

Pediastrum boryanum Immobilized on Rice Husk Ash Silica as Biosorbent for Fluoride Removal from Drinking Water

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Abstract

Objectives: Biosorption is an environmentally friendly approach for the removal of organic and inorganic compounds from aqueous solutions. Fluoride concentration in drinking water above $1.5 \text{ mg}\cdot\text{L}^{-1}$ is harmful to human health. The aim of this study was to develop an algae immobilization method using silica gel extracted from renewable rice husk ash and test the biosorbent in defluoridation of water. **Methods:** *Pediastrumboryanum* was immobilized using sodium silicate extracted from rice husk ash. The method involved suspending the biomass in a sodium silicate rich filtrate prepared through alkaline leaching of rice husk ash. The immobilization was achieved through acid precipitation of silica. The biosorbent was used in the defluoridation of water and had improved mechanical properties. **Findings:** The maximum adsorption capacity was $25.641 \text{ mg}\cdot\text{g}^{-1}$ at pH 5. Experimental data fitted well into the Langmuir adsorption isotherm ($R^2 = 0.9987$) although Freundlich adsorption isotherm ($R^2=0.9898$) could also be used to describe biosorption processes. The biosorption process was of the pseudo-second order kinetics with $R^2 \geq 0.9988$. FT-IR spectra revealed the presence of $-\text{OH}$, $-\text{NH}$, $\text{C}-\text{O}-\text{C}$ and $-\text{C}=\text{O}$ functional groups. **Application:** This study demonstrates the feasibility to immobilize *Pediastrumboryanum* using sodium silicate extracted from renewable bio-waste instead of using commercially available sodium silicate. Experimental results present the possibility to application of the biosorbent in the defluoridation of water.

Keywords: Biosorbent, Defluoridation, Immobilization, Isotherm, *Pediastrum boryanum*

1. Introduction

Report by the World Health Organization¹ recommends levels of $0.5 \text{ mg}\cdot\text{L}^{-1}$ fluoride in drinking water as beneficial to health but levels in excess of $1.5 \text{ mg}\cdot\text{L}^{-1}$ may be harmful. At higher concentrations exceeding $1.5 \text{ mg}\cdot\text{L}^{-1}$ one may suffer from dental fluorosis and above $3.0 \text{ mg}\cdot\text{L}^{-1}$ skeletal fluorosis². Other health problems associated with drinking water with high fluoride concentration include lowering of Intelligent Quotient (IQ) and long term damage to brain, liver, thyroid and kidney plus a host of other health problems^{3,4}. Major sources of fluorides in drinking water have been reported as mining activities such

as phosphate rock and apatite mining, agricultural and industrial activities e.g., phosphate fertilizers, aluminum and electroplating and glass manufacturing⁵. Studies on underground water quality in various communities neighboring these activities have shown the presence of varying levels of fluorides.⁶⁻⁸ A number of technologies on fluoride removal have been developed and these can broadly be classified into chemical addition and precipitation methods, adsorption and ion exchange methods and methods based on membrane separation⁹. Of these defluoridation methods, adsorption methods appear to be more versatile, economic and hence have attracted a lot of research interest^{10,11}. Bio-sorption methods are a

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class of adsorption methods based on biomass that have been studied by a number of researchers with varying degrees of success as illustrated with selected examples in Table 1.

Table 1. Selected examples of biosorbents used in defluoridation of water

Bio-sorbent	q_{max}	References
Silica- <i>Pediastrum boryanum</i> biosorbent	29.76 mg·g ⁻¹	Current study
Tamarind seed	6.37 mg·g ⁻¹	12
Waste fungus (<i>Pleurotus ostreatus</i> 1804)	1.272 mg·g ⁻¹	13
Algae <i>Spirogyra IO1</i>	1.272 mg·g ⁻¹	14
Neem charcoal	1.27 mg·g ⁻¹	15
Tamarind (<i>Tamarindus indica</i>) fruit cover	4.14 mg·g ⁻¹	16

This study reports the use of silica gel immobilized *Pediastrum boryanum* based biosorbent for defluoridation of drinking water. Sodium silicate used in the immobilization was extracted from rice husk ash through alkaline leaching and was designed to improve mechanical properties, a problem normally encountered in such biosorbents. Reports by other researchers suggest a number of bio-mass immobilization techniques and these include use of alginate, sodium silicate synthetic and natural polymers^{17,18}.

