

# Adsorption of fluoride from aqueous solution by *Emblica officinalis* seed powder and *Manikara zapota* seed powder - A comparative study

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## ABSTRACT

The removal of fluoride ion in aqueous solution by using naturally and abundantly available low cost biosorbents of *Emblica officinalis* seed powder (EOSP) and *Manikara zapota* seed powder (MZSP) is studied. The results of fluoride adsorption were compared. Further, the biosorbents were characterized by FTIR, SEM and surface area analysis. The effect of various operating parameters such as pH, contact time, concentration of fluoride and amount of biosorbent were studied to find the adsorption efficiency. The equilibrium data were used to study the kinetics of defluoridation process such as pseudo first order, pseudo-second order and Weber–Morris intraparticle diffusion models. The adsorption data were analyzed using Langmuir and Freundlich adsorption isotherms. Break through curves were obtained from column flow adsorption data. The maximum monolayer adsorption of fluoride on EOSP and MZSP as found to be 30.8 and 43.8 mg/g. The experimental results showed that MZSP had more potential than EOSP for removal of fluoride ion in drinking water.

**Keywords:** Adsorption; EOSP; MZSP; Fluoride; Isotherms; Kinetics

## 1. INTRODUCTION

Groundwater constitutes 97% of global freshwater and is single largest supply of drinking water in many parts of the world. Now-a-days, quality of groundwater is impaired by many natural constituents, of which fluoride stands first as a pollutant of geogenic origin in many countries.

Fluorine (F) known as tiger of chemistry, is highly reactive and most electronegative element which reacts with most of the organic and inorganic substances. Presence of fluoride is considered as necessary devil which shows both beneficial and detrimental effects of fluoride on human health. The fluoride research in the past decades suggests that concentration below 1 mg/L are beneficial in the prevention of dental caries or tooth decay, but above 1.5 mg/L increase the severity of the incurable disease fluorosis. Various techniques and materials were tried throughout the world for defluoridation of water. Extensive research has been carried out for removal of fluoride from water. These methods are based on the principle of ion-exchange [1], precipitation-coagulation [2,3], membrane separation process [4], nanofiltration [5] and adsorption [6].

Among various methods used for the defluoridation, adsorption is generally preferred due to low cost, simplicity of design and operation [7,8]. Different adsorbents like *Cynodon dactylon*, *Azadirachta Indica* and *Acacia Arabica* leaves, wood or bone charcoal, citrus fruits, *Moringa indica* bark, corn cobs, tamarind seeds [9-15] in modified or natural form are studied for effective removal of fluorine.

In the present study EOSP and MZSP is used for defluoridation of drinking water. *Phyllanthus emblica* Linn (or) *Emblica officinalis* Gaertn, commonly known as Indian gooseberry or Amla is one of the most important medicinal plants in Indian traditional systems of medicine (Ayurveda, Unani and Siddha). Amla fruit is widely used in the Indian system of medicine as diuretic, laxative, liver tonic, refrigerant, stomachic, restorative, anti-pyretic, hair tonic, ulcer preventive and for common cold, fever; as alone or in combination with other plants. Phytochemical studies on amla disclosed major chemical constituents including tannins, alkaloids, polyphenols, vitamins and minerals [16].

*Manilkara zapota*, also known as Sapodilla, is very commonly distributed in Indian subcontinent. It is an important member of Sapotaceous family as it is well known all over the world for its traditional medicinal uses. The fruit of sapodilla is a brown coloured berry, nearly round and varies from 5-10 cm in width. Some Sapodilla fruits are seedless but normally they produce 3-12 seeds per fruit. They are hard and brown or black in colour with one white margin. The seeds contain some phytochemicals like saponin, achras saponin and the bitter saptinine [17].

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

NaF was used in this study as adsorbents. The NaF, HCl and NaOH were obtained from Merck with analytical grade. High pure water is prepared in the laboratory itself by double distillation of deionised

water in quartz distillation plant (Bhanu Scientific Company, Bangalore, India). Measuring electrical conductivity checks purity of distilled water. This water is used for cleaning of adsorbents and glassware and for preparation of stock solutions, standard solutions and for the dilution of samples.

