

Adsorption of Fluoride from Drinking Water on Magnesium substituted Hydroxyapatite

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Abstract. In the present study performance of synthesized adsorbent was investigated for fluoride removal from drinking water under batch mode operations. Magnesium substituted Hydroxyapatite (Mg-HAp) which is a calcium-magnesium based adsorbent was characterized using XRD. The effect of different parameters such as pH, initial fluoride concentration, contact time and co-existing ions (Bicarbonate, Sulphate, Chloride, Nitrate) were studied to understand the adsorption behavior of sorbent under various conditions. Adsorption kinetics followed a typical kinetic curve and pseudo second order rate model described the kinetic sorption process indicating that chemical adsorption, rather than mass transfer, is the rate determining step. Equilibrium was reached in less than 24 hours of contact time and equilibrium data followed Freundlich isotherm model more closely as compared to Langmuir isotherm model. Leaching of Calcium & Magnesium (Ca-Mg) was found to be insignificant as hardness at in all treated samples was found to be increased by 12.13 mg/L as CaCO₃. An increase in equilibrium pH from 6.5 to 8.7 reduced the uptake capacity by 41% and similar trend was observed for leaching of Ca-Mg. The presence of coexisting anions reduced the uptake capacity negligibly.

Keywords: Adsorption, Defluoridation, Magnesium substituted Hydroxyapatite, Drinking Water

1. Introduction

Fluoride (F⁻) contaminated drinking water is a major problem due to its effect on human health and it is estimated that more than 200 million people worldwide rely on drinking water with F⁻ concentrations that exceed the WHO guideline of 1.5 mg/L (Bhatnagar et al., 2011).

Till now many adsorbents for F⁻ removal from water solutions have been developed using copper or by impregnating aluminum, lanthanum and zirconium on various other adsorbents. All these adsorbents have a limitation that during adsorption there is a possibility that the coated elements may leach out in the treated water and can make it unfit for drinking purpose (Bansiwal et al., 2010). So far, aluminum has been reported to be a neurotoxin (Walton, 2011), Lanthanum to be mutagenic and genotoxic (Yongxing et al., 2000). Zirconium has also been reported to have health effects (Ghosh et al., 1992) and Copper has been categorized as heavy metal by the scientific community.

In the present work magnesium substituted hydroxyapatite (Mg-HAp) which is a calcium and magnesium (Ca-Mg) based adsorbent was chemically synthesized and employed to remove F⁻ ions from aqueous solution in batch mode. As the adsorbent is Ca-Mg based so even if it leaches out at equilibrium it will not impart any toxicity to treated water.

2. Materials and Methods

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2.1 Synthesis of Mg-HAp and characterization

For synthesis of Mg-HAp, Ca(OH)_2 , Mg(OH)_2 , and solid $(\text{NH}_4)_2\text{HPO}_4$ (all analytical grade, MERCK Ltd, Mumbai)

were used as reactants. Suspensions from powder mixtures of 22 g Ca(OH)_2 and 1 g Mg(OH)_2 was prepared in 350 ml deionized water. Subsequently, 27 g of $(\text{NH}_4)_2\text{PO}_4$ powder was added slowly with vigorous stirring for 10 minutes. Flushing of any unreacted Ca(OH)_2 and Mg(OH)_2 was accomplished by 3 cycles of washing the slurry with deionized water followed by centrifuging at 4500 rpm for 10 minutes. The washed solid phase was dried in oven at 70°C for 4 hours and then ground to powder with grain size less than 0.425 mm (Suchanek et al., 2004). Material was characterized using XRD (Rigaku D-Max IC XRD unit). X-ray powder diffraction patterns were analyzed which confirmed the synthesized material as magnesium substituted hydroxyapatite.

