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Biosorption of fluoride from aqueous solution by white–rot fungus *Pleurotus eryngii* ATCC 90888

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ABSTRACT

In present study the biosorption characteristics of fluoride anions from aqueous solution using white rot fungus (*Pleurotus eryngii*) were investigated as a function of pH, initial fluoride concentration, biosorbent dose, temperature, and contact time. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of fluoride ions by *P. eryngii* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The monolayer biosorption capacity of *P. eryngii* biomass for fluoride ions was found to be 66.6 mg g^{-1}. Thermodynamic parameters such as ΔH°, ΔS° and ΔG° indicate that the removal of fluoride ions by fungal biomass was endothermic and spontaneous in nature. Experimental data were also analyzed in terms of kinetic characteristics and it was found that biosorption process of fluoride ion followed well pseudo-second order model, where intra-particle diffusion was not the only rate-controlling step. The surface and sorption characteristics were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and Fourier transform infrared (FTIR) spectrometry. In order to check the practical utility of the studied biosorbent, batch studies were carried out with fluoride contaminated water samples collected from a fluoride-endemic area. Eventually, this fungal biomass recommended to be used as a suitable, environment friendly and low cost biosorbent for removal of fluoride ion concentration to standard permissible limit.

1. Introduction

Fluoride contamination in groundwater has been recognized as one of the serious problems worldwide (Amini et al., 2008). The natural or anthropogenic sources are the major cause of excess fluoride levels in drinking water. The permissible limit of fluoride in drinking water is 1.5 mg L^{-1} as per World Health Organization (WHO) guidelines (WHO, 2011). According to the WHO more than 260 million people are consuming drinking water worldwide with fluoride contents higher than permissible limit. The consumption of drinking water with fluoride concentration above this limit may increase the prevalence of dental and skeletal fluorosis in children and adults. Recent surveys carried out to investigate the quality of groundwater in Pakistan, indicated that some areas in the dry zone have the fluoride problem in endemics proportions. Predominantly the locality of district Tharparkar, Sindh (Mithi, Diplo, Chachro, and Nagarparkar) is severely affected by fluoride contamination. People in these areas depend heavily on underground water due to unavailability of other water resources. Several reports have shown high fluoride contamination in the water of aforementioned areas of Pakistan and proven to be the major source of fluorosis (Rafique et al., 2008, 2009).

Various methods for defluoridation have been reported in literature such as adsorption (Raichur and Basu, 2001), chemical treatment (Reardon and Wang, 2000), ion exchange (Singh et al., 1999), membrane separation (Amer et al., 2001), and electrolytic defluoridation (Mameri et al., 2001), etc. Among these processes, adsorption has been reported to be an effective and economical method for removal of fluoride ions (Mohan et al., 2002). Recently, more focus has been given by the scientists in using various naturally occurring biosorbents in adsorption process. Biosorption utilizes the ability of biological materials to accumulate metal ions from water by either metabolically mediated or physico-chemical pathways of uptake. Biosorption offers advantages of low cost, minimization of the quantity of chemical or biological sludge to be disposed, high efficacy in dilute effluents, environmental friendly properties, regeneration of biosorbent, and possibility of metal recovery (Ahalya et al., 2003).

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Application of biosorbents from microbial sources such as, *Spirogyra* sp.-IO2 (Mohan et al., 2007), *Pleurotus ostreatus* (Ramanaiah et al., 2007), *Aspergillus penicilloides*, *Mucor racemosus* (Prajapat et al., 2010), and *Anabaena fertilissima* (Bhatnagar et al., 2002) for fluoride removal have been reported. In current study, the biosorption capacity of white – rot fungus (*Pleurotus eryngii*) is evaluated first time in literature for removal of fluoride from ground water samples. Following the experimental optimizations, the biosorbent was applied successfully for defluoridation of real water samples from endemic areas of Tharparkar district, Sindh, Pakistan. Afterword it has been revealed from the obtained results that *P. eryngii* is a better choice and suitable biosorbent for removal of fluoride from aqueous systems then the earlier reported materials.

2. Materials and methods

2.1. Chemicals

Analytical grade anhydrous sodium fluoride salt (purity 99%) was procured from Sigma Aldrich (Madrid, Spain). All other reagents were of high purity available.

2.2. Fluoride stock solution

Stock solution of fluoride (1000 mg L^{-1}) was prepared by dissolving 2.21 g of sodium fluoride in 1000 ml of deionized water. The stock solution was then appropriately diluted to get the test solution of desired fluoride concentration.

2.3. Preparation of the biosorbent

Strain of *P. eryngii* ATCC® 90888™ was obtained from Edible Fungi Institute, Shanghai Academy of Agricultural Sciences, Shanghai, China. Fungal culture was routinely maintained on potato dextrose agar (PDA) slants. To produce the mycelial biomass for biosorption experiments, the seed cultures were prepared by loop inoculation and incubating the fungus in glucose peptone medium. The formulation of liquid medium prepared in laboratory composed of g L^{-1}; Glucose (50), Peptone (5), KH_2PO_4 (5) and NaCl (5), adjusted to pH 6.0 ± 0.2 and incubated for 28 days at 27 ± 2 °C. The resultant fungal biomass was washed with deionized water and dried at 60 °C for 24 h. Dried biomass was crushed to a particle size of 0.18 mm and stored in screw capped falcon tubes for subsequent use in the fluoride biosorption experiment. No impregnation or activation process was done before using fungal biosorbent. The fungal biomass was subjected to elemental analysis which reveals that fungal biomass is composed of C 45.42%, H 6.58%, N 3.88%, O 44.01% and S 0.11%.

2.4. Point of zero charge (pH_{PZC})

The point of zero charge is the pH value at which the number of cations and anions present on the surface are equal, so that the surface has no electrical charge. pH_{PZC} of the biosorbent was determined by the solid addition method (Mahmood et al., 2011). Briefly 50 ml of 0.1 M KNO_3 solution was transferred into a series of 100 ml conical flask. The initial pH (pH_i) values of the solution were adjusted from 2.0 to 12.0 by adding either 0.1 N HCl or NaOH. Then 0.1 g of *P. eryngii* biomass was added to each flask and shaken for 48 h at ambient temperature. After 48 h the final pH values of the supernatant liquid was noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_i - pH_f$) was plotted against the pH_i. The point of intersection of the resulting curve with abscissa at which pH = 0 gave the pH_{PZC}.

