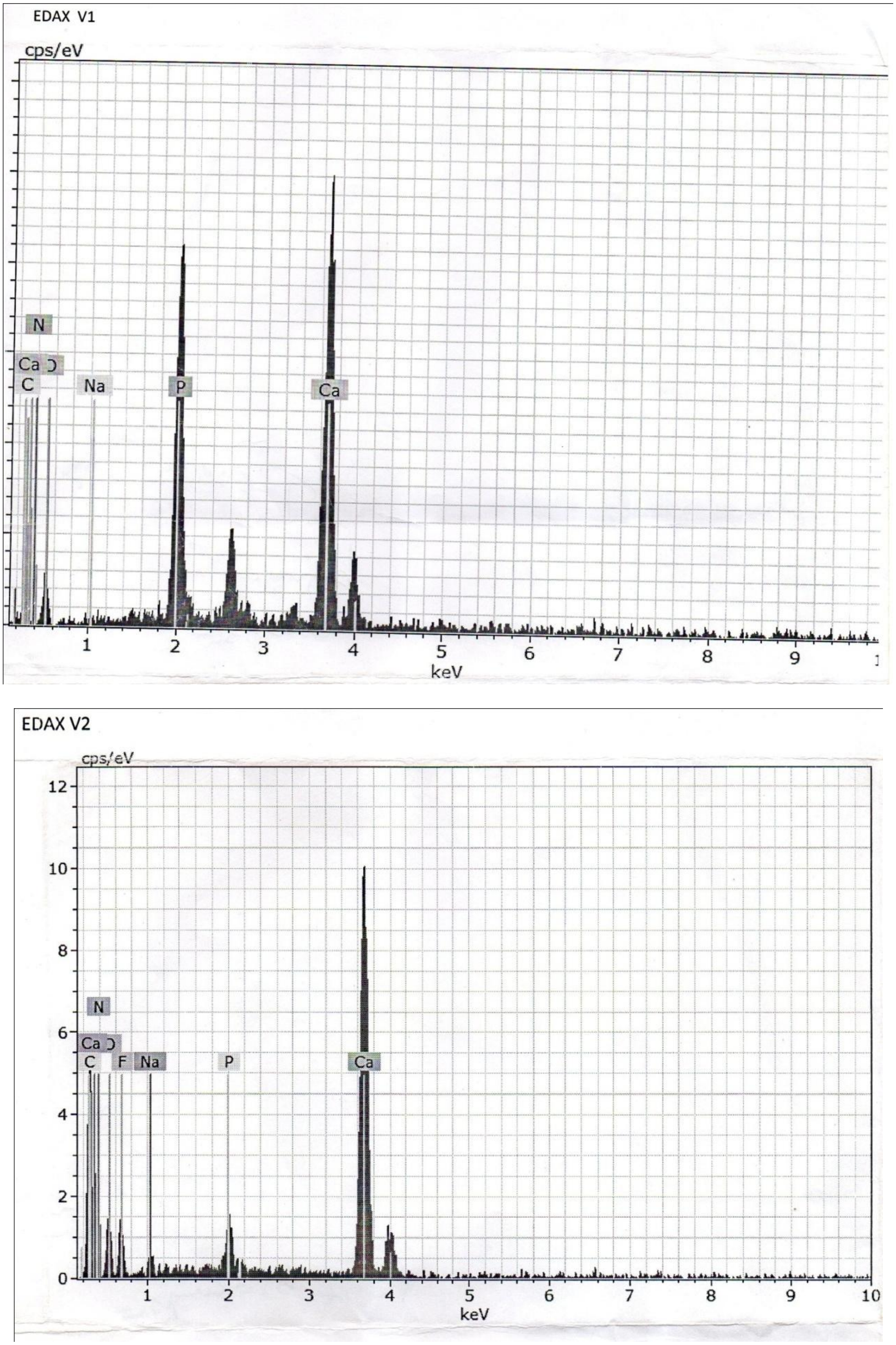


Figure 4:- EDAX spectra of (a) MOH@n-HAp/Alg and (b) fluoride sorbed MOH@n-HAp/Alg biocomposite

pH_{zpc} analysis:-

The pH_{zpc} value of MOH@n-HAp/Alg biocomposite was found to be around 7.45. As shown in Figure 5, the DC of MOH@n-HAp/Alg biocomposite was influenced by the solution pH and it indicates that the maximum fluoride sorption capacity obtained at around pH 7 and then decreased sharply with increase in pH. The change in the pH_{zpc} the biocomposite will confirm the surface morphological changes in the composite.