## 2.2. Preparation of adsorbents

Sapota and Amla are purchased from local market in Nellore (A.P.) Seeds are separated, washed with tap water then with deionized water. The seeds are sundried for 5 days, powdered using mixer grinder and sieved. Then the powder is collected and stored in airtight container.

## 2.3. Preparation of Fluoride stock solution

The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1000 mL of double distilled water, such that each ml of solution contains 1 mg of F. The exact concentration of fluoride ion solution is calculated on mass basis and expressed in terms of mg/L. The required lower concentrations 10, 15 and 20 mg/L are prepared by dilution of the stock solution. All precautions are taken to minimize the loss due to evaporation during the preparation of solutions and subsequent measurements. The stock solutions are prepared fresh for each experiment as the concentration of the stock solution may change on long standing.

## 3. RESULTS AND DISCUSSION

### 3.1. FTIR Spectral Analysis

The important role of FTIR is characterization of sorbents or describes the functional groups involved in the mechanism of adsorption process. The FTIR spectra of EOSP and MZSP before and after fluoride adsorption are shown in Fig. 1. The FTIR spectra of EOSP (Fig. 1(a)) show peaks at  $3433\text{ cm}^{-1}$  and  $1053\text{ cm}^{-1}$  due to the presence of hydroxyl and alcohol groups, respectively. Fig. 1(b) shows the FTIR spectrum of EOSP loaded with fluoride. An interesting phenomenon is the sharp shift in the position and intensity of the bands after fluoride binding. The peak appears at  $1000 - 1100\text{ cm}^{-1}$  indicates the presence of C - F stretching. The FTIR spectrum of MZSP biosorbent (Fig. 1(c)) indicates the presence of predominant peaks at  $3437\text{ cm}^{-1}$  (-OH and -NH stretching vibrations),  $2922\text{ cm}^{-1}$  (-CH stretching vibration),  $1383\text{ cm}^{-1}$  (-NH deformation vibration), and  $1047\text{ cm}^{-1}$  (-CO stretching vibration). This reveals that all functional groups originally present on EOSP and MZSP are still present even after coating process and are available for interaction with fluoride. Fig. 1(d) represents the FTIR spectra of fluoride loaded MZSP, indicating the shift in the position and intensity of the peaks upon fluoride binding.

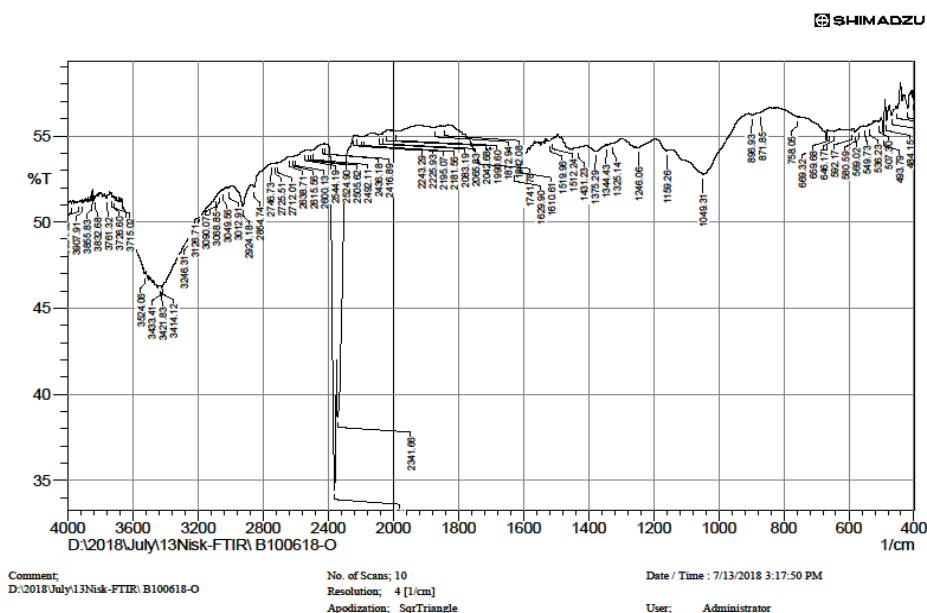


Fig. 1(a). FTIR Spectra of EOSP.