2.5. Instrumentation

Innova 4230 Incubator shaker (New Brunswick Scientific Co; Huntingdon, UK) was used for the batch experiments. pH meter (InoLab-WTW GmbH; Weilheim, Germany) with glass electrode and internal reference electrode was used for pH measurements. The Ion-Chromatograph (Ω Metrohm; Herisau, Switzerland) instrument 861 Advance Compact with 833 IC liquid handling unit equipped with self-regenerating suppressor consists of a double gradient peristaltic pump along with conductivity detector was used for fluoride analysis. The anion column (4.0 mm × 250 mm) METROSEP A SUPP 4-250 with carbonate and bicarbonate buffer mobile phase was used. Chemical and morphological characterization of *P. eryngii* before and after fluoride sorption was studied by SEM equipped with EDX analyzer (JEOL; Tokyo, Japan). FTIR spectra were recorded on a Nicolet 5700 FTIR spectrometer (Thermo Electron; USA) as KBr pellets and elemental analysis was performed with elemental analyzer (Flash EA 1112; Rodano-Milan, Italy).

2.6. Batch biosorption experiment

In order to optimize the experimental conditions a series of biosorption experiments were conducted in batches. The extent of biosorption was studied by varying several parameters such as pH (2–7), fluoride ion concentrations (5–25 mg L^{-1}), biomass dosages (0.1–0.5 g), temperature (288–303 K) and contact time (60–300 min).

The biosorption capacity i.e. amount of fluoride ion biosorbed on *P. eryngii* was calculated by following equation:

$$Q = \frac{(C_o - C_e)V}{M}$$

where Q is the fluoride ion uptake (mg g^{-1}), V is the solution volume (L), C_o and C_e are the initial and equilibrium fluoride concentrations in the solution (mg L^{-1}) respectively, and M is the mass of biosorbent (g).

Langmuir, Freundlich and D–R isotherms were also studied for varying concentrations of fluoride ions (5, 10, 15, 20, and 25 mg L^{-1}) at constant temperature (303 K). Thermodynamic studies were carried out at four different temperatures: 288, 293, 298 and 303 K (agitation: 100 rpm; biosorbent dosage: 0.2 g; fluoride ion concentration: 5 mg L^{-1}; pH: 2.0; contact time: 240 min). Sorption kinetics were determined by analyzing uptake of the fluoride from aqueous solution at different time intervals i.e. 60, 90, 120, 150, 180, 210, 240, 270, and 300 min (agitation: 100 rpm; biosorbent dosage: 0.2 g; fluoride ion concentration: 5 mg L^{-1}; pH 2.0).

For desorption studies, 0.1 M of different desorbing agents (i.e. HCl, NaOH, HNO_3, H_2SO_4 and EDTA) were checked with 0.2 g fluoride loaded biosorbent at 30 °C. Reusability of the biosorbent was conducted by introducing biosorbent again in the fresh fluoride solution. This procedure was repeated for consecutive adsorption desorption cycles. The desorption ratio was calculated from the amount of fluoride ion initially loaded on the biosorbent and the final fluoride ion concentration in the desorption medium.

3. Results and discussion

3.1. Characterization of the biosorbent

3.1.1. SEM and EDX studies

SEM images of untreated sample of *P. eryngii* exhibit non-adhesive and matt appearance (Fig. 1a) without well-defined porous structure (only few pores on the surface). After biosorption, surface of *P. eryngii* become adhesive in appearance as evident from Fig. 1b. Elemental composition of pure and fluoride-loaded biomass analyzed by SEM/EDX is shown in Fig. 1c and d. The weight

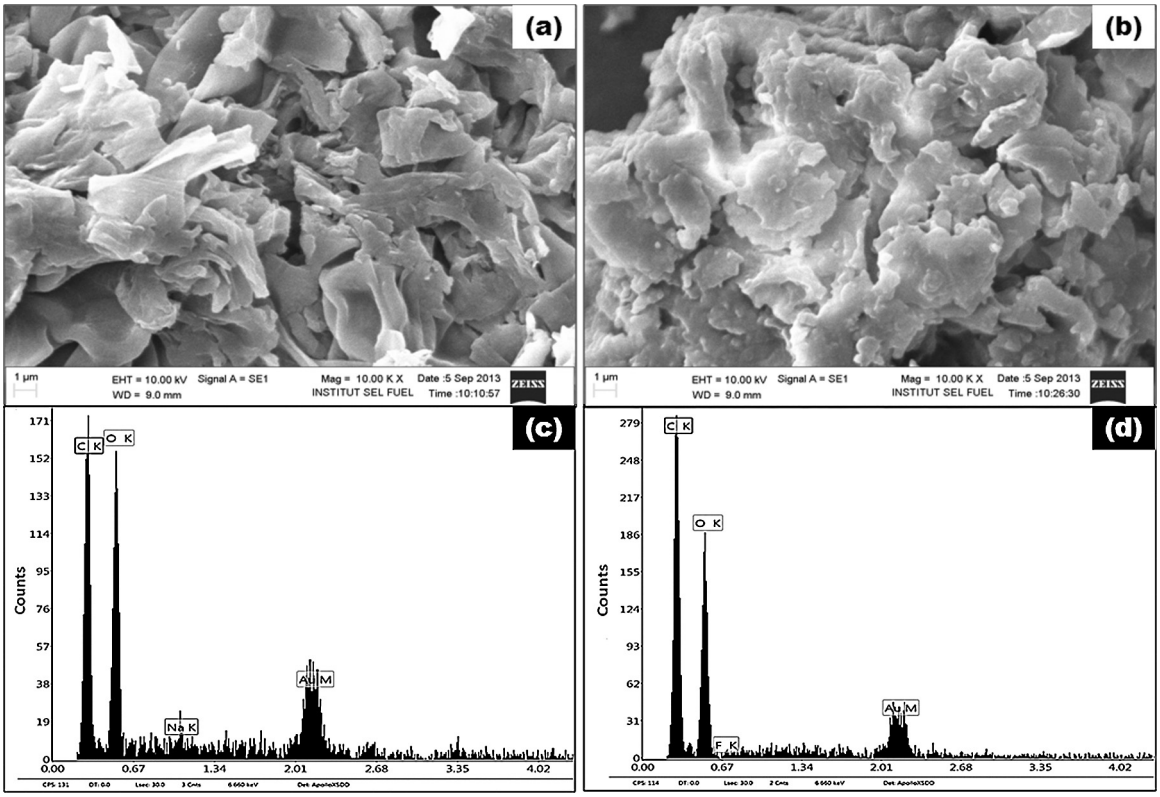

Fig. 1. SEM/EDX images of *P. eryngii* biomass: (a) and (c) are unloaded; while (b) and (d) are fluoride-loaded pattern of fungal biosorbent.

percent of fluoride-loaded fungal biomass gives fluoride peak (0.32% in weight) apart from C (34.85%) and O (22.18%) peaks. The presence of prominent fluoride peak indicates that fluoride is superficially biosorbed on the surface of *P. eryngii*.