2.2. Batch Studies

Batch sorption experiments were conducted in order to study the effect of different controlling parameters like pH, initial F^- concentration, contact time and coexisting ions on defluoridation capacity of Mg-HAp. After adding required quantity of adsorbent dose (1 g/L in all samples), fluoride spiked solutions were kept in a rotating shaker at 36 rpm at room temperature $30 \pm 2^\circ\text{C}$ for a specified contact time. The supernatant of sample was filtered through laboratory filter paper and analyzed for residual fluoride concentration. Fluoride analysis was carried out using UV spectrophotometer (V 530, Jasco) as per SPADNS method (APHA, 1998). During experiments, deionized water, NaF and other applicable chemicals like NaHCO_3 , H_2SO_4 and NaOH were used. Except Mg-HAp all other chemicals were analytical grade.

In order to develop an adsorption isotherm, fluoride sorption equilibrium studies were conducted by varying initial F^- concentration from 1.5- 13 mg/L. To study the effect of pH, solution pH was varied from 6 to 9 using 0.01 N HCl and NaOH, as groundwater pH varies in this range only. To investigate the effect of co existing anions on fluoride uptake capacity, experiments were conducted in which concentration of competing anions (Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-) was varied in the range of 0-500 mg/L.

3. Results and Discussion

3.1 Adsorption Kinetics

For kinetics study, the initial F^- concentration in water solution was adjusted to 5.5 mg/L. F^- removal followed a typical kinetic curve (as shown in Fig. 1). In first 30 minutes 25.68 % removal was achieved and equilibrium was reached in less than 24 hours with 47.94 % removal. For all other experiments the contact time was kept 24 hours.

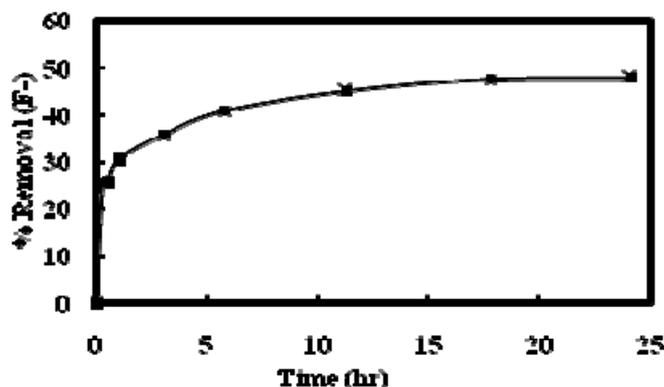


Fig.1. Adsorption kinetics of F^- onto Mg-HAp at initial pH 6.0 and initial F^- concentration of 5.5 mg/L

In order to analyze kinetics of F⁻ onto the sorbent, two popular kinetic models namely, the Lagergren equation and the Pseudo second order equation were used. The rate constants for respective equations are shown in Table 1. The coefficient of determination for the pseudo-second-order adsorption model (R²=0.998) is higher than that obtained from the Lagergren first-order kinetics (R²=0.966). The calculated equilibrium adsorption capacity q_e (2.71 mg/g) is consistent with the experimental value q_{exp} (2.66 mg/g). Therefore, it is possible to conclude that the Mg-HAp followed a second-order kinetic model which indicates that chemisorption, rather than mass transfer, is the rate limiting step (Kang et al., 2011).

Table 1 Adsorption rate constant for different kinetic models

Initial F ⁻ conc. (mg/L)	Measured q _{e,exp} (mg/g)	Lagergren Equation			Pseudo Second Order		
		K _{Lag} (1/h)	q _e (mg/g)	R ²	K _{PSS} g/(mg h)	q _e (mg/g)	R ²
5.51	2.66	0.101	1.210	0.966	0.52	2.71	0.998

3.2 Adsorption Equilibrium

Equilibrium studies were carried out to determine the conditions for maximum F⁻ removal on Mg-HAp. It was observed that adsorption capacity reaches an equilibrium value beyond which there is negligible change in the residual F⁻ concentration. The distribution of F⁻ between the liquid phase and the solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by two model equations namely Freundlich and Langmuir equations (Ghorai and Pant, 2005). The Freundlich model, which is an indicative of surface heterogeneity of the sorbent, is given by the following linearized equation

$$\text{Log}q_e = \text{Log}k_f + \frac{1}{n}\text{Log}C_e$$

where k and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The Langmuir equation, which is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}}$$

where q_{max} is the maximum amount of the F⁻ ion per unit weight of Mg-HAp to form a complete monolayer on the surface and b is a constant related to the affinity of the binding sites. All the values of isotherm model parameters are shown in Table 2.