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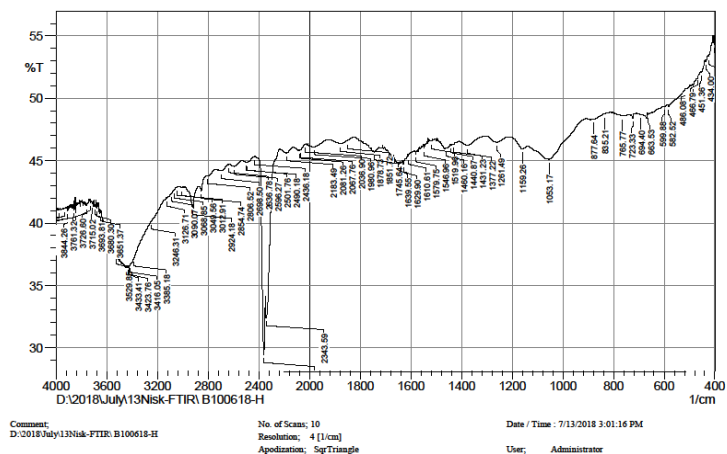


Fig. 1(b). FTIR Spectra of EOSP loaded with fluoride.

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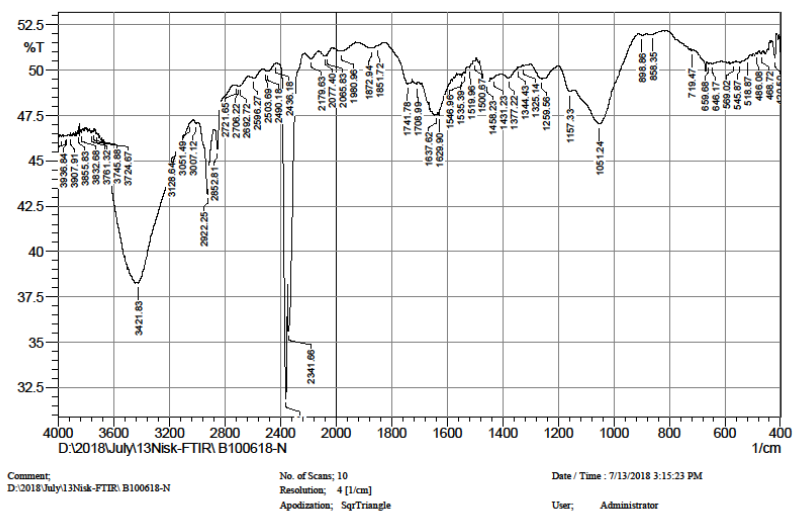


Fig. 1(c). FTIR Spectra of MZSP.

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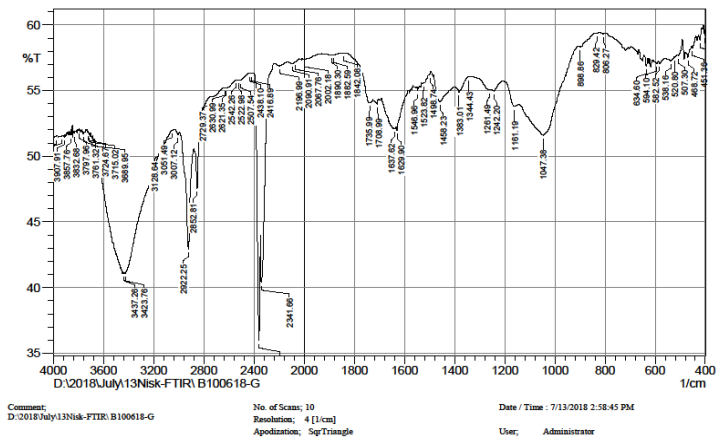
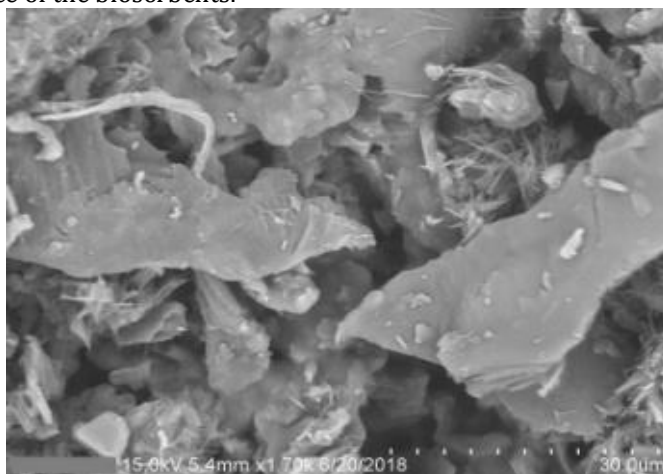