3.1.2. FT-IR studies

In order to determine the characteristic functional groups responsible for biosorption of fluoride ions by *P. eryngii*, FTIR spectroscopy was utilized as a powerful tool. Biosorption of fluoride has resulted in several changes such as the disappearance of some bands, shifts and decrease in the percentage of transmittance in the IR spectra of the solid surface in the range 4000–500 cm^{-1}. Interpretations of the spectra were based on the information acquired from literature (Simonescu and Ferdes, 2012).

The FTIR spectra of the biosorbent before and after fluoride sorption are shown in Fig. 2. Very strong broad band at the region of 3500–3200 cm^{-1} is the overlapping peak of —NH_2 and —OH stretching vibrations (Viswanathan et al., 2009). The peak around 2923.0 and 2852.3 cm^{-1} is due to the presence of aliphatic (—CH_2) groups in the biomass. The strong bands at 1724.6 and 1654.1 cm^{-1} may be due to involvement of double bond structures such as C=C or C=O groups. The peaks at 1558.0 and 1457.1 cm^{-1} attributed to N—H bending in the amine group. The band observed at 1043.8 cm^{-1} was assigned to the C—O stretching of alcohols and carboxylic acids. Thus, *P. eryngii* contains hydroxyl, carboxyl, and amine groups on its surface as important sorption sites.

The peaks for —NH_2 were shifted from 1558.0 and 1457.1 to 1539.4 and 1456.1 cm^{-1} in fluoride loaded biomass. This decrease in the wave number of the peaks may indicate the interaction of —NH_2 group of biomass with fluoride ions. The hydrogen bonding in amines is weaker than that of hydroxyl groups, so —NH_2 stretching bands are not as broad or intense as —OH stretching bands (Smith, 1998). A slight broadening of —NH_2 stretching band in the fluoride sorbed *P. eryngii* (Fig. 2a) may be taken as an indicative of hydrogen bonding between the protonated amine (—NH_3^+) and fluoride (Smith, 1998). Similar results were reported by other authors while studying fluoride sorption on chelating ion exchange resins (Viswanathan et al., 2009). After sorption of fluoride, the carboxyl peak that observed in unloaded fungal biomass at 1724.6 cm^{-1} becomes very sharp and shifts to higher wave number 1747.1 cm^{-1}. This could be due to the interaction of hydrogen atoms in the carboxylic group and fluoride ions. Consequently, new bands appear at 1078.0, and 999.7 cm^{-1} after fluoride biosorption (Fig. 2b), may indicate the presence of —C—F stretching modes.

3.2. Influence of pH

The solution pH is one of the main factors which affect the biosorption capacity. The fungal cell wall contains a high amount of polysaccharides and some of them are associated with proteins and other components (Ramanaiah et al., 2007). These biomacromolecules on the fungal cell surfaces have several functional groups (such as amino, carboxyl, thiol, and phosphate groups) and biosorption phenomena depend on the protonation or deprotonation of these functional groups on the surface of the cell wall (Ilhami et al., 2005). The ionic form of fluoride in solution and the electrical charge of the fungal cell wall components (i.e. functional groups carrying polysaccharides and proteins) depend on the solution pH (Ramanaiah et al., 2007). To study the effect of pH on fluoride sorption (5 mg L^{-1}) by *P. eryngii*, studies were performed at various solution pH (i.e. 2–7) as shown in Fig. 3a. The pH_{pzc} of *P. eryngii* was found to be 5.75 which suggests that defluoridation capacity of the fungal biosorbent is appreciable in acidic range ($pH < pH_{pzc}$). At pH 2, the maximum percentage (81.2%) of fluoride removal was achieved. While increase in pH decreases the sorption capacity of fluoride. The same trend has been reported in *Moringa indica* based activated carbon (Karthikeyan and Ilango, 2007).