2. Experimental

2.1 Sample Preparation

Fresh green algae, *Pediastrum boryanum*, was harvested from a fish pond near Silveria Dam in Bikita District of Masvingo Province, Zimbabwe. The algae was rinsed with tap water and then with distilled water to remove any particulate matter. It was then sundried for two weeks followed by drying at 80°C in a drying oven over night. The biomass was ground in a laboratory mill and sieved through a 50-µm sieve.

Rice Husks (RH) were donated by communal farmers from Nyajena District of Masvingo Province. The rice husks (20 g) were first leached with 1M HCl for one hour before being ignited in a muffle furnace at 650°C for two

hours. The resultant white ash was used for sodium silicate extraction.

2.2 Immobilization of *Pediastrum boryanum*

The immobilization procedure was adapted from the literature¹⁹ and methods for Rice Husk Ash (RHA) extraction²⁰. In an optimized procedure 12.5 g RHA containing more than 85% SiO₂ by XRF analysis was refluxed in 50 ml of 2M NaOH solution for three hours. The reaction products were allowed to cool and filtered to remove any suspended solids. The sodium silicate rich filtrate was used to immobilize the green algae. *Pediastrum boryanum* powder (2 g) was suspended in the filtrate. Under vigorous stirring 2M HCl was gradually added until the pH reached 5.5. Vigorous stirring continued until the mixture became viscous. This was then allowed to stand and gel over 48 hours. The resultant composite material was washed with distilled water to remove sodium chloride. The biosorbent was then dried at 80 °C overnight and was ready for bio-sorption experiments. The procedure for preparing RHA silica gel immobilized *Pediastrum boryanum* biosorbent is illustrated in the reaction schemes in Figure 1.

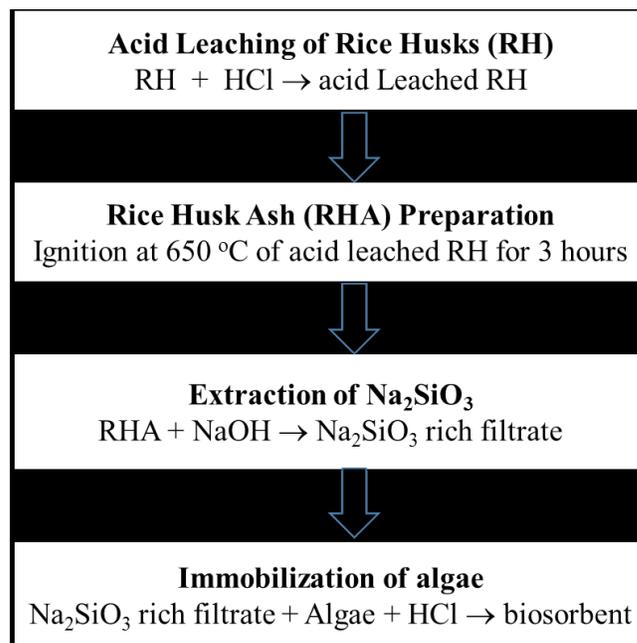


Figure 1. Reaction schemes for the preparation of RHA silica gel immobilized *Pediastrum boryanum* biosorbent.

The biosorbent was characterized using a Nicolet iS5 MIR FT-IR spectrophotometer equipped with an ATR iD7 and OMNIC software manufactured by Thermo Fisher Scientific GmbH, Germany. The spectra were recorded between 4000 and 400 cm^{-1} in order to establish the surface functionality of the biosorbent and hence assist in the understanding of biosorption mechanism.

2.3 Adsorption Experiments

Fluoride solutions of 3, 10, 20, 50 and 100 ppm were prepared by serial dilution of a 200 ppm NaF stock solution. The fluoride concentration before and after defluoridation were determined using fluoride ion selective electrode. A Total Ionic Strength Adjustment Buffer (TISAB) solution was used to maintain pH at 5.5 and eliminate any interference by complexing ions. Defluoridation was optimized in terms of pH, contact time, adsorbent dosage, initial concentration and temperature. Experimental data was fitted into the Langmuir and Freundlich adsorption isotherm models. Adsorption kinetics was modeled using the pseudo-first and pseudo-second order kinetics. Removal Efficiencies (RE), adsorption capacities (q_t) and adsorption capacities at equilibrium (q_e) were calculated using Equation (1), (2), and (3) respectively.

$$RE = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{m} \quad q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

Where c_o is the initial fluoride concentration in $\text{mg}\cdot\text{L}^{-1}$, c_t fluoride concentration at time t in $\text{mg}\cdot\text{L}^{-1}$, c_e equilibrium fluoride concentration in $\text{mg}\cdot\text{L}^{-1}$, m mass of adsorbent in g and V volume of fluoride solution in L.