Both Langmuir and Freundlich isotherm models could fit the fluoride adsorption process on Mg-HAp, but the applicability of isotherm equation was compared by evaluating the coefficient of determination R². The equilibrium data followed Freundlich isotherm more closely as compared to Langmuir isotherm model with coefficient of determination 0.983 (refer Table 2). Freundlich isotherm plot for adsorption of F⁻ is shown in Fig.3. Leaching in treated samples was found to be insignificant as hardness was found to be increased by 12.13 mg/L as CaCO₃. Adsorption capacity of Mg-HAp is compared (as shown in Fig.5) with Granular Zirconium-Iron oxide, GZI (Dou et al., 2011), Copper Oxide Coated Alumina, COCA (Bansiwal et al., 2010), Alum Impregnated Activated Alumina, AIAA (Tripathy et al., 2006), Hydroxyapatite, HAp (Jimenez-Reyes and Solache-Ri'os, 2010), Manganese Oxide Coated Alumina, MOCA (Maliyekkal et al., 2006), Activated Alumina, AA (Maliyekkal et al., 2006), Lanthanum Incorporated Chitosan Beads, LCB (Bansiwal et al., 2009) at equilibrium concentration of 1mg/L and 5 mg/L and it is observed that uptake capacity of Mg-HAp is more than HAp, MOCA, AA, LCB and comparable to COCA, AIAA. GZI has slightly more uptake capacity than Mg-HAp.

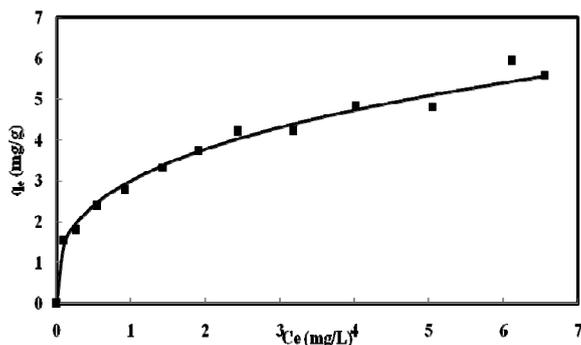


Fig. 2. Freundlich isotherm plot for adsorption of fluoride

3.3 Effect of pH

Solution pH is one of the main factors which affect the sorption capacity of a sorbent. To study the effect of pH on uptake capacity of Mg-HAp, studies were performed on fluoride removal at various solution pH (ranging from ~6-9) keeping other parameters constant. The average initial concentration of F^- was adjusted to ~10 mg/L. Fig.3 shows the effect of pH on F^- sorption onto Mg-HAp. Results showed adsorption capacity of 8.8 mg/g at pH 6.5 and it decreased by 41% at pH 8.7. The progressive decrease in the amount of F^- adsorbed under alkaline pH conditions is probably due to competition for adsorption sites between F^- and OH^- (Chen et al, 2010). If the surface charge of the Mg-HAp was to decrease continuously with the increasing concentration of OH^- , the attractive interactions between the F^- and the adsorbent surface could be adversely affected (Keng et al . 2011). Leaching of Ca-Mg followed a decreasing trend on increasing pH as hardness at pH 6.5 was 31.3 mg/L as $CaCO_3$ and it decreased by 68.7% at pH 8.7.