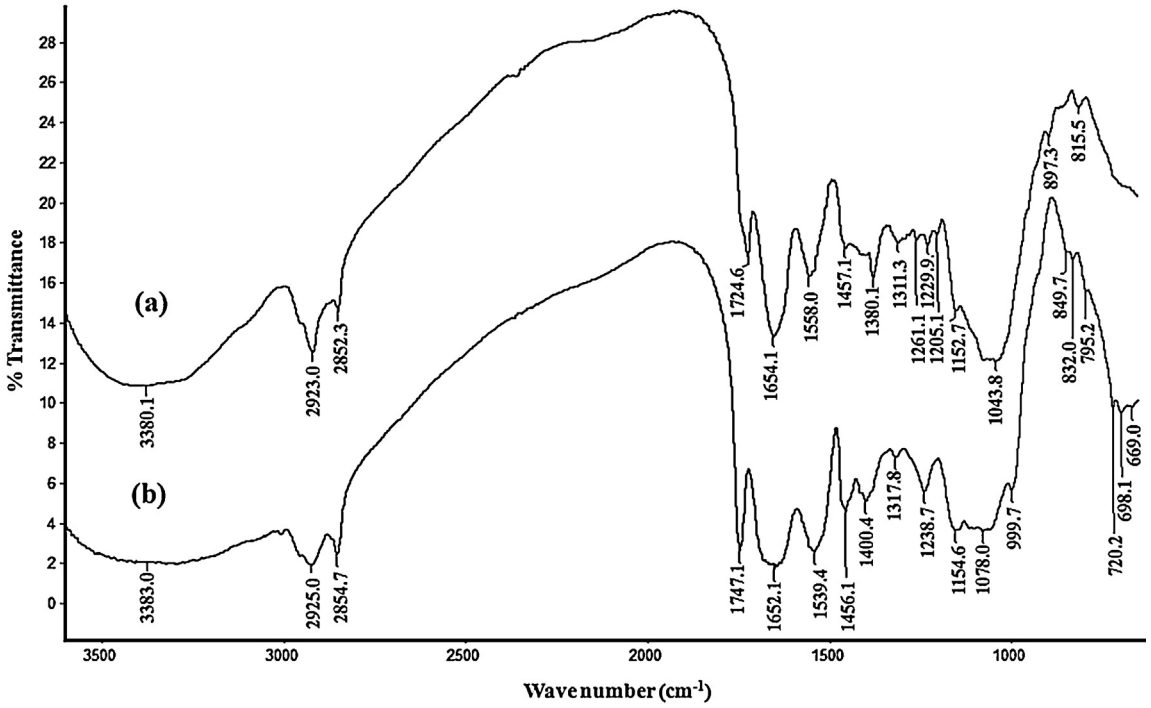

Fig. 2. FTIR spectra of *P. eryngii* (a) before and (b) after fluoride sorption.

At acidic pH due to the protonated effect of surface functionalities including amino, carboxyl, thiol, etc, positive charges impart on the surface (Ilhami et al., 2005; Karthikeyan and llango, 2007; Alagumuthu and Rajan, 2010) and hence increase the biosorption of negatively charged fluoride ions at lower pH.

3.3. Influence of initial fluoride concentration

The effect of initial fluoride concentration was studied by varying fluoride concentration from 5 to 25 mg L^{-1} at pH 2. Maximum biosorption (92%) was achieved at 5 mg L^{-1}, which shows that all

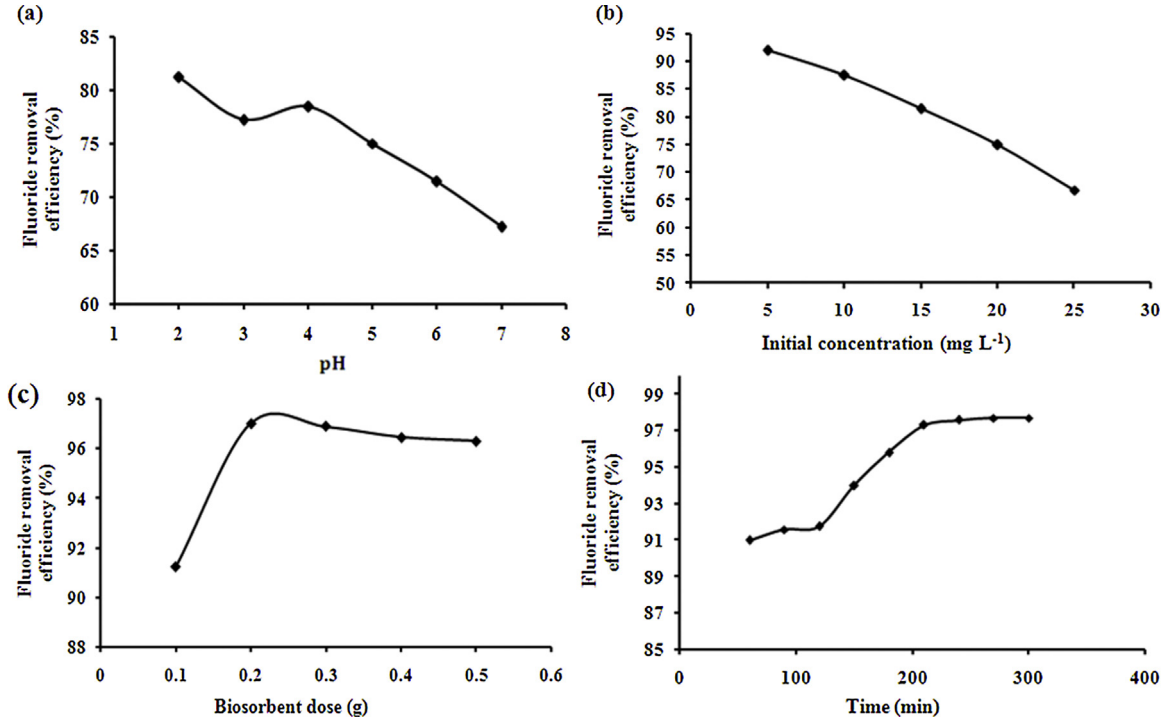

Fig. 3. (a) Percentage removal of fluoride concentration as a function of pH (biosorbent dose: 0.1 g; initial concentration: 5.0 mg L^{-1}; temperature: 30 °C; contact time: 240 min; agitation: 100 rpm). (b) Effect of concentration of fluoride on their percent removal over *P. eryngii* (pH: 2.0; biosorbent dose: 0.1 g; temperature: 30 °C; contact time: 240 min; agitation: 100 rpm). (c) Percentage removal of fluoride concentration as a function of biosorbent dose (pH: 2.0; initial concentration: 5.0 mg L^{-1}; temperature: 30 °C; contact time: 240 min; agitation: 100 rpm). (d) Percentage removal of fluoride concentration as a function of contact time (pH: 2.0; biosorbent dose: 0.2 g; initial concentration: 5.0 mg L^{-1}; temperature: 30 °C; agitation: 100 rpm).

fluoride ions present in the solution would interact with binding sites (Fig. 3b). At higher concentration, more fluoride ions are left unabsorbed in the solution due to the saturation of binding sites (Chakrabarty and Sarma, 2012). Similar types of results are reported for fluoride removal by many authors (Viswanathan and Meenakshi, 2008).

3.4. Influence of biosorbent dose

Biosorbent dose is an important parameter owing to its effect on efficiency and on the amount of fluoride removed per unit weight of biomass. Biosorbent dosages was varied from 0.1 to 0.5 g under optimum conditions (pH: 2.0; concentration: 5 mg L^{-1}; temperature: 30 °C; time: 240 min.; agitation: 100 rpm). At 0.2 g of biosorbent maximum fluoride removal (97.03%) was obtained and remains constant with the increase in dosage of biosorbent (Fig. 3c). Therefore 0.2 g of the biomass was taken as the optimized dose for fluoride removal and used for further experiments. The increase in fluoride removal with increase in biosorbent dose is due to the greater availability of exchangeable sites or surface area of the biosorbent. By further increment in sorbent dose, the removal capacity was not increased possibly due to the aggregation of available binding sites.