2. Results and Discussion

2.1 Analysis of FT-IR Spectra

FT-IR spectra of biosorbent before and after defluoridation are shown in Figure 2. A broad absorption band in the range 3500-3000 cm^{-1} is associated with $-\text{OH}$ and $-\text{NHR}$ of the silanols and biomaterial respectively. A small absorption band between 1650 cm^{-1} can be assigned to carbonyl groups of amino acids of the biomaterial.

Characteristic strong Si-O-Si absorption band can be observed at 1000 cm^{-1} and may be overlapped by C-O-C of the biomass. Other researchers have also observed similar absorption bands with different biosorbents^{21,22}.

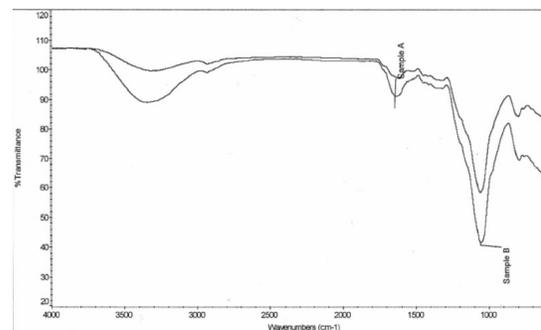


Figure 2. FT-IR spectra silica gel immobilized *Pediasium boryanum* biosorbent. (a) Before adsorption. (b) After adsorption.

2.2 Effect of pH

Adsorption processes with biosorbents are strongly influenced by the pH of adsorbate solution mainly due to the functional groups on the biosorbent. The effect of pH on the removal efficiency was investigated between pH 5 and 8. From Figure 3, it can be observed that the removal efficiency rose sharply between pH 5 and 7 and again dropped sharply to 40.9 % at pH 8. The maximum removal efficiency was 80.5% at pH7. Further studies were therefore performed at optimum pH 7. A similar trend was observed in a similar study and was attributed to the positively charged biosorbent surface which promoted coulombic attraction of fluoride ions²³.

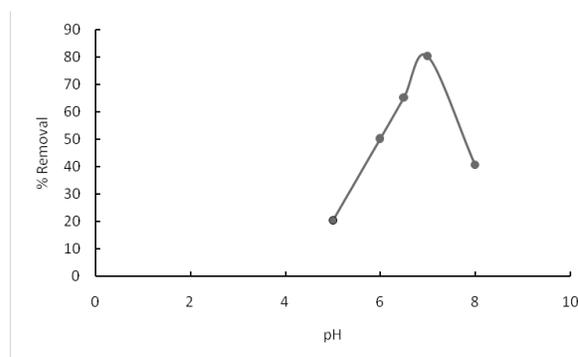


Figure 3. Effect of pH on the fluoride removal efficiency ($c_o = 3 \text{ mg}\cdot\text{g}^{-1}$, agitation speed = 135 rpm, bio-sorbent dosage = 0.8 g, $t = 100 \text{ min}$, $T = 305 \text{ K}$).

2.3 Effect of Contact Time

The effect of contact time is very important in optimizing adsorption processes. The results of this study are illustrated in Figure 4. From the diagram it can be observed that the removal efficiency rose fast in the first 20 minutes and then gradually until the 90th minute. Thereafter no further increases in the removal efficiency were observed. Hence adsorption capacity and fluoride concentration at 90 minutes were chosen as the adsorption capacity at equilibrium (q_e) and equilibrium concentration (c_e). The rise in the removal efficiency in the 90 minutes can be attributed to available adsorption sites on the biosorbent surface. A similar biosorption trend was observed in a similar study that used *Phyllanthus emblica* as a biosorbent²⁴.

