Nature Environment and Pollution Technology *An International Quarterly Scientific Journal*	Vol. 8	No. 2	pp. 231-236	2009

Original Research Paper

Removal of Fluoride from Aqueous Solution Using a Waste Material

G. Babu Rao, G. Kalyani, B. Vijaya Saradhi* and Y. Prasanna Kumar**
Department of Chemical Engineering, GMR Institute of Technology, Rajam-532 127, A.P.
*****Department of Civil Engineering, A.U. College of Engineering, Visakhapatnam-530 003, A.P.
******Department of Chemical Engineering, Vignan's Engineering College, Vadlamudi-522 213, A.P.

Key Words:
Fluoride
Biosorption
Algae
Ulva fasciata Biosorbent

ABSTRACT

This communication presents results pertaining to the adsorptive studies carried out on fluoride removal onto an algal biosorbent (*Ulva fasciata*). Batch sorption studies were performed and the results revealed that biosorbent demonstrated ability to adsorb the fluoride. Influence of varying conditions for removal of fluoride such as the fluoride concentration, the dosage of adsorbent, the size of adsorbent, and the concentration of metal solution was investigated. Experimental data showed good fit with the Langmuir's adsorption isotherm model. Maximum fluoride sorption was observed at 30°C operating temperature.

INTRODUCTION

Fluoride ion in water exhibits unique properties as its concentration in optimum dose in drinking water is advantageous to health and excess concentration beyond the prescribed limits affects the health adversely. High fluoride concentration in groundwaters and surface waters in many parts of the world is a cause of great concern. High fluoride in drinking water was reported from different geographical regions. The problem of excessive fluoride in groundwater in India was first detected in Nellore of Andhra Pradesh in 1937 (Short et al. 1937). According to an estimate, 25 million people in 19 states and union territories have already been affected and another 66 million are at risk including 6 million children below the age of 14 years. Though fluoride enters the body mainly through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake. A fluoride ion is attracted by positively charged calcium in teeth and bones, due to its strong electro-negativity. Major health problems caused by fluoride are dental fluorosis (teeth mottling), skeletal fluorosis (deformation of bones) and nonskeletal fluorosis (Susheela et al. 1993, WHO 1985). It can interfere with carbohydrates, lipids, protein, vitamins, enzymes and mineral metabolism when the dosage is high. In some parts of India, the fluoride levels are below 0.5 mg/L, while at certain places, fluoride levels are as high as 35 mg/L (Handa 1975).

Defluoridation is performed by adsorption, chemical treatment, ion exchange, membrane separation, electrolytic defluoridation, and electrodialysis, etc. Among various processes, adsorption was reported to be effective. Investigators reported various types of adsorbents namely activated carbon, minerals, fish bone charcoal, coconut shell carbon and rice husk carbon, with different degrees of success. Recently considerable interest was observed on the application of biosorbent materials for removal of various pollutants. Biosorbent materials can passively bind large amounts of metal(s) or organic pollutants, a phenomenon commonly referred to as biosorption. Biosorbents are attractive since naturally occurring biomass or spent biomass can be effectively utilized (Volesky & Holan 1995). Besides this, biosorption offers advantages of low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed, high efficiency in dilute effluents, no nutrient requirements and environmental friendly and economical viable. It provides a cost-effective solution for industrial water management (Arjun Khandare et al. 2004). Application of biosorbents/biomass from various microbial sources, leaf based adsorbents and water hyacinth was reported by various investigators (Venkata Mohan et al. 2003, Ram Chandra Murthy et al. 2003, Udaya Simha et al. 2002, Mariappan et al. 2000, Prakasam et al. 1998). Limited number of studies were available on the treatment by algal species (fresh and marine water) in spite of their ubiquitous distribution and their central role in fixation and turnover of carbon. Keeping the above points in view, batch adsorption studies were carried out on the sorption of fluoride from aqueous phases using commonly available marine alga *Ulva fasciata*. The adsorption studies were carried out under various experimental conditions and the results obtained are presented in this communication. Algae are traditionally food supplement and are generally safe. The alga *Ulva fasciata,* used as biosorbent in this experiment, generally grows profusely on rocks of the tidal zone of costal belt and its availability is easy without any practical investment. Thus, using *Ulva fasciata* as biosorbent is environmentally safe and practically economical.

MATERIALS AND METHODS

Preparation of adsorbent: The green coloured marine alga *Ulva fasciata,* used in the present study, was collected from the coastal belt of Visakhapatnam. The collected algae were washed with deionized water several times to remove impurities. The washing process was continued till the wash water contains no dirt. The washed algae were then completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent after cutting into small pieces and powdering (75-212 µm particle size).