3.5. Biosorption isotherm models

The biosorption isotherm expresses the specific relation between the concentration of fluoride and its degree to accumulate on biosorbent surface at constant temperature. The equilibrium data were analyzed by the linear regression of isotherm models, viz., Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm.

3.5.1. Langmuir biosorption isotherm

The Langmuir isotherm theory assumes monolayer coverage of sorbate (fluoride) over a homogeneous biosorbent surface. The linearized form of Langmuir isotherm model:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q}$$

where C_{ads} is the amount of fluoride ion biosorbed per unit mass of biosorbent (mg g^{-1}), C_e is the amount of fluoride ion in liquid phase at equilibrium (mg L^{-1}), Q is the monolayer biosorption capacity (mg g^{-1}) and b is the Langmuir biosorption constant related to the free energy of biosorption (L mg^{-1}). The related parameters obtained by calculation are shown in Table 1.

Langmuir biosorption isotherm equation could be expressed in terms of a dimensionless constant called a separation factor or equilibrium factor 'R_L', which is defined by the following equation:

$$R_L = \frac{1}{(1 + bC_o)}$$

where R_L is the dimensionless constant separation factor, b is the Langmuir's constant (L mg^{-1}), and C_o is the initial concentration of fluoride ion (mg g^{-1}). All the values of R_L were between 0 and 1 suggesting biosorption is favorable at the conditions being applied (Meenakshi and Viswanathan, 2007).

The Langmuir biosorption capacities obtained in the present study were compared with those reported earlier (Table 2). The value of fluoride uptake by *P. eryngii* fungal biomass found in this work is significantly higher than that of other biosorbents. Therefore, the present study shows that *P. eryngii* is an effective low-cost biosorbent for the removal of fluoride from aqueous solutions.

3.5.2. Freundlich biosorption isotherm

This is an empirical equation that describes biosorption in heterogeneous systems and exponential distribution of sites and energy. The linearized Freundlich biosorption isotherm is given in the following equation:

$$\log C_{ads} = \log K_f + \frac{1}{n}\log C_e$$

where C_{ads} is the amount of fluoride biosorbed per unit weight of the biosorbent (mg g^{-1}), C_e is the equilibrium concentration of fluoride in solution (mg L^{-1}), K_f is a measure of biosorption capacity and n is the biosorption intensity related to the distribution of bonded ions on the sorbent surface. The value of n is found to be greater than unity for biomass, indicating that biosorption of fluoride is favorable (Sag and Kutsal, 1995).

3.5.3. Dubinin–Radushkevich (D–R) biosorption isotherm

In order to evaluate the adsorption type, equilibrium data were applied to D–R isotherm with following equation:

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2$$

where C_{ads} is the amount of fluoride biosorbed in mol g^{-1}, X_m is the D–R monolayer biosorption capacity (mol g^{-1}), β is a constant related to free energy (mol^2 kJ^{-2}) and ε is Polanyi potential which is related as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

where T is temperature (K), R the gas constant (8.314 J mol^{-1} K^{-1}) and C_e is the equilibrium concentration of fluoride (mol L^{-1}). The biosorption energy E (kJ mol^{-1}) can be obtained by equation:

$$E = \frac{1}{\sqrt{-2\beta}}$$

The calculated parameters of D–R model are presented in Table 1. The value of E was greater than 8 kJ mol^{-1}, indicates that the interaction of fungal biomass with fluoride ions is chemisorption in nature.

From Table 1, it was established that experimental data fit the selected adsorption isotherms in the following order: Langmuir > Freundlich > D–R. Higher values of correlation coefficient (R^2) indicate that the Langmuir model is more suitable for describing the sorption equilibrium of fluoride on *P. eryngii*.

3.6. Thermodynamic studies

The uptake of fluoride is highly dependent on temperature. The percentage biosorption of fluoride increased from 78.38 to 97.0% when the temperature changes in the range of 288–303 K (15–30 °C). This is due to the fact that biosorption get accelerated at higher temperature, which in turn indicate endothermic nature of reaction.

The respective change in standard Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) was evaluated from the thermodynamic study as follows:

$$\Delta G^\circ = -RT \ln K_c$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

where ΔG° is the standard free energy change (kJ mol^{-1}), R is the universal gas constant (0.008314 kJ mol^{-1} K^{-1}), and T is the absolute temperature (K), K_c is an equilibrium constant, ΔH° is change in standard enthalpy (kJ mol^{-1}), and ΔS° is change in standard entropy (kJ mol^{-1} K^{-1}). The values of ΔH° and ΔS° were computed from the slope and intercept of ln K_c versus $1/T$ (K^{-1}) by Van't Hoff

Table 1
Fluoride biosorption: Langmuir, Freundlich and D–R isotherm constants (initial fluoride concentration range = 5–25 mg L^{-1}).

Langmuir				Freundlich			D–R		
Q (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_f (mg g^{-1})	n	R^2	X_m (mol g^{-1})	E (kJ mol^{-1})	R^2
66.6	1.5	0.025–0.117	0.998	36.72	2.33	0.976	0.0037	2.056	0.911

Table 2
Comparison of biosorption capacity of *P. eryngii* fungal biomass for fluoride ion with other reported biosorbents.

Biosorbent	Biosorption capacity (mg g^{-1})	References
Used tea leaves	0.51	Methodis and Selvapathy (2005)
Spirodela polyrrhiza	0.91	Shirke and Chandra (1991)
Rice husk	0.820	VivekVardhan and Karthikeyan (2011)
Pleurotus ostreatus – 1804	1.272	Ramanaiah et al. (2007)
Spirogyra IO1	1.272	Mohan et al. (2007)
Moringa indica based activated carbon	0.23	Karthikeyan and llango (2007)
Ca-treated *Chlorococcum humicola*	4.5	Bhatnagar et al. (2002)
Pleurotus eryngii ATCC 90888	**66.6**	Present study

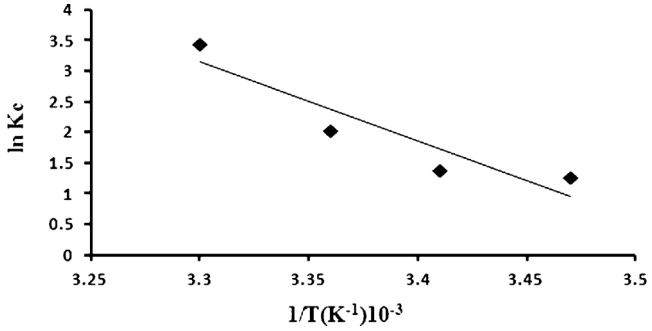

Fig. 4. Van't Hoff plot, log K_c versus 1/T.

plot as shown in Fig. 4. The negative values of ΔG° (Table 3) indicate the spontaneity of the biosorption reaction, emphasizing that biosorption is more favorable at higher temperature.

