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 mg·L$^{-1}$ is harmful to human health. The aim of this study was to develop algae immobilization method using silica gel extracted from renewable rice husk ash and test the biosorbent in defluoridation of water. **Methods:** *Pediastrum boryanum* 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 mg·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 –OH, -NH, C-O-C and –C=O functional groups. **Application:** This study demonstrate the feasibility to immobilize *Pediastrum boryanum* 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 Organization$^1$ recommends levels of 0.5 mg·L$^{-1}$ fluoride in drinking water as beneficial to health but levels in excess of 1.5 mg·L$^{-1}$ may be harmful. At higher concentrations exceeding 1.5 mg·L$^{-1}$ one may suffer from dental fluorosis and above 3.0 mg·L$^{-1}$ skeletal fluorosis. 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$^{24}$. 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 manufacturing$^3$. 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 separation$^2$. 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
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                              | \( q_{\text{max}} \) (mg g\(^{-1}\)) | References |
|-----------------------------------------|--------------------------------------|------------|
| Silica-Pediastrum boryanum biosorbent   | 29.76                                 | Current study |
| Tamarind seed                           | 6.37                                 | 12         |
| Waste fungus (Pleurotus ostreatus 1804) | 1.272                                | 13         |
| Algae Spirogyra IO1                     | 1.272                                | 14         |
| Neem charcoal                           | 1.27                                 | 15         |
| Tamarind (Tamarindus indica) fruit cover | 4.14                                 | 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.

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 literature and methods for Rice Husk Ash (RHA) extraction. In an optimized procedure 12.5 g RHA containing more than 85% SiO\(_2\) 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.

20

![Reaction schemes for the preparation of RHA silica gel immobilized *Pediastrum boryanum* biosorbent.](image-url)
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.

\[
RE = \frac{C_o - C_t}{C_o} \times 100
\]

\[
q_t = \frac{(C_o - C_t)V}{m}
\]

\[
q_e = \frac{(C_o - C_e)V}{m}
\]

Where \(C_o\) is the initial fluoride concentration in mg L\(^{-1}\), \(C_t\) fluoride concentration at time \(t\) in mg L\(^{-1}\), \(C_e\) equilibrium fluoride concentration in mg 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 –OH and –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].

![FT-IR spectra silica gel immobilized Pediastrum boryanum biosorbent. (a) Before adsorption. (b) After adsorption.](image)

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 ions[23].

![Effect of pH on the fluoride removal efficiency](image)

\[
RE = \frac{C_o - C_t}{C_o} \times 100
\]

\[
q_t = \frac{(C_o - C_t)V}{m}
\]

\[
q_e = \frac{(C_o - C_e)V}{m}
\]
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 biosorbent.\(^{24}\)

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

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 up to 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_o = 3 \, \text{mg.g}^{-1}, \text{pH } 7, t = 100 \, \text{min}, \text{agitation speed} = 135 \, \text{rpm}, T = 305 \, \text{K}).](image)

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 researchers.\(^{25}\) 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 \( 1/q_e \) versus \( 1/c_e \) was used to determine Langmuir adsorption isotherm parameters. The result is illustrated in Figure 6.

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

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{K_L q_{\text{max}}} \tag{5}
\]

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

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

\[
\frac{q_e}{C_e} = K_L q_{\text{max}} - K_L q_e \tag{8}
\]

![Figure 6. Langmuir adsorption isotherm for fluoride removal.](image)

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 adsorptions parameters may be obtained from the linear plots of \( \log q_e \) versus \( \log c_e \). A plot is shown in Figure 7.

\[
q_e = K_F c_e^{1/n} \tag{9}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{10}
\]

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 L∙mg\(^{-1}\) and 6.6374 mg∙L\(^{1/n}\) ∙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 mg∙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 \textit{Pediastrum boryanum}\textsubscript{b}biosorbent was modelled using the pseudo-first and pseudo-second order kinetic models\(^{35}\). 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 \( t \).

\[
\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{11}
\]

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{12}
\]

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.

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{13}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}
\]

A summary of pseudo-first and pseudo-second order kinetic 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.

| Initial fluoride concentration | Pseudo-first order parameters | 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 (R² = 0.9987) than the Freundlich adsorption isotherm (R² = 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.

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