Effect of pH:-

The pH had some significant influence on sorption of fluoride by MOH@n-HAp/Alg biocomposite, because it can affect the surface charge of the adsorbent. The adsorption of fluoride ions onto the biocomposite adsorbents was analyzed at five different initial pH levels, viz., 2,4,6,7 and 9 and keeping other parameters as constant. The pH of the working solution was controlled by adding dilute HCl/NaOH solution. In **Figure 5** the biosorbent was effective in the pH range 6.0 and 7.5 with a maximum sorption of 85% at pH 7.1 and the extent of sorption of fluoride decreased considerably above pH 7.5 or below pH4. Some sorption was >80% at the natural pH of aqueous sodium fluoride solution as prepared therefore, all the subsequent experiments were carried out without adjusting the pH of the fluoride solution. The effects of pH on fluoride adsorption by MOH@n-HAp/Alg is similar to what has been observed for fluoride adsorption onto various other adsorbents like lanthanum incorporated Chitosan beads(A. Banswal et al, 2009), tamarind fruit cover(N.P. Kumar et al, 2012) and neem leaf powder(Ranjan Kr Bharali et al, 2015). The increase in the pH value decreases the sorption of fluoride as the deprotonation on the sorbent commences. This results in decreasing the electrostatic force at attraction between the sorbent and sorbate ions. To understand the fluoride sorption behavior under different pH values, the following reactions are considered(M.S. Onyango et al, 2006, M.S. Onyango et al, 2006).

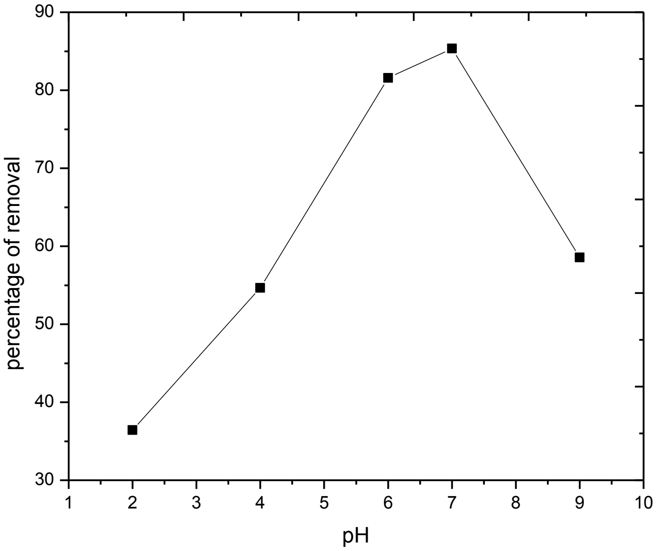


Figure 5:- Effect of solution pH on the MOH@n-HAp/Alg composite in presence of 13mg/L initial fluoride concentration, 0.1g dosage with 60 min. contact time at 301K.

$HF \leftrightarrow H^+ + F^-$

$MOH@n\text{-}HAp/Alg\text{-}OH + H^+ \leftrightarrow MOH@n\text{-}HAp/Alg\text{-}OH_2^+$

$MOH@n\text{-}HAp/Alg\text{-}OH + OH^- \leftrightarrow MOH@n\text{-}HAp/Alg\text{-}O^-$

$MOH@n\text{-}HAp/Alg\text{-}OH_2^+ + F^- \leftrightarrow MOH@n\text{-}HAp/Alg\text{-}F + H_2O$

$MOH@n\text{-}HAp/Alg\text{-}OH + F^- \leftrightarrow MOH@n\text{-}HAp/Alg\text{-}F + OH^-$

Effect of Contact time:-

The effect of contact time on fluoride sorption by MOH@n-HAp/Alg is shown in Figure 6. It was found that the extent of sorption increased with the increase in time(min.) upto 60 min. and after this time interval, the sorption was almost constant. This indicated that the contact time for MOH@n-HAp/Alg biocomposite-fluoride interactions to reach equilibrium was just over 60min. Therefore, this time interval was maintained constant for the next set of experiments. The amount of adsorption is higher in initial stages may be due to the fact that initially all the sorption sites were vacant and can adsorb more fluoride ions from solution phase(S.Kumar et al, 2008).