Similarly, the values of enthalpy of a biosorption process can be used to distinguish between chemical and physical biosorption. For chemical biosorption, enthalpy value ranges from 83 to 830 kJ mol^{-1} (Gopal and Elango, 2007). Thus, the value of ΔH° obtained in present study confirms that biosorption is endothermic in nature and exhibits chemical mechanism. The positive value of ΔS° indicates strong affinity of biosorbent toward fluoride molecule and shows increasing randomness at the solid/liquid interface during biosorption (Eren, 2008).

3.7. Kinetic study

Fig. 3d illustrates the removal of fluoride by fungal biomass as a function of contact time (60–300 min) at 30 °C. The fluoride removal efficiency was increased linearly up to 240 min and thereafter it remains constant indicating the attainment of biosorption equilibrium. Therefore 240 min was fixed as optimum contact time for the defluoridation with maximum fluoride removal of 97.7%.

Kinetics of fluoride ion biosorption governs the rate which determines the residence time and efficiency of a biosorbent. In order to investigate the mechanism of biosorption process, the two main types of biosorption kinetic models, namely reaction based (pseudo-first and pseudo-second order model) and diffusion based (intra particle diffusion) models were adopted to fit the experimental data.

Table 3
Themodynamic parameters for fluoride biosorption on *P. eryngii* at various temperatures.

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
288	−3.083	+107.10	0.379
293	−3.414		
298	−5.084		
303	−8.752		

3.7.1. Reaction based models

The pseudo-first order rate equation is given as:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303}$$

where q_t and q_e are the amount of fluoride (mg g^{-1}) biosorbed at time 't' and equilibrium respectively, k_1 is the rate constant of the pseudo-first order biosorption process (min^{-1}). Straight line plots of $\ln(q_e - q_t)$ against t were used to determine the rate constant k_1, and adsorption capacity. From results it was concluded that biosorption of fluoride on fungal biomass did not follow pseudo-first order kinetics.

The pseudo-second order equation is expressed as:

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

$$h = k q_e^2$$

where h (mg g^{-1} min^{-1}) is the initial biosorption rate at time 't' and k_2 is the rate constant of pseudo-second order biosorption (g mg^{-1} min^{-1}).

From Table 4, it was found that there is an agreement between experimental and calculated q_e values for the pseudo second-order model. Hence, the pseudo second-order model better represents the sorption kinetics.

3.7.2. Diffusion based models

In a solid–liquid biosorption process, the transfer of solute was characterized by particle diffusion control. The possible contribution of intra particle diffusion on fluoride biosorption is described by Weber–Morris model as:

$$q_t = k_{id}\sqrt{t} + C$$

where k_{id} is the intraparticle diffusion rate constant (mg g^{-1} $min^{1/2}$) and C is constant related to thickness of boundary layer. The values of k_{id} and C obtained from slope of q_t versus $t^{1/2}$ (Fig. 5) are 0.002 mg g^{-1} $min^{-0.5}$ and 0.209 respectively. In addition, the straight line did not pass through its origin which shows that besides intra particle diffusion other mechanisms are also involved in rate determining step.

Table 4
Kinetic parameters for fluoride biosorption on *P. eryngii*. (experimentally obtained $q_{e,exp}$. value is 0.244 mg g^{-1} for 5 mg L^{-1} initial fluoride concentration).

Pseudo-first order model			Pseudo-second order model			
k_1 (min^{-1})	$q_{e,cal.}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{,cal.}$ (mg g^{-1})	h (mg g^{-1} min^{-1})	R^2
0.051	0.132	0.843	0.438	0.252	0.028	0.999

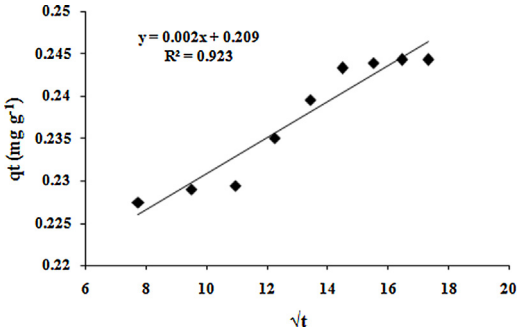

Fig. 5. Morris–Weber/Intra-particle diffusion plot for fluoride ion biosorption onto *P. eryngii* biomass at 30 °C.

3.8. Effect of co-existing anions on fluoride biosorption

Interference experiments were performed to find out the interference of other species with the binding of target ion on the biomass. The fluoride-contaminated water may contain several other anions which can compete with the sorption of fluoride. The interference studies were carried out in the presence of various co-ions viz., Cl^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and CO_3^{2-} in 1–10 folds (binary mixture: fluoride ion 2 mg L^{-1} with co-ions 2, 4, 10 and 20 mg L^{-1}). Results are presented in Fig. 6, which shows tolerable effect with 1:1 fold of co-ions, whereas increasing concentration retarded the fluoride removal capacity in different extent. The order of interference in the presence of anions for fluoride removal is: $CO_3^{2-} > NO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-} > Br^-$.

The fluoride sorption amount decreased quickly from 100 to 69.45% in the presence of 10 fold carbonate. The higher concentration of carbonate may decrease fluoride removal due to the high columbic repulsive forces, which reduce the probability of fluoride interactions with the active sites. In general, the presence of competitive anions may decrease the attraction between fluoride and biomass surface, because like charges repel each other and they cause to increase columbic repulsive forces. The results are in good agreement with Kumar et al. (2009).