Chemical and metal solution: Stock solution of fluoride was prepared by dissolving 2.21g of sodium fluoride (AR grade) in 1000 mL of double glass distilled water. The stock solution was then appropriately diluted to get the test solution of desired fluoride concentration.

Analysis of fluoride: The residual fluoride concentration in the aqueous phase was analysed by standard methods.

The results are given as a unit of adsorbed and unadsorbed metal concentrations per gram of adsorbent in solution at equilibrium and calculated by:

$$q_e = \frac{(C_o - C_{eq})V}{X} \quad ...(1)$$

Where X is the adsorbent concentration (g/L), q_e is the adsorbed metal ion quantity per gram of adsorbent at equilibrium (mg/g), C_o is the initial metal concentration (mg/L), C_{eq} is the metal concentration at equilibrium (mg/L) and V is the working solution volume.

Metal adsorption experiments: Adsorption experiments were conducted at 30°C in batch with 0.1 g of the *Ulva fasciata* in a 30 mL of working solution volume. The flasks were then shaked at 180 rpm.

Adsorption equilibrium: Equilibrium studies were carried out by agitating 30 mL of fluoride solution of initial concentrations varying from 5-25 mg/L with 0.1 to 0.5 g of algae at room temperature for 45 minutes at a constant stirring speed at a pH of 6.

During the adsorption, a rapid equilibrium is established between adsorbed metal ions on the algal cell *qe* and unadsorbed metal ions in solution (C_{eq}). This equilibrium can be represented by the Langmuir (Langmuir 1916) or Freundlich (Freundlich 1906) adsorption isotherms, which are widely used to analyse data for water and wastewater treatment applications. The Langmuir equation, which is valid for monolayer adsorption on to a surface a finite number of identical sites, is given by:

$$q_e = \frac{Q_{\max} b C_{eq}}{1 + b C_{eq}} \quad ...(2)$$

Where Q_{max} is the maximum amount of the metal ion per unit weight of algae to form a complete monolayer on the surface bound at high C_{eq} (mg/g), and *b* is a constant related to the affinity of the binding sites (L/mg) Q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments. Q_{max} and *b* can be determined from the linear plot of C_{eq}/q_e vs. C_{eq}

The empirical Freundlich equation based on adsorption on a heterogeneous surface is given by

$$q_e = K_F C_{eq}^n \quad ...(3)$$

Where K_F and *n* are Freundlich constants characteristic of the system. K_F and *n* are indicators of adsorption capacity and adsorption intensity, respectively. Eq. (3) can be linearized in logarithmic form and Freundlich constants can be determined. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

RESULTS AND DISCUSSION

The effect of contact time: Fig. 1 shows the effect of contact time on the adsorption of fluoride by adsorbent from aqueous solution. The rate of fluoride adsorption by the nonliving cells was very rapid, reaching almost 90% of the maximum adsorption capacity within 45 min of contact time and the adsorption does not change significantly with further increase in contact time. Microbial metal uptake by nonliving cells, which is metabolism-independent passive binding process to cell walls (adsorption), and to other external surfaces, and is generally considered as a rapid process, taking place within a few minutes. The rapid metal sorption is also highly desirable for successful deployment of the biosorbents for practical applications.

Effect of algal concentration: The effect of variation of *Ulva fasciata* algal cells dosage on fluoride uptake and fluoride % removal is shown in Fig.2. It shows that while the percentage removal of fluoride increases with the increase in adsorbent dosage, fluoride uptake increases by increasing adsorbent dose. The increase in metal uptake by increasing adsorbent dose is attributed to many reasons, such as availability of solute, electrostatic interactions, interference between binding sites, and reduced mixing at high biomass densities. Thus, the adsorption sites remain unsaturated during the sorption process due to a lower adsorptive capacity utilization of the sorbent, which decreases the adsorption efficiency. Some of these reasons contributed also in limiting the maximum percentage removal, thus 100% removal was not attained. This suggests that a more economical design for the removal of heavy metal ions can be carried out using small batches of sorbent rather than in a single batch.

The influence of adsorbent dosage in removal of fluoride is shown in Fig. 2. The increase in