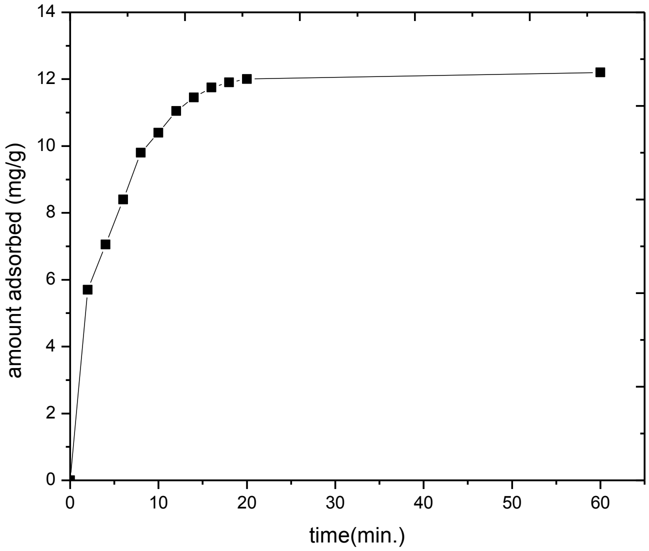


Figure 6:- Effect of contact time on the DC of MOH@n-HAp/Alg biocomposites in presence of 3mg/L initial fluoride concentration, 0.1g dosage with neutral pH at 301K.