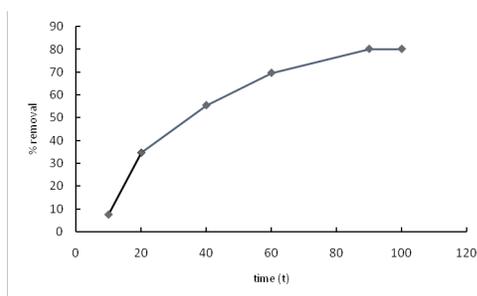


Figure 4. Effect of contact time on the removal efficiency ($c_0 = 3 \text{ mg}\cdot\text{g}^{-1}$, pH 7, agitation speed = 135 rpm, biosorbent dosage = 0.8 g, $t = 100 \text{ min}$, $T = 305 \text{ K}$).

2.4 Effect of Biosorbent Dosage

Figure 5 shows the effect of biosorbent dosage on fluoride removal efficiency. There was a steep rise in the removal efficiency with increase dosage upto a biosorbent dosage of 0.5 g with a maximum removal efficiency of 79.1%. No further increase in the removal efficiency at biosorbent dosage of above 0.8 g was observed. The maximum removal efficiency was 80.5%.

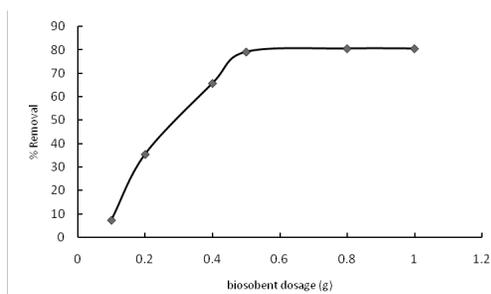


Figure 5. Effect of adsorbent dosage ($c_0 = 3 \text{ mg}\cdot\text{g}^{-1}$, pH 7, $t = 100 \text{ min}$, agitation speed = 135 rpm, $T = 305 \text{ K}$).

2.5 Adsorption Isotherms

Adsorption isotherms are used to describe equilibrium relationship between the quantity of adsorbate and concentration or pressure in the bulk fluid phase at constant temperature. Adsorption isotherm models based on different assumptions have over the years been developed by different researchers²⁰. This study fitted its experimental data on to the Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption isotherm assumes a mono molecular layer adsorption on energetically homogeneous surface. The Langmuir adsorption isotherm is represented by Equation (4). Equation (4) can be linearized to give equation 5, 6, 7 and 8. A linear plot of $\frac{1}{q_e}$ versus $\frac{1}{c_e}$ equation 6 was used to determine Langmuir adsorption isotherm parameters. The result is illustrated in Figure 6.

$$q_e = \frac{K_L C_e}{1 + K_L C_e} \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{K_L q_{max}} \tag{5}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}} \right) \frac{1}{C_e} + \frac{1}{q_{max}} \tag{6}$$

$$q_e = q_{max} - \left(\frac{1}{K_L} \right) \frac{q_e}{C_e} \tag{7}$$

$$\frac{q_e}{C_e} = K_L q_{max} - K_L q_e \tag{8}$$

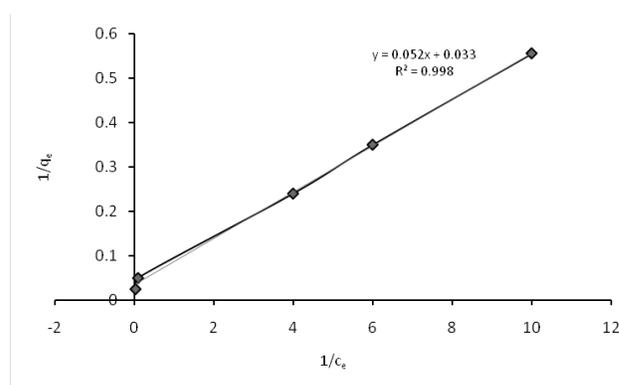


Figure 6. Langmuir adsorption isotherm for fluoride removal.

The Freundlich adsorption isotherm is used to describe adsorption phenomena on a heterogeneous surface and is expressed using Equation (9). The linearized form of

this isotherm is represented by Equation (10). Freundlich adsorption parameters may be obtained from the linear plots of $\log q_e$ versus $\log c_e$. A plot is shown in Figure 7.

$$q_e = K_F c_e^{\frac{1}{n}} \quad (9)$$

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (10)$$

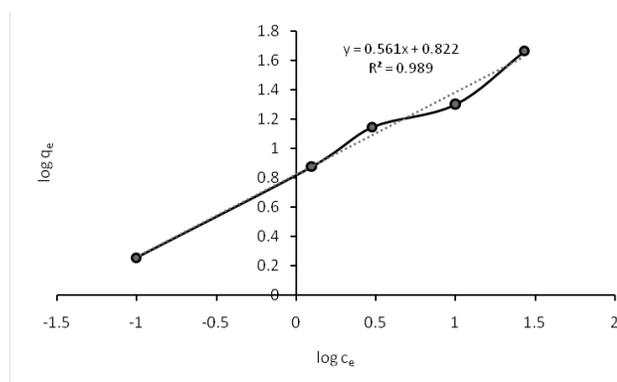


Figure 7. Freundlich adsorption isotherm for fluoride removal.

The Langmuir and Freundlich isotherm parameters K_F and K_L were found to be $0.7647 \text{ L}\cdot\text{mg}^{-1}$ and $6.6374 \text{ mg}\cdot\text{L}^{-1} \cdot \text{g}^{-1}$ respectively. From the R^2 values of both adsorption isotherms it can be concluded that experimental data fitted better into the Langmuir adsorption isotherm ($R^2 = 0.9987$) than the Freundlich adsorption isotherm ($R^2 = 0.9898$) although the Freundlich adsorption isotherm could also be used to model the defluoridation of water. From the Langmuir adsorption isotherm, it can be concluded that the RHA silica immobilized biosorbent had a maximum adsorption capacity of $25.641 \text{ mg}\cdot\text{g}^{-1}$ under optimum conditions.

2.6 Kinetic Studies

Kinetic parameters of any adsorption process are very important in designing and sizing an adsorption plant. The defluoridation of drinking water using RHA silica immobilized *Pediastrum boryanum* biosorbent was modelled using the pseudo-first and pseudo-second order kinetic models²⁵. The pseudo-first order kinetics is expressed in Equation (11). The linearized form of this equation is represented by Equation (12). Pseudo-first order parameters can be obtained from a linear plot of $\log(q_e - q_t)$ versus t .

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (11)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (12)$$

The pseudo-second order kinetics is expressed in Equation (13). The linearized form of this equation is expressed in Equation (14). Pseudo-second order parameters for the defluoridation can be obtained from the linear plot of $\frac{t}{q_t}$ versus t . The results of the pseudo first and pseudo second order plots are shown in Table 2.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

A summary of pseudo-first and pseudo-second order parameters is shown in Table 2. A comparison of R^2 values shows that the adsorption kinetics was more of a pseudo-second order than pseudo-first order rate.

Table 2. Comparison of pseudo-first and pseudo-second order kinetic parameters

Initial fluoride concentration	Pseudo-first order parameter			Pseudo-second order parameters		
	R^2	k_1	q_e	R^2	k_2	q_e
10	0.9741	0.02993	0.4911	0.9988	0.3066	0.6389
20	0.9814	0.0253	0.5689	0.999	0.1944	1.0846
50	0.9303	0.0299	0.8949	0.9966	0.0616	1.7064
100	0.9839	0.0201	1.2275	0.9927	0.0230	3.6101

3. Conclusion

The study demonstrated the feasibility of immobilizing *Pediastrum boryanum* using rice husk ash as a silica source. It may also conclude that any bio-waste rich in silica may be used to immobilize alga based biosorbent. The biosorbent had a maximum adsorption capacity of 25.641 mg·g⁻¹ at a neutral pH 7. Experimental data fitted more into the Langmuir adsorption isotherm model ($R^2 = 0.9987$) than the Freundlich adsorption isotherm ($R^2 = 0.9898$) although the latter could also be used for the same. Pseudo-second order kinetic model described better the adsorption processes than the pseudo-first order kinetic model. The FT-IR spectra revealed the presence of -NHR, -OH, -C=O, C-O-C and Si-O-Si vibrational modes.

4. References

- World Health Organization: Fluorides, Environmental Health Criteria; 2010. p. 227.
- Yadav RN, Yadav R, Dagar NK, Gupta P, Singh P, Chandrawat MPS. Removal of fluoride in drinking water by green chemical approach. *Journal of Current Chemistry Pharmaceutical Science*. 2012; 2(1):69–75.
- Lavecchia R, Medici F, Pigg L, Rinaldi G, Zuurro A. Fluoride removal from water by adsorption on a high alumina content bauxite. *Chemical Engineering Transactions*. 2012; 26:225–30.
- Teotia SPS, Teotia M, Singh KP. Highlights of forty years of research on endemic skeletal fluorosis in India. 4th International Workshop on fluorosis Prevention and Defluoridation of Water; 2004. p. 107–25.
- Roy S, Dass G. Fluoride contamination in drinking water—A review. *Resources and Environment*. 2013; 3(3):53–8.
- Bhatnagar A, Kumar E, Sillanpää M. Fluoride removal from water by adsorption—A review. *Chemical Engineering Journal*. 2011; 171:811–40.
- Singh G, Kamal RK. Assessment of groundwater quality in the mining area of Goa, India. *Indian Journal of Science and Technology*. 2015; 8(6):588–95.
- Llyaraja K, Eqyaabal MDZ. Study of groundwater quality in Cooum Belt. *Indian Journal of Science and Technology*. 2015; 8(2):1–8.
- Jamode AV, Sapkal VS, Jamode VS. Defluoridation of water using inexpensive adsorbents. *Journal Indian Inst of Science*. 2004; 84:163–71.
- Shrivastava BK, Vani A. A comparative study of defluoridation technologies in India. *Asian J Exp Sci*. 2009; 23(1):269–74.
- Haghighat GA, Dehghani MH, Nasser S, Mahvi AH, Rastkari N. Comparison of carbon nanotubes and activated alumina efficiencies in fluoride removal from drinking water. *Indian Journal of Science and Technology*. 2012; 5(S3):2432–5.
- Murugan M, Subramanian E. Studies on defluoridation of water by tamarind seed, an unconventional biosorbent. *Journal of Water and Health*. 2006; 4(4):453–61.
- Ramanaiah SV, Mohan SV, Sarma PN. Adsorptive removal of fluoride from aqueous phase using waste fungus (*Pleurotus ostreatus 1804*) biosorbent: Kinetics evaluation. *Ecol Eng*. 2007; 31:47–56.
- Mohan SV, Ramanaiah SV, Rajkumar B, Sarma PN. Biosorption of fluoride from aqueous phase on to algal *Spirogyra* IO1 and evaluation of adsorption kinetics. *Bioresource Technology*. 2007; 98(5):1006–11.
- Chakrabarty S, Sarma HP. Defluoridation of contaminated drinking water using neem charcoal adsorbent: Kinetic and equilibrium studies. *International Journal of Chem Tech Research*. 2012; 4(2):511–6.
- Kumar NP, Kumar NS, Krishnaiah A. Defluoridation of water using tamarind (*Tamarindus indica*) fruit cover: Kinetic and equilibrium studies. *J Chil Chem Soc*. 2012; 57(3):1224–31.
- Soltman U, Matys S, Kieszig G, Pompe W, Bättcher H. Algae-Silica hybrid materials for biosorption of heavy metals. *Journal of Water and Protection*. 2010; 1:115–22.
- Moreno-Garrido I. Microalgae immobilization: Current techniques and uses. *Bioresource Technology*. 2008; 99(10):3949–64.
- Rangasaytorn N, Pokethitiyook P, Upatham ES, Lanza GR. Cadmium biosorption by cells of *Spirulina Plantensis* YISTR 8217 immobilized in alginate and silica gel. *Environ Int*. 2004; 30:57–63.
- Kalpathy U, Procter A, Shultz J. An improved method for production of silica from rice hull ash. *Bioresource Technology*. 2003; 85(3):285–9.
- El Jamal MM, Ncibi MC. Biosorption of methylene blue by *Chaetophoraelegans* algae: Kinetic, equilibrium and thermodynamic studies. *Acta Chim Slov*. 2012; 59(1):24–31.
- Miretzky P, Muñoz C, Carrillo-Chávez A. Fluoride removal from aqueous solution by Ca-pretreated microphytebiomas. *Environment Chemical*. 2008; 5:68–72.
- Harikuma PSP, Jaseela C, Megha T. Defluoridation of water using biosorbents. *Natural Science*. 2012; 4(4):245–51.
- Veeraputhiran V, Alagumuthu G. Treatment of high fluoride drinking water using bioadsorbents. *Research Journal of Chemical Science*. 2011; 1(4):49–54.
- Foo KY, Hameed BH. Insights into the modelling of adsorption isotherm system. *Chemical Engineering Journal*. 2010; 156(1):2–10.