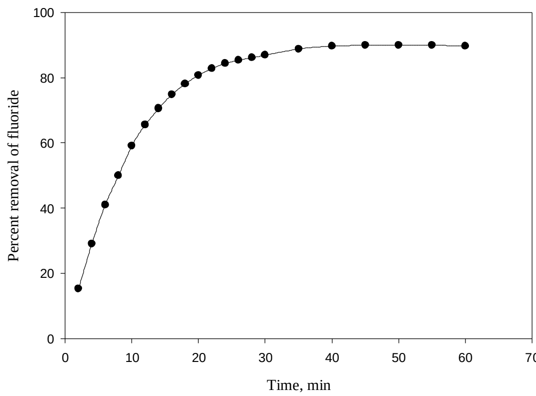

Fig:1 Effect of contact time on the percentage removal of fluoride

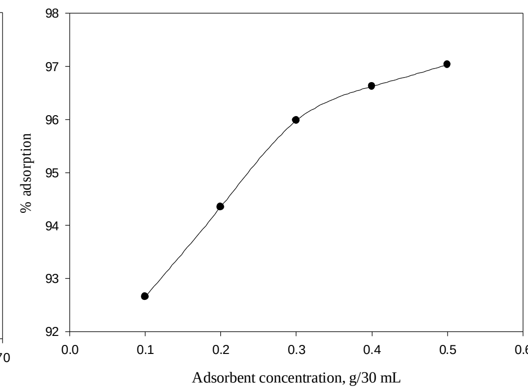

Fig:2 Effect of adsorbent concentration on percentage adsorption

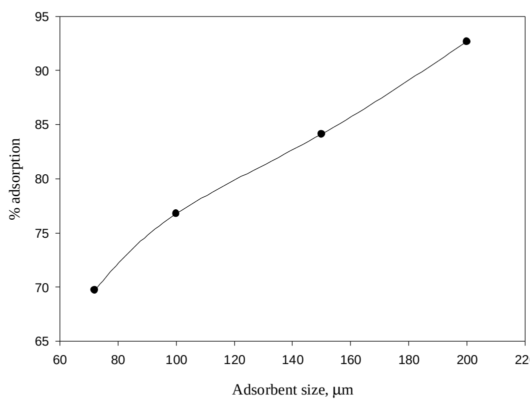

Fig: 3 Effect of adsorbent size on percentage adsorption

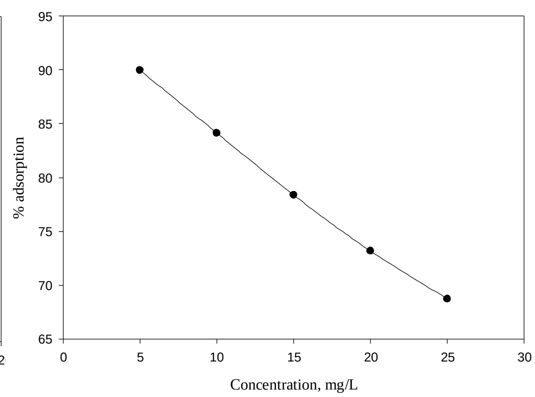

Fig:4 Effect of metal concentration on percentage adsorption

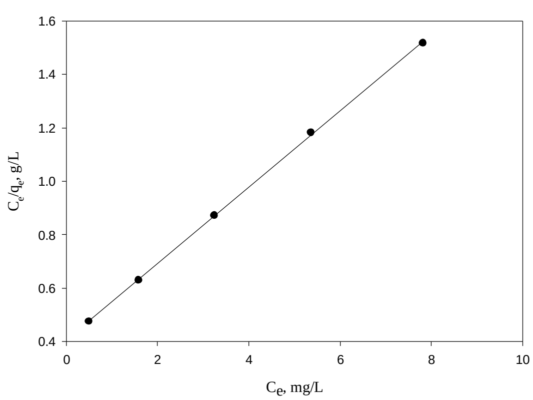

Fig:5 Langmuir Adsorption Isotherm

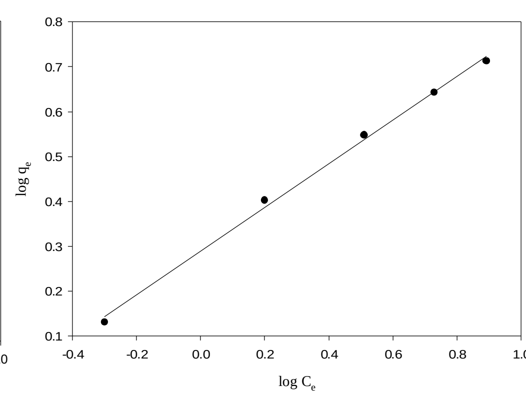

Fig:6 Freundlich Adsorption Isotherm

adsorbent dosage from 0.1 to 0.5 g resulted in an increase in adsorption of fluoride. This is because of the availability of more binding sites for complexation of fluoride ions.

Effect of particle size: The effect of different adsorbent particle sizes (72-200 µm) on percentage removal of fluoride was investigated. Fig.3 reveals that the adsorptions of fluoride on *Ulva fasciata* decreases with the increased particle size from 72 to 200 µm at an initial concentration of 5 mg/L. It is well known that decreasing the particle size of the adsorbent increases the surface area, which in turn increases in adsorption capacity.