Effect of Co-anions:-

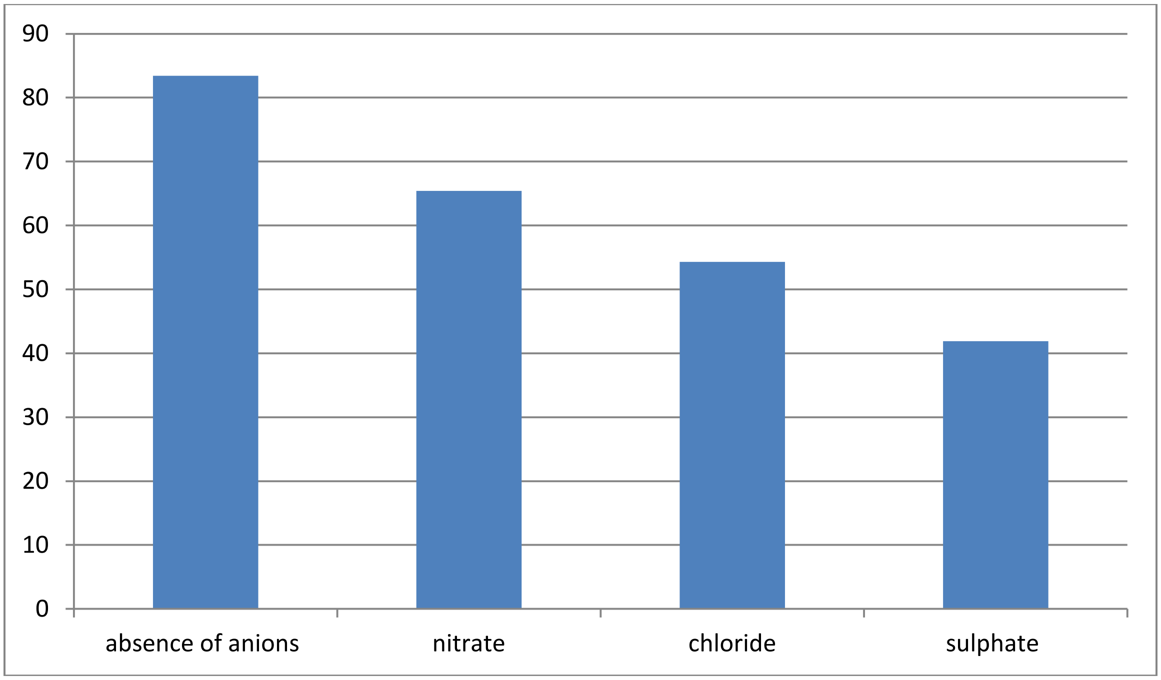


Figure 7:- Effect of presence of co-anions

The drinking water contains other anions in addition to fluoride. It is necessary to test the influence of these co-anions on the MOH@n-HAp/Alg biocomposites. The co-anions like chloride, nitrate and sulphate are normally present in water. The effect of the amount of adsorption of the biocomposite with the fixed initial concentration of co-anions as 5mg/L, 5mg/L as the initial fluoride concentration and by keeping all other parameters as constant. In **Figure 7** shows the percentage removal of fluoride in the presence of anions. It is clear that the fluoride removal is slightly decreased in the presence of chloride, sulphate and nitrate which may be due to high columbic repulsive forces and the size, charge, polarizability and electronegativity differences etc(S.S.Tripathy and A.M. Raichur, 2008). The preference of the sorption of anions by biocomposite may be the following order, fluoride >nitrate>chloride>sulphate.

Thermodynamic Studies:-
The values of thermodynamic parameters are shown in Table 3 and it help to test the spontaneous occurrence of a given process as well as the viability of the operation at a given temperature. Thermodynamic parameters like standard free energy change(ΔG^o), standard enthalpy change(ΔH^o) and standard entropy change (ΔS^o) were calculated by using standard method. The negative values of ΔG^o for the biocomposite confirm the spontaneous nature of fluoride sorption. The positive value of ΔH^o indicates that the defluoridation was governed by endothermic in nature. Biocomposite showed positive value of ΔS^o which is a measure of randomness at the solid/liquid interface during fluoride sorption indicates the fluoride sorption is irreversible and stable. The E_a value calculated from the slope of the plot was found to be –5.062kJ/mol lesser E_a value faster the reaction.

Table 1:- Thermodynamic parameters of the bioadsorbent

Temp.(K)	ΔG^o kJ/mol	ΔH^o kJ/mol	ΔS^o kJ/mol	E_a kJ/mol
301	-39.04	4.86	0.029	-5.062
311	-41.89			
321	-44.84			

Adsorption isotherm analysis:-
The equilibrium data for fluoride sorption onto biocomposite are shown in Table 2. The equilibrium data have been analyzed by the linear regression of isotherm model equations viz., Langmuir(I. Langmuir, 1916), Freundlich(H.M.F. Freundlich, 1906), Temkin(Temkin, M.J and Pyzhev, V, 1940) and D-R isotherm(M.M. Dubinin, 1960).

Table 2:- Various isotherm parameters of MOH@n-HAp/Alg biocomposites

Isotherms	Langmuir	Freundlich	Temkin	D-R
Parameters	Q_0=121.0	n= 0.8423	K_T=2.85	q_m=10320.5
	b =0.1507	1/n =1.215	B_T= 44.22	β=-2.49X10^{-7}
	R_L= 0.481	K_F= 22.14	r = 0.9801	E=1.42
	r = 0.7456	r = 0.9843	sd=5.12E1	r =0.9277
	sd =7.62E-5	sd = 0.0093		sd = 0.2199

The linear plot of C_e vs C_e/q_e indicates the applicability of Langmuir isotherm. The calculated values of Q_o and b are listed in table 2. The R_L values lie in the range between 0 and 1 indicates the sorption process was favourable. The applicability of Fruendlich equation was indicated by the linear plot of log C_e vs log q_e. The obtained ‘n’ and K_F values are in table 2. The values of n lies between 1 and 10 represent favourable condition for sorption. Temkin isotherm was carried out by plotting lnC_e vs q_e (Fig. The value of K_T and B_T were determined from the slope and intercept of the linear plot and are listed in table 2. The high ‘r’ values and the lower sd values indicate the applicability of particular isotherm. The linear plot of ε^2 vs lnq_e indicates the applicability of D-R isotherms. The values of q_m, β and E are shown in table 2. The E value ranges from 1 to 8 kJ/mol for physical sorption and from 9 to 16 kJ/mol for chemical adsorption(A.Sari et al, 2007, R.Donat et al, 2005). From the result the value of E which is 1.42 kJ/mol may suggest that the mechanism for the fluoride sorption on biocomposite is of physical sorption in nature.

Sorption kinetic studies:-
The sorption kinetics describes the sorbate uptake rate that can determine the residence time of sorbate at the solid-solution interface. The sorption processes are analyzed by using reaction based models, including pseudo-first order (A.A. Khan and R.P. Singh, 1987) models and pseudo-second order (S. Langergen, 1898) models. The linear plots of log(q_e-q) against ‘t’ give straight line indicate the applicability of pseudo-first-order model. The slope of the straight line plot of log(q_e-q) against ‘t’ sorption at different temperatures viz. 301, 311 and 321K give the value of the pseudo-first order rate constant(k_{ad}) and r values are listed in Table 3. The pseudo-second-order equation can be found out experimentally by plotting t/q_t against ‘t’. The values of q_e, k_2 and ‘r’ if the pseudo-second-order model were obtained from the plots of t/q_t vs t for fluoride sorption at different temperatures viz 301, 311 and 321K of the composite are presented in table 3. The values of q_e increase with the increase in temperature indicating the fluoride

sorption increases with increase in temperature. The higher 'r' values obtained for pseudo-second-order model than pseudo-first-order model indicate the applicability of the pseudo-second-order model than pseudo-first-order model. For a solid-liquid sorption process, the solute transfer in usually characterized by intra-particle diffusion control (W.J. Weber and J.C.Morris, 1964). The straight line plot of q_t vs $t^{1/2}$ indicates the applicability of intraparticle diffusion model. The k_{ad}, k_2, k_{id} and 'r' values are illustrated in table 3. Based on the sd values shown in Table 3, it is clear that the lower sd values of pseudo-second-order is suitable for describing the sorption kinetics of fluoride on MOH@n-HAp/Alg biocomposite.

Table 3:- Kinetic model for MOH@n-HAp/Alg biocomposite

Kinetic model	Parameters	301K					
		3mg/L	5mg/L	7mg/L	9mg/L	11mg/L	13mg/L
First order	k_{ad}	0.151	0.200	0.065	0.167	0.131	0.169
	r	0.937	0.996	0.986	0.958	0.965	0.908
	sd	0.0149	0.198	0.007	0.152	0.080	0.378
Second order	q_e	22.98	14.32	27.17	43.47	51.28	60.97
	k_2 ($X10^{-3}$)	8.35	19.00	11.00	4.90	4.57	4.54
	r	0.981	0.998	0.988	0.987	0.987	0.988
	sd	0.005	0.024	0.010	0.005	0.003	0.002
Intra particle diffusion	k_{id}	0.686	1.129	1.147	2.09	2.37	2.62
	r	0.869	0.999	0.999	0.986	0.996	0.999
	sd	5.11	0.127	0.126	4.85	1.696	0.308

Field Study:-

In order to test the suitability of MOH@n-Hap/Alg biocomposite at field conditions, fluoride contaminated water was collected in a nearby village. About 0.05g of the bio composite was added to 100 mL of fluoride water sample and the contents were shaken with constant time at room temperature. The obtained results are presented in Table 4. There is a significant reduction in the levels of other water quality parameters in addition to fluoride. It is evident from the result that the biocomposite can be effectively employed for removing the fluoride from water.

Table 4:- Field trial results of the biocomposite

Water quality parameter	Before treatment	After treatment
F^- (mg/L)	3.14	1.94
p^H	6.91	7.16
Total hardness (mg/L)	200	176
Total dissolved solid (mg/L)	126	95

Conclusions:-

In this study, the following conclusions were drawn: the DCs of biocomposite was influenced by the pH of the medium and slightly lowered in the presence of co-anions. The sorption of fluoride onto MOH@n-HAp/Alg biocomposite follows Freundlich Isotherm. The nature of fluoride removal was spontaneous and endothermic. The kinetics of the reaction followed pseudo-second-order model. Field studies indicated that the biocomposite could be used as effective fluoride removal sorbents. The developed MOH@n-HAp/Alg biocomposite could be an effective, eco-friendly and economical biocomposite for the removal of fluoride in water.

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