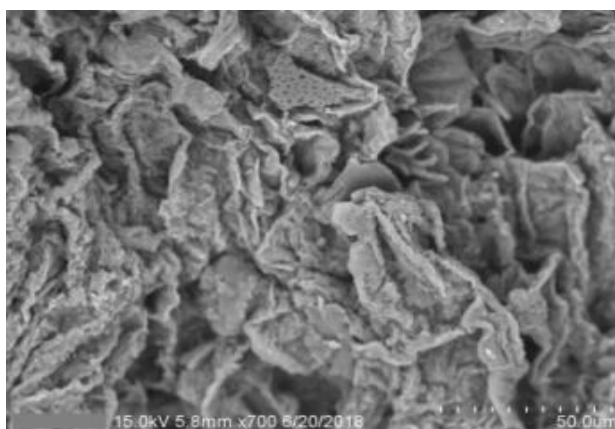
Fig. 1(d). FTIR Spectra of MZSP loaded with fluoride.

### 3.2. SEM analysis

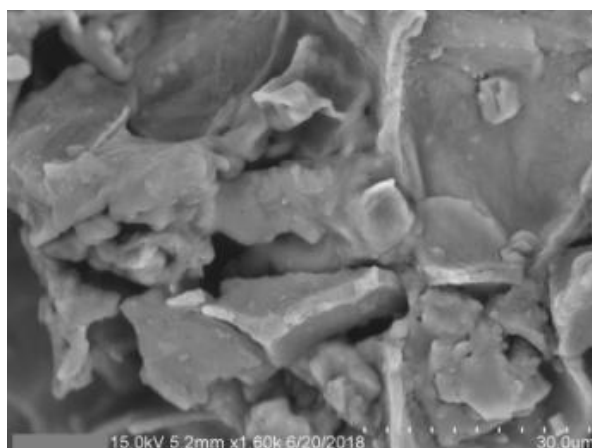
Scanning electron microscopy (SEM) images were recorded using a soft ware controlled digital scanning electron microscope. In order to study the surface of adsorbent before and after adsorption SEM images were obtained. SEM images of the biosorbents before and after fluoride sorption of EOSP are shown in Fig. 2(a) and 2(b), respectively. The respective SEM images of MZSP before and after treatment are shown in Fig 2(c) and Fig. 2(d), respectively. An examination of the SEM micrographs indicates the surface is irregular, contains number of pores and also has broken edges. Comparison of these micrographs before and after fluoride sorption indicates the surface is swollen and that there is no significant change in the morphology of the surface of the biosorbents.



**Fig. 2(a). SEM image of EOSP.**



**Fig. 2(b). SEM image of EOSP loaded with fluoride.**



**Fig. 2(c). SEM image of MZSP.**

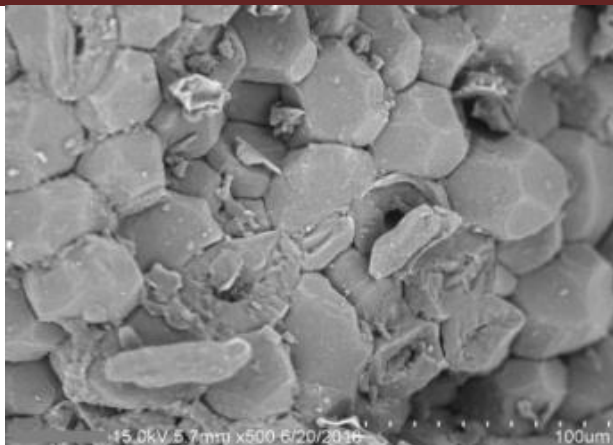


Fig. 2(d). SEM image of MZSP loaded with fluoride.

**3.3. Surface area analysis**

Influence of the surface properties on the extent of adsorption is evaluated by measuring the surface area ( $44.6 \text{ m}^2 \text{ g}^{-1}$  for EOSP and  $78.3 \text{ m}^2 \text{ g}^{-1}$  for MZSP) and pore volume ( $0.202 \text{ cm}^3$  for EOSP and  $0.231 \text{ cm}^3$  for MZSP). Porosity influences the activity and physical interaction of solids with liquids and gases and fluorine adsorption. It was observed that EOSP has more surface area and porosity than MZSP.

**3.4. Effect of pH**

One of the most important factors controlling the adsorption of fluoride is pH. pH can influence the surface charge of adsorbent and the degree of ionization of fluoride ions. Thus the role of hydrogen ion concentration is examined with 100 ml solution of 10 mg/L of fluoride in contact with 0.5 g of adsorbent in the pH range 1-8 at room temperature. The influence of pH on the sorption rate is shown in Fig. 3. It is observed that the maximum % removal is observed at pH 6 (79%) and pH 4 (65%) for MZSP and EOSP, respectively. The fluoride removal is observed to increase upto a certain pH value followed by reduction when further pH increases. The progressive decrease of fluoride uptake at alkaline pH could be mainly due to the electrostatic (attraction between positively charged surface ions and fluoride ions) repulsion of fluoride to the negatively charged surface of EOSP and MZSP, and the competition of hydroxyl ions with fluoride ions for active sites.

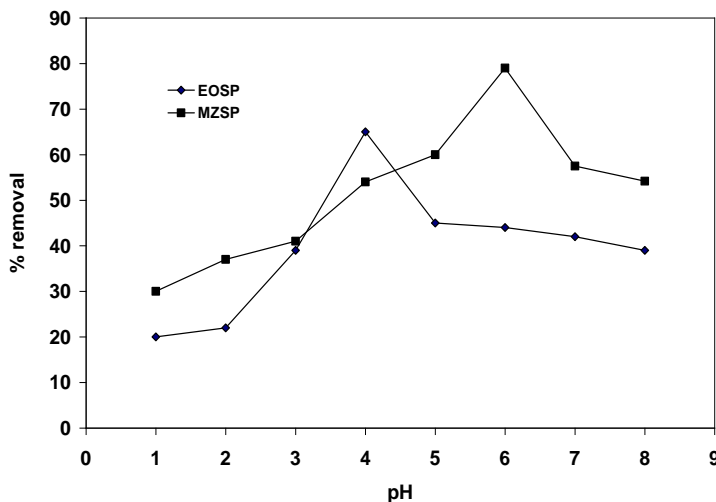


Fig.3: Effect of pH on biosorption of fluoride on of EOSP and MZSP.

**3.5. Effect of contact time**

The contact time between adsorbents and adsorbents were carried out by varying from 0 to 150 minutes to assess the optimum contact time required for the process to attain equilibrium. The effect of contact time on adsorption capacity of fluoride is depicted in Fig. 4 and 5. The results illustrated that the extent of adsorption increases rapidly with time initially and attained equilibrium for all the concentrations of fluoride ion studied at 120 minutes. After this equilibrium period, the amount of fluoride adsorbed does not change significantly with time.

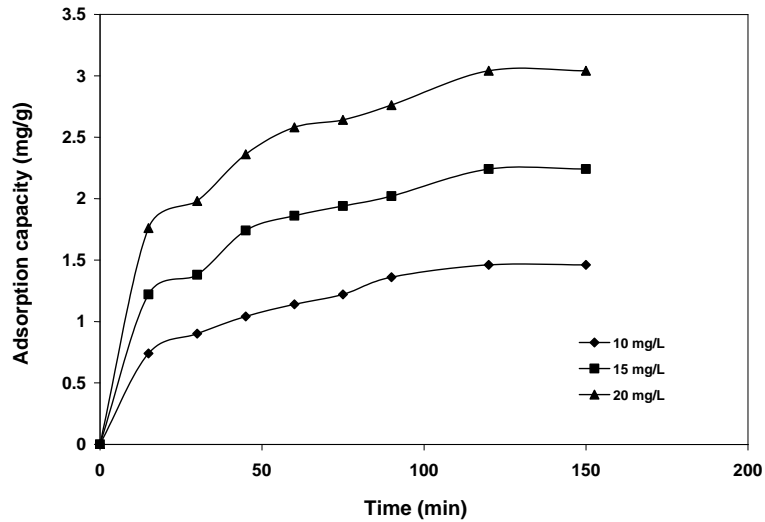


Fig. 4: Effect of time on biosorption of fluoride on EOSP.

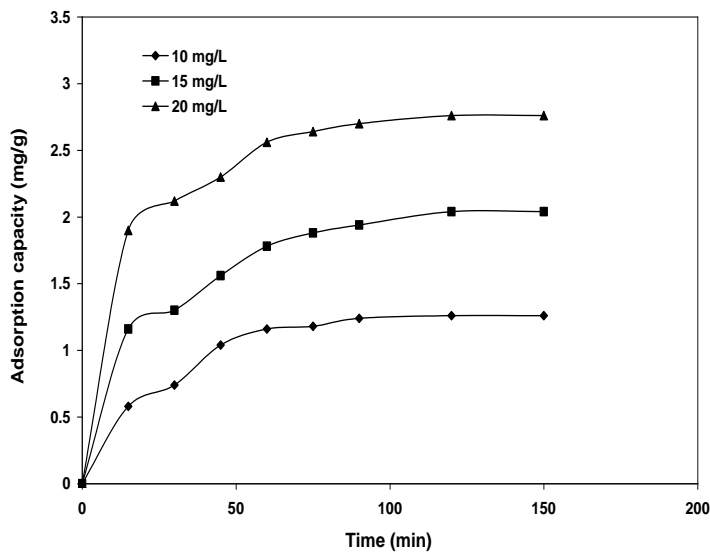


Fig. 5: Effect of time on biosorption of fluoride on MZSP.

### 3.6. Sorption Dynamics

The sorption kinetics of fluoride on the biosorbents is studied on the basis of pseudo first order [18], pseudo second order kinetic [19] and intraparticle diffusion [20] models. Pseudo first order kinetic equation or Lagergren rate equation is expressed as,

$$\log(q_e - q_t) = \log q_e - k_1 t \tag{1}$$

Pseudo second order equation may be expressed as;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Where  $q_e$  and  $q_t$  are the amount of fluoride adsorbed per unit mass of adsorbent (mg/g) at equilibrium and any time  $t$  (min),  $k_1$  (1/min) and  $k_2$  (g/mg. min) are the rate constants of first and second order sorption respectively.  $k_1$  is calculated according to the linear plot of  $\log(q_e - q_t)$  versus  $t$  and  $k_2$  is determined by plotting  $t/q_t$  against  $t$ . The rate constants of pseudo-first order and pseudo-second order kinetic models are shown in Tables 1 and 2.

The adsorption data on EOSP and MZSP followed pseudo second order kinetic model. It was found that the value of correlation coefficient  $R^2$  for the pseudo-second-order adsorption model is relatively high.

The larger  $k_2$  value, the slower the adsorption rate. Therefore, the values of the pseudo second order rate follow the order  $MZSP > EOSP$ .

**Diffusion based models**

In order to study the contribution of the intraparticle diffusion in the fluoride adsorption process on EOSP and MZSP, rate constant of intraparticle diffusion is calculated by using Weber-Morris intraparticle diffusion model represented as

$$q_e = k_{id}t^{0.5} + C \tag{3}$$

Where  $k_{id}$  is the intraparticle diffusion rate constant ( $mg/g \text{ min}^{-0.5}$ ) and C is the intercept. It can be seen that all the plots have an initial curved portion, followed by a linear portion and a plateau regions. The initial curved portion was attributed to the diffusion of fluoride through the solution to the external surface of both EOSP and MZSP. The linear portion of curves describes the intraparticle diffusion of fluoride on EOSP and MZSP and final plateau region indicates equilibrium uptake. The rate constants of Weber-Morris intraparticle diffusion model are shown in Table 3. Based on the results it may be concluded surface adsorption and intra particle diffusion contribute to the rate determining step.

**Table 1: Legergren first-order rate constants for fluoride biosorption.**

Initial concentration (mg/L)	EOSP		MZSP	
	$k_1$	$R^2$	$k_1$	$R^2$
10	0.03823	0.9753	0.0263	0.9140
15	0.03316	0.9794	0.0221	0.9841
20	0.03063	0.9823	0.0216	0.9844

**Table 2: Pseudo second-order rate constants for fluoride biosorption.**

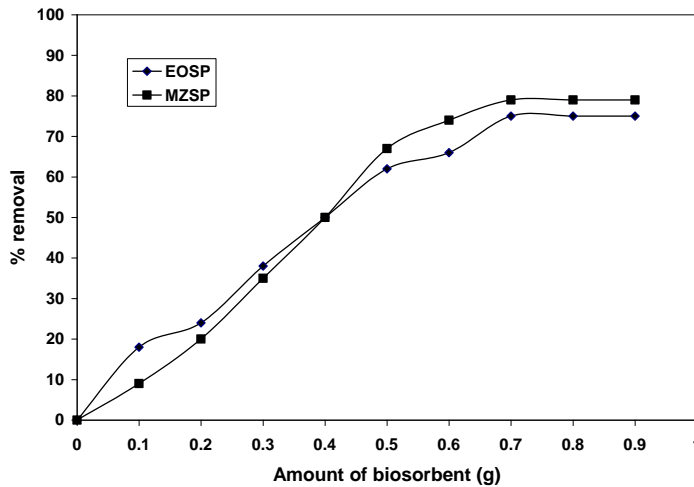
Initial concentration (mg/L)	EOSP			MZSP		
	$Q_e$ (mg/g)	$k_2$	$R^2$	$Q_e$ (mg/g)	$k_2$	$R^2$
10	1.4876	0.0305	0.9897	1.7256	0.0218	0.9918
15	2.3294	0.0223	0.9960	2.5694	0.0178	0.9948
20	2.9762	0.0322	0.9986	3.4294	0.0150	0.9955

**Table 3: Weber-Morris rate constants for fluoride biosorption.**

Initial concentration (mg/L)	EOSP			MZSP		
	$k_{id}$	C	$R^2$	$k_{id}$	C	$R^2$
10	0.1067	0.1647	0.8977	0.1189	0.1751	0.9486
15	0.1630	0.3367	0.9026	0.1793	0.3294	0.9231
20	0.2078	0.6836	0.8107	0.2393	0.5087	0.9063

**3.7. Effect of Adsorbent Dose**

The influence of biosorbent dose on fluoride removal is studied by varying the amount of adsorbent from 0.1 to 0.9 g while keeping all other variables (pH, agitation time and concentration) constant. It is observed that percentage removal of fluoride increases with the increase in adsorbent dose shown in Fig. 6. This behavior is attributed to the greater available surface area with the rise in adsorbent dosage and greater availability of exchangeable sites for the ions. The maximum fluoride ion removal efficiencies are 75% with EOSP and 79% with MZSP. This suggests that the fluoride ion can be removed effectively by using < 1 g of the biosorbent. The reduction in adsorption capacity with increase in the adsorbent dose is mainly due to overlapping of active sites thus decreasing the net surface area for adsorption. Adsorption capacity decreases from 1.8 to 0.83 mg/g and 1.34 to 0.88 mg/g for fluoride with EOSP and MZSP respectively.



**Fig.6: Effect of adsorbent dose on biosorption of fluoride on EOSP and MZSP.**

### 3.8. Adsorption Isotherm models

Initial concentration of fluoride ion can influence the fluoride removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bond fluoride ions. Adsorption capacity of fluoride on EOSP and MZSP is carried out at different initial fluoride concentrations (10-60 mg/L). It was observed that fluoride removal efficiency decreased with increasing initial fluoride concentration and reached equilibrium at 30 mg/L. This is due to the fact that initial concentration contributes to the driving force to overcome mass transfer resistance of ions between the adsorbent and bulk fluid phases. Higher initial concentration enhances the mass transfer driving force, thus increasing the uptake of fluoride ion. In addition, increasing initial fluoride ion concentrations increases number of collisions between fluoride ions and adsorbents thus enhancing the adsorption capacity.

#### Langmuir isotherm

The process of adsorption is usually studied through graphs known as adsorption isotherms it shows the relationship between the amounts of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solutions. The Langmuir equation is applied for the estimation of maximum adsorption capacity of the adsorbent for the removal of fluoride in aqueous solutions corresponding to complete monolayer coverage on the biosorbent surface. Langmuir isotherm [21] model assumes that adsorption sites are energetically same with monolayer formation and is represented as

$$Q_e = \frac{Q^o b C_e}{1 + b C_e} \tag{4}$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount of fluoride adsorbed for unit weight of EOSP or MZSP,  $b$  is Langmuir constant related to the energy of adsorption and  $Q^o$  represents Langmuir constant related to the adsorption of adsorption capacity when the surface is fully covered with fluoride.

In order to predict the efficiency in adsorption process, dimensionless equilibrium parameter constant, separation factor ( $R_L$ ), is defined by

$$R_L = \frac{1}{1 + b C_o} \tag{5}$$

Where  $b$  is the Langmuir constant (L/mg) and  $C_o$  is the initial fluoride concentration (mg/L). If the  $R_L < 1$ , it represents favorable adsorption and if the  $R_L > 1$ , it represents unfavorable adsorption. The values of  $R_L$  for sorption of fluoride on EOSP and MZSP are less than 1 and greater than 0, indicating the favorable uptake of fluoride by the biosorbents.

#### Freundlich Isotherm

The Freundlich model is chosen to estimate the adsorption intensity of the sorbent towards the biosorbent on heterogeneity EOSP surfaces. The Freundlich isotherm [22] is represented by the equation:



$$Q_e = K_f C_e^{1/n} \quad (6)$$

Where  $K_f$  is a measure of adsorption capacity, and  $1/n$  is the adsorption intensity. The parameters of Langmuir and Freundlich adsorption isotherms, evaluated from the linear plots are presented in Table 4 along with the correlation coefficients. Though both the isotherms are capable of representing the data satisfactorily, the Langmuir model gives a better representation

**Table 4: Langmuir and Freundlich isotherm constants for fluoride biosorption.**

Biosorbent	Langmuir			Freundlich			
	$Q^o$ (mg/g)	$b$ (L/mg)	$R^2$	$K_f$	$1/n$	$n$	$R^2$
EOSP	30.8	0.012	0.998	0.485	0.933	1.074	0.997
MZSP	43.8	0.009	0.998	0.482	0.953	1.059	0.998

#### 4. CONCLUSIONS

The results of this study indicate that the MZSP is an effective adsorbent for removal of fluoride from aqueous solution than EOSP. Adsorptive removal of fluoride is influenced by pH of the solution as well as on the initial concentration of fluoride ion. The maximum fluoride removal was obtained in the pH range of 4 for EOSP and 6 for MZSP. From the kinetic studies, it is found that fluoride removal is complex and both the surface adsorption as well as intraparticle diffusion contributes to the rate-determining step. The equilibrium data were fitted to Langmuir and Freundlich adsorption isotherms. The maximum monolayer adsorption of fluoride on EOSP and MZSP found to be 30.8 and 43.8 mg/g.

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