3.4. Effect of Co-existing ions

In practical situations, various ions coexist along with target contaminants, which may equally compete for the adsorption sites. Hence this study experimentally determined the defluoridation capacity of Mg-HAp in the presence of common anions such as Cl^- , SO_4^{2-} , NO_3^- and HCO_3^- . In order to study the effect, initial concentration of these anions was varied from 0-500 mg/L with all other parameters constant. Initial fluoride concentration was adjusted to

Table 2 Isotherm model parameters

Adsorbent	Langmuir Isotherm Model			Freundlich Isotherm Model		
	R^2	b (L/mg)	q_{max} (mg/g)	R^2	K_f ($mg^{(n-1/n)}g^{-1}L^{(1/n)}$)	1/n
Mg-HAp	0.968	1.04	6.211	0.983	3.01	0.325

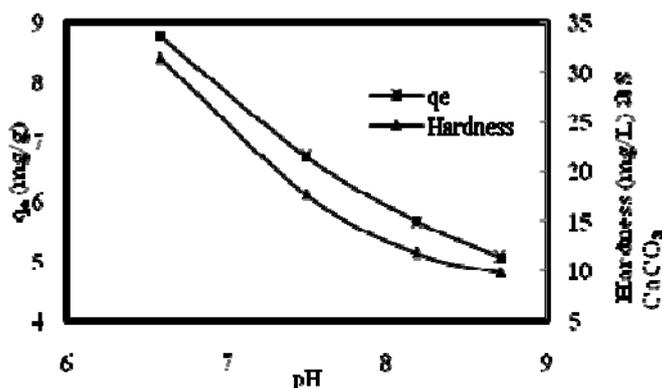


Fig.3. Effect of pH on fluoride removal by Mg-HAp

~4.5 mg/L. Fig.4 indicates that the fluoride removal decreases as the concentration of coexisting anions increases in the aqueous phase. Uptake capacity of Mg-HAp was decreased by 14% when concentration of HCO_3^- was varied from 0 to 500 mg/L. Similar trend was observed for SO_4^{2-} , NO_3^- with a 16% and 13% decrease in the uptake capacity respectively. Presence of Cl^- decreased the uptake capacity by 0.9%.

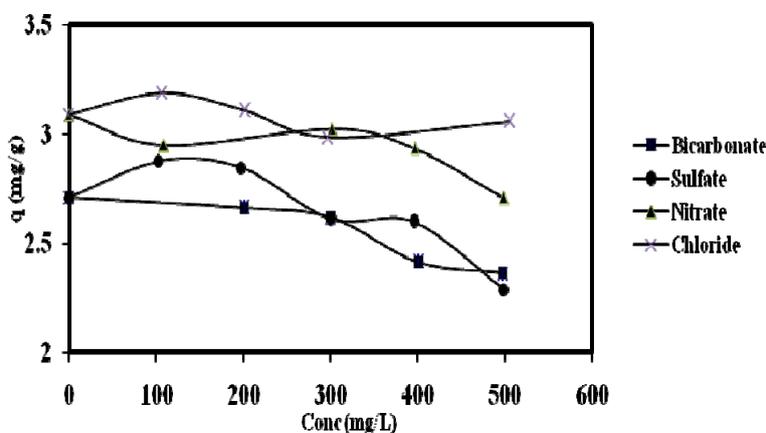


Fig.4. Effect of Co-existing anions on uptake capacity of Mg-HAp

4 Conclusions

The conclusions drawn based on the above study are given below. The removal of F^- from aqueous greatly depends on initial concentration, contact time, pH and presence of co-existing anions. The adsorption kinetic data followed pseudo second order rate model and adsorption equilibrium data followed Freundlich isotherm model with a better fit. Adsorption capacity of Mg-HAp is more than various adsorbents as compared in the paper. The pH conditions of the initial solution influenced the adsorption capacity of Mg-HAp significantly. Presence of co-existing anions does not affect the defluoridation capacity appreciably. Hardness at equilibrium was negligible which indicates low leaching characteristics. Hence, Mg-HAp, a calcium-magnesium based adsorbent, was found to possess excellent defluoridation capacity.