Effect of initial metal ion concentration: Several experiments were undertaken to study the effect of initial fluoride concentration on the fluoride removal from the solution. The results obtained are shown in Fig. 4. The data show that the metal uptake increases and percentage adsorption of the fluoride decreases with increase in initial metal ion concentration. This increase is a result of the increase in the driving force, i.e., concentration gradient. However, the percentage adsorption of fluoride ions on *Ulva fasciata* was decreased. Though, an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of fluoride displays an opposite trend.

At lower concentrations, all fluoride ions present in solution could interact with the binding sites and, thus, the percentage adsorption was higher than that at higher initial fluoride ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

Adsorption equilibrium: The adsorption equilibrium defines the distribution of a solute phase between the liquid phases and solid phases after the adsorption reaction reached equilibrium condition. In the present study, equilibrium studies were carried out at room temperature 28 ± 2°C. The equilibrium data were analysed using two of the most commonly used isotherm equations, Freundlich and Langmuir isotherm models.

The equilibrium data were very well represented by all the two equilibrium models (Fig. 5 and 6). The best-fit equilibrium model was determined based on the linear regression correlation coefficient R^2. It was observed that the adsorption data were very well represented by Langmuir isotherm with an average higher correlation coefficient of 0.9989. The higher R^2 value for Langmuir isotherm confirms the approximation of equilibrium data to Henry's law at lower initial concentration.

CONCLUSIONS

Following conclusions can be drawn from study on the removal of fluoride ion from aqueous solution using adsorption technique. The biomass of the *Ulva fasciata* demonstrated a good capacity of fluoride adsorption, highlighting its potential for water.

- The data obtained from the adsorption of fluoride ions on the *Ulva fasciata* showed that a contact time of 45 minutes was sufficient to achieve equilibrium.
- It was observed that the percentage adsorption of the metals decreases with increase in the initial metal ion concentration.
- It reveals that the effect of different adsorbent particle sizes on the adsorption of fluoride is significant. The adsorption of the metal decreases with increase in particle size of *Ulva fasciata*.
- The amount of fluoride adsorbed increases with an increase in adsorbent dosage of *Ulva fasciata*.

- The experimental data gave good fit with Langmuir isotherm and the adsorption coefficient agreed well with conditions of favourable adsorption.

REFERENCES

Arjun Khandare, L., Uday Kumar, P., Shankar, G., Venkaiah, K. and Laxmaiah, N. 2004. Additional beneficial effects of tamarind ingestion over defluoridated water supply to adolescent boys in a fluorotic area. Nutrition, 20: 433-436.

Freundlich, H.M.F.1906. Zeitschrift fur Physikalische Chemie. Leipzig, 57A: 385-470.

Handa, B.K. 1975. Geochemistry and genesis or fluoride containing groundwater in India. Ground Water, 13: 278-281.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc., 38(11): 2221-2295.

Mariappan, P., Yegnaraman, V. and Vasudevan, T. 2000. Defluoridation using low cost activated carbons. IJEP, 22(2): 154-160.

Prakasam, R.S., Chandra Reddy, P.L., Manisha, A. and Ramakrishna, S.V. 1998. Defluoridation of drinking water using *Eichhornia* sp. IJEP, 19(2): 119-124.

Ram Chandra Murthy, T., Jeyakar, A., Chellaraj, R., Edison Raja, T., Venkatachalam, R., Sangeetha and Sivaraj, C. 2003. Fluoride estimation in potable water in Tiruchirapalli Rock-Port area - Dental fluorosis survey and defluoridation with *Phyllanthus emblica*. IJEP, 239(3): 317-320.

Short, H.E., Mc Robert, G.R., Bernard, T.W. and Mannadiyar, A.S. 1937. Endemic fluorosis in the Madras Presidency. Ind. J. Med. Res., 25: 553-561.

Susheela, A.K., Kumar, A., Betnagar, M. and Bahadur, M. 1993. Prevalence of endemic fluorosis with gastro-intestinal manifestations in people living in some north-Indian villages. Fluoride, 26: 97-104.

Venkata Mohan, S., Vijaya Bhaskar, Y. and Karthikeyan, J. 2003. Biological decolorization of simulated azo dye in aqueous phase by algae *Spirogyra* species. Int. J. Environ. Pollut., 21(3): 211-222.

Volesky, B. and Holan, Z.R. 1995. Biosorption of heavy metals. Biotechnol. Prog., 11: 235-250.

Udaya Simha, L., Panigrahy, B. and Ramakrishna, S.V. 2002. Preliminary studies on fluoride adsorption by water hyacinth. IJEP, 22(5): 506-511.

WHO, 1985. Health Criteria and Other Supporting Information, Guidelines for Drinking Water Quality. CBS Publishers and Distributors, New Delhi.