A slight interference was obtained in the presence of nitrate, chloride, sulfate and phosphate; however bromide had virtually

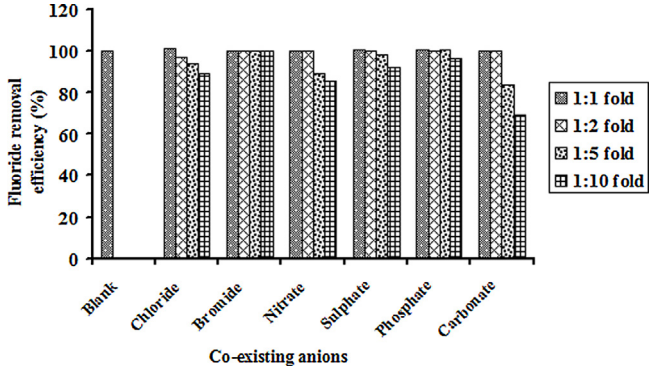

Fig. 6. Effect of co-existing anions on fluoride removal (pH: 2.0; biosorbent dose: 0.2 g; initial fluoride concentration: 2.0 mg L^{-1}; contact time: 240 min; and temperature: 30 °C).

Table 5
The physico-chemical parameters of real water samples.

S. no.	Water quality parameters	S-1	S-2	S-3
1.	Fluoride (mg L^{-1})	2.4	0.69	3.37
2.	pH	7.9	7.2	8.1
3.	TDS (mg L^{-1})	1855	550	1214
4.	EC (μS cm^{-1})	3850	1144	2520
5.	Hardness (mg L^{-1})	2.26	1.76	3.38
6.	Chloride (mg L^{-1})	1000	187.5	675
7.	Sulphate (mg L^{-1})	707.7	411.5	625.4
8.	Bicarbonate (mg L^{-1})	462	203	435

no impact on fluoride sorption. The observed increase in sorption could be due to the increase in ionic strength of the solution or a weakening of lateral repulsion between adsorbed fluoride ions.

3.9. Desorption and regeneration of biosorbent

Water purification by biosorption technology is economical with the regeneration of biosorbent. Moreover, reuse of biosorbent helps in reducing environmental impacts related with biosorbent disposal.

It is found that alkaline solution desorption capacity was higher compared to acidic ones. For *P. eryngii* the order of desorption was NaOH > HCl > H_2SO_4 > HNO_3 > EDTA. Out of the six eluents, NaOH identified as the best eluent as it desorbed 97.6% fluoride ions (Fig. 7a).

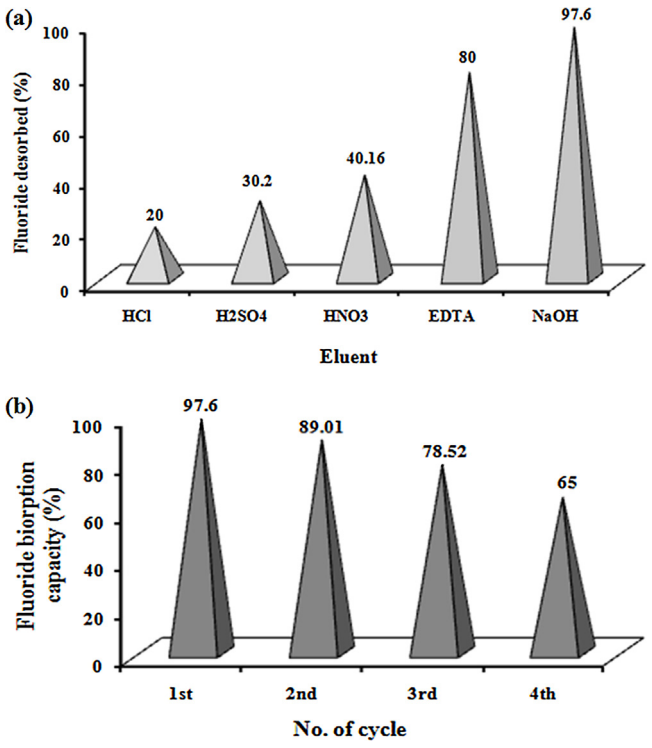

Fig. 7. (a) Desorption of fluoride by different desorbing agents (initial fluoride concentration 2.0 mg L^{-1}; biosorbent dose: 0.2 g; contact time 30 min; and temperature 30 °C). (b) Desorption efficiency of *P. eryngii* with cycle number.

Table 6
Field trial results of biosorption studies using real field water.

Sample I.D	Sampling site[a]	F^- initial concentration (mg L^{-1})	F^- final concentration (mg L^{-1})	Removal efficiency (%)
S-1	Mithi	2.4	0.835	65.2
S-2	Diplo	0.69	0.227	67.01
S-3	Nagarparkar	3.37	1.205	64.24

[a] Tharparkar district, Pakistan.

The biomass was washed with deionized water, filtered and dried at 60 °C for next sorption experiment. This sorption–desorption cyclic study was carried out for four consecutive cycles. In fourth cycle the fluoride biosorption capacity was decreased approx. 30% from 97.6% (Fig. 7b). Decrease in biosorption capacity is possibly due to the decomposition of surface active sites as evident from previous studies (Khan et al., 2012). Furthermore, resultant fungal biomass can easily be disposed off because it is biodegradable in nature.

3.10. Application to real water samples

In order to gain the practical utility of the studied biosorbent, batch studies were performed to evaluate their viability for real field application. Three water samples from fluorosis affected areas of Tharparkar district, Pakistan were collected; the physicochemical parameters are reported in Table 5. The sorption studies performed at natural pH values shows after biosorption the fluoride levels in the ground water samples were decreased well below the permissible limits of WHO drinking water standards as depicted in Table 6.

4. Conclusions

In this study, a novel biosorbent, *P. eryngii* has been prepared and examined for its potential in removing fluoride from drinking water system. The biosorption of fluoride on fungal biomass was achieved at pH 2.0. Experimental equilibrium data best fit to the Langmuir isotherm in contrast with Freundlich and D–R isotherm models, indicating monolayer biosorption on a homogenous surface. Thermodynamic parameters reveal that sorption of fluoride is spontaneous and endothermic in nature. Modeling of biosorption kinetics showed good agreement of experimental data with the pseudo-second order kinetic model. The fungal biomass has also shown encouraging results with ground water sample collected from endemic areas of Tharparkar district, Pakistan. It was found that *P. eryngii* could be a promising alternative biosorbent for defluoridation of water from real water samples to levels below the WHO recommended value.

Conflict of interest

The authors declare that there are no conflicts of interest.

References

Ahalya, N., Ramachandra, T.V., Kanamadi, R.D., 2003. Biosorption of heavy metals. Res. J. Chem. Environ. 7, 20–30.