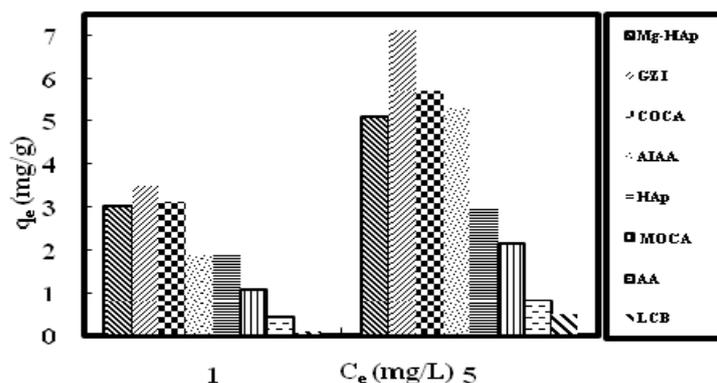


Fig.5. Adsorption capacity of different adsorbent at pH 7 ± 0.5

References:

- [1] A. Bansiwala, D. Thakre, N. Labhshetwar, S. Meshram, S. Rayalu. Fluoride removal using lanthanum incorporated chitosan beads. *Colloids and Surfaces B: Biointerfaces*. 2009, 74(1): 216–224.
- [2] A. Bansiwala, P. Pillewan, R.B. Biniwale, S.S. Rayalu. Copper oxide incorporated mesoporous alumina for defluoridation of drinking water. *Microporous and Mesoporous Materials*. 2010, 129(1-2): 54–61.
- [3] A. Bhatnagar, E. Kumar, M. Sillanpää. Fluoride removal from water by adsorption -A review. *Chemical Engineering Journal*. 2011, 171(3): 811–840.

- [4] APHA. Standard Methods for the Examination of Water and Wastewater. 18th ed. American Public Health Association, American Water Works Association Washington, DC, USA. 1998.
- [5] J. Kang, B. Li, J. Song, D. Li, J. Yang, W. Zhan, D. Liu. Defluoridation of water using calcined magnesia/pullulan composite. *Chemical Engineering Journal*. 2011, 166(2): 765–771.
- [6] J.R. Walton. Bioavailable Aluminum: Its Effects on Human Health. *Encyclopedia of Environmental Health*. 2011: 331–342.
- [7] M. Jiménez-Reyes and M. Solache-Ríos Sorption behavior of fluoride ions from aqueous solutions by hydroxyapatite. *Journal of Hazardous Materials*. 2010, 180(1-3): 297–302.
- [8] N. Chen, Z. Zhang, C. Feng, N. Sugiura, M. Li, R. Chen. Fluoride removal from water by granular ceramic adsorption. *Journal of Colloid and Interface Science*. 2010, 348(2): 579–584.
- [9] S. Ghorai and K.K. Pant. Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Separation and Purification Technology*. 2005, 42(3): 265–271.
- [10] S. Ghosh, A. Sharma, G. Talukder. Zirconium. *Biological Trace Element Research*. 1992, 35(3): 247–271.
- [11] S.M. Maliyekkal, A.K. Sharma, L. Philip, Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water. *Water Research*. 2006, 40(19): 3497–3506.
- [12] S.S. Tripathy, J. Bersillon, K. Gopal. Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. *Separation and Purification Technology*. 2006, 50(3): 310–317.
- [13] W. Yongxing, W. Xiaorong, H. Zichun. Genotoxicity of lanthanum (III) and gadolinium (III) in human peripheral blood lymphocytes. *Bulletin of Environmental Contamination and Toxicology*. 2000, 64(4): 611–616.
- [14] W.L. Suchanek, K. Byrappa, P. Shuk, R.E. Riman, V.F. Janas, K.S. TenHuisen. Preparation of magnesium-substituted hydroxyapatite powders by the mechanochemical-hydrothermal method. *Biomaterials*. 2004, 25(19): 4647–4657.
- [15] X. Dou, Y. Zhang, H. Wang, T. Wang, Y. Wang. Performance of granular zirconium-iron oxide in the removal of fluoride from drinking water. *Water Research*. 2011, 45(12): 3571–3578.