Alagumuthu, G., Rajan, M., 2010. Kinetic and equilibrium studies on fluoride removal by zirconium (IV) – impregnated ground nutshell carbon. Hem. Ind. 64, 295–304.

Amer, Z., Bariou, B., Mameri, N., Taky, M., Nicolas, S., Elimidaoui, A., 2001. Fluoride removal from brakish water by electro dialysis. Desalination 133, 215–223.

Amini, M., Mueller, K., Abbaspour, K.C., Rosenberg, T., Afyuni, M., Moller, K.N., Sarr, M., Johnson, C.A., 2008. Statistical modeling of global geogenic fluoride contamination in ground waters. Environ. Sci. Technol. 42, 3662–3668.

Bhatnagar, M., Bhatnagar, A., Jha, S., 2002. Interactive biosorption by micro algal biomass as a tool for fluoride removal. Biotechnol. Lett. 24, 1079–1081.

Chakrabarty, S., Sarma, H.P., 2012. Defluoridation of contaminated drinking water using neem charcoal adsorbent: kinetics and equilibrium studies. Int. J. ChemTech Res. 4, 511–516.

Eren, E., 2008. Removal of copper ions by modified Unye clay, Turkey. J. Hazard. Mater. 159, 235–244.

Gopal, V., Elango, K.P., 2007. Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris. J. Hazard. Mater. 141, 98–105.

Ilhami, T., Gulay, B., Emine, Y., Gokben, B., 2005. Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae *Chlamydomonas reinhardtii*. J. Environ. Manag. 77, 85–92.

Karthikeyan, G., Ilango, S.S., 2007. Fluoride sorption using *Moringa indica* based activated carbon. Iran. J. Environ. Health 4, 21–28.

Khan, M.A., Ngabura, M., Choong, T.S.Y., Masood, M., 2012. Biosorption and desorption of Nickel on oil cake: batch and column studies. Bioresour. Technol. 103, 35–42.

Kumar, E., Bhatnagar, M., Jung, W., Lee, S.H., Kim, S.J., Lee, G., Song, H.M., Choi, J.Y., Jeon, B.H., 2009. Defluoridation from aqueous solutions by granular ferric hydroxide (GFH). Water Res. 43, 490–498.

Mahmood, T., Saddique, M.T., Naeem, A., Westerhoff, P., Mustafa, S., Alum, A., 2011. Comparison of different methods for the point of zero charge determination of NiO. Ind. Eng. Chem. Res. 50, 10017–10023.

Mameri, N., Lounici, H., Belhocine, D., Grib, H., Prion, D.L., Yahiat, Y., 2001. Defluoridation of Sahara water by small electro coagulation using bipolar aluminium electrodes. Sep. Purif. Technol. 24, 113–119.

Meenakshi, S., Viswanathan, N., 2007. Identification of selective ion exchange resin for fluoride sorption. J. Colloid Interface Sci. 308, 438–450.

Methodis, P.A., Selvapathy, P., 2005. Studies on removal of fluoride from water by used tea leaves carbon. In: Third International Conference on Plants and Environmental Pollution, Lucknow, India.

Mohan, S.V., Rao, C.N., Prasad, K.K., Karthikeyan, J., 2002. Treatment of simulated reactive yellow 22 (azo) dye effluents using *Spirogyra* species. Waste Manag. 22, 575–582.

Mohan, S.V., Ramanaiah, S.V., Rajkumar, B., Sarma, P.N., 2007. Removal of fluoride from aqueous phase by biosorption onto algal biosorbent *Spirogyra* sp.-IO2: sorption mechanism elucidation. J. Hazard. Mater. 141, 465–474.

Prajapat, R., Bhatnagar, A., Gaur, K.R., Bajpai, V., 2010. Fluoride removal from water by sorbing on plant and fungal biomass. Int. J. Biotechnol. 1, 43–46.

Rafique, T., Naseem, S., Bhanger, M.I., Usmani, T.H., 2008. Fluoride ion contamination in the groundwater of Mithi sub-district, the Thar Desert, Pakistan. Environ. Geol. 56, 317–326.

Rafique, T., Naseem, S., Usmani, T.H., Bashir, E., Khan, F.A., Bhanger, M.I., 2009. Geochemical factors controlling the occurrence of high fluoride groundwater in the Nagar Parkar area, Sindh, Pakistan. J. Hazard. Mater. 171, 424–430.

Raichur, A.M., Basu, M.J., 2001. Adsorption of fluoride onto mixed rare earth oxides. Sep. Purif. Technol. 24, 121–127.

Ramanaiah, S.V., Mohan, S.V., Sarma, P.N., 2007. Adsorptive removal of fluoride from aqueous phase using waste fungus (*Pleurotus ostreatus* 1804) biosorbent: kinetics evaluation. Ecol. Eng. 31, 47–56.

Reardon, E.J., Wang, Y., 2000. Limestone reactor for fluoride removal from waste water. Environ. Sci. Technol. 34, 3247–3253.

Sag, Y., Kutsal, T., 1995. Biosorption of heavy-metals by zoogloea-ramigera – use of adsorption-isotherms and a comparison of biosorption characteristics. Biochem. Eng. J. 60, 181–188.

Shirke, P.A., Chandra, P., 1991. Flouride uptake by duck-weed *Spirodela polyrrhiza*. Flouride 24, 109–112.

Simonescu, C.M., Ferdes, M., 2012. Fungal biomass for Cu(II) uptake from aqueous system. Pol. J. Environ. Stud. 21, 1831–1839.

Singh, G., Kumar, B., Sen, P.K., Maunder, J., 1999. Removal of fluoride from spent pot liner leachate using ion exchange. Water Environ. Res. 71, 36–42.

Smith, B.C., 1998. Infrared Spectral Interpretation: A Systematic Approach, 1st ed. CRC Press, London.

Viswanathan, N., Meenakshi, S., 2008. Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads. J. Colloid Interface Sci. 322, 375–383.

Viswanathan, N., Sundaram, C.S., Meenakshi, S., 2009. Removal of fluoride from aqueous solution using protonated chitosan beads. J. Hazard. Mater. 161, 423–430.

VivekVardhan, C.M., Karthikeyan, J., 2011. Removal of fluoride from water using low-cost materials. IWTJ 1, 1–12.

WHO – World Health Organization, 2011. Guidelines for Drinking Water Quality, 4th ed, http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf