Lead Biosorption by Biosorbent Materials of Marine Brown Algae *U. pinnatifida, H. fusiformis, and S. fulvellum*

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Biosorbents of nonliving, dried marine brown algae *Undaria pinnatifida, Hizikia fusiformis,* and *Sargassum fulvellum* were investigated for their lead biosorption performances.

As the amount of biosorbent added was increased, the lead removal by biosorbent materials increased but the lead biosorption capacities decreased. However the lead biosorption capacity by the biosorbent materials increased with increasing initial lead concentration and pH in the range of C_o 10~500 mg/L. Among the biosorbent materials used in this study, the lead biosorption capacity in the solutions with no pH adjustment decreased in the following sequence: *U. pinnatifida* > *H. fusiformis* > *S. fulvellum.* Equilibrium parameters based on Langmuir and Freundlich isotherm were determined. It was found that the lead biosorption by biosorbent materials were expressed by the Langmuir isotherm better than the Freundlich isotherm.

Key words : lead, biosorption, biosorbent, *Undaria pinnatifida, Hizikia fusiformis, Sargassum fulvellum,* Langmuir isotherm, Freundlich isotherm

Introduction

The toxicology of lead has been extensively studied. Inorganic lead (Pb^{2+}) is a general metabolic poison and enzyme inhibitor. Organic lead as TML (tetra methyl lead) or TEL (tetra ethyl lead), is even more poisonous than inorganic lead. Lead poisoning of children has been linked to even contemporary earthenware glazed surfaces (Kein et al., 1970) and pigments of older paints (Copeland, 1971). By far the most urgent contemporary problem is the control of lead emissions from motor vehicle exhausts and the control of lead pollution is one of the most important environmental problems facing us today.

Conventional methods for removing lead from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, membrane technologies, and evaporation recovery. These processes may be ineffective or extremely expensive, especially in the treatments of the solution containing low concentrations (1~100 mg/L).

Recently, marine algae are being examined for their metal biosorbent properties, some of them showing an exciting potential. Some earlier studies have indicated that the nonliving algal biosorbent may be even more effective in sequestering and accumulating metallic elements than the living cells and tissues. Rice (1956) compared the biosorption of metal by dead and live algal cells, and found that the ability of the cell mass to sequester metallic ions is greater when it is dead. Hassall (1963) also obtained higher accumulations of metals by dead algal cells than by living ones. This indicated changes in the nature of the cell surface (Crist et al., 1981) along with the absence of active transport or rather perhaps rejection and particulate ingestion.

The cell wall constituents of marine algae play an important role in biosorbent metal biosorption and binding. Hope and Walker (1975) reported that the cell walls of algae are often porous in their structure which allows molecules and ions to pass freely through. They also noted that the cell membrane of most algae is permeable to neutral molecules, but not to ions. In addition to the porosity of the algal cell wall structure, the algal cell constituents can provide an array of chemical ligands binding functional groups to take up metallic ions. Differences in the cell constituents and in the composition and structure of the cell wall of widely different algal species can serve as a basis for sequestering, even selectively, many different metallic species(Kam et al., 1997).

In this paper, for the purpose of identifying effective biosorbent types among easily available and preferably

abundant sources, the lead biosorption performances by the biosorbents of nonliving, dried marine brown algae *U. pinnatifida, H. fusiformis, and S. fulvellum* were investigated.

Materials and Methods

Test algae

The marine brown algae (*Phaeophyta*), *Undaria pinnatifida, Hizikia fusiformis,* and *Sargassum fulvellum* obtained from the market were employed as biosorbents. These materials were throughly washed with water, stored in a refrigerator for three days, and then stored in the freezing dryer for 2 days. The biosorbent materials of brown algae in which water was completely removed by those procedures were ground, sieved (70, 100 mesh), and stored in the desiccator.

Chemicals

Analytical grades of $Pb(NO_3)_2$ (Aldrich Chem. Co., USA), Na_2CO_3 (Hayashi Pure Chem. Co., Japan), HNO_3 (Hori Pharm. Co., Japan), and NaOH (Yakuri Pure Chem. Co., Japan) were used. Reagents solutions were made with deionized distilled water. The stock solution of lead ion was prepared as 1000 mg/L and diluted as desired concentrations (10~500 mg/L) with water, respectively.

Methods

Batch reactor experiments had been performed to investigate the effects of initial lead solution concentration, biosorbent amount and pH. Biosorbent with known amount and metal solution with known concentration were placed in a 1-liter flask container, and stirred with a magnetic stirrer. During the experiment, 2 ㎖ of sample in the solution was taken at a given time interval and centrifugated at 4000 rpm for 10 min, and then the supernatant was used to measure the residual lead ion concentrations. A water bath was used to maintain constant temperature during experimentation. All experimental vessels were pyrex glass and all glasswares were leached in 14% nitric acid and washed with distilled water prior to use.

For the biosorption isotherm experiments, a relationship between the equilibrium concentration and the amount of lead ion adsorbed per unit mass of biosorbent was obtained by employing a series of tests.

The concentrations of lead in solution was determined by an Atomic Absorption Spectrophotometer (GBC 904 AA) at 217.0 nm.

Adsorption from aqueous solution at equilibrium is usually correlated by one of the two following adsorption isotherm relationships, the Langmuir isotherm and the Freundlich isotherm.

The Langmuir model, considered valid for mono-layer adsorption on a surface containing a finite number of identical sites (McKay et al. 1982), assumes uniform energies of adsorption over the surface and no transmigration of adsorbate in the plane of the surface.

The Langmuir expression can be represented by:

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{b \cdot q_{max}} \cdot \frac{1}{C_e} \quad (1)$$

A plot of $1/q$ against $1/C_e$ should be a straight line.

For a biosorption system, the Freundlich isotherm can be represented by:

$$q = KC_e^{1/n} \quad (2)$$

The above Freundlich equation is often linearized by taking the natural logarithm of both sides of the equation to give:

$$\log q = \log K + 1/n \log C_e \quad (3)$$

The magnitude of n is an indication of system suitability, with values of $n>2$ representing favourable adsorption conditions (Treybal, 1980). If the isotherm model fits the data, then estimations of K and n can be obtained from the plot of log q against $\log C_e$.

The amount of lead biosorbed (q) for the construction of biosorption isotherms can be determined as follows:

$$q = V(C_o - C_e)/1000M \quad (4)$$

Results and Discussion

This work used three types of marine brown algae biomass (dead) as biosorbent materials used for binding

lead. There is a scientific and practical interest in locating the active sites of biopolymeric structures of the biomass that are responsible for the sorption. Recently, Kloareg et al. (1986) outlined the semispeculative model of the structure of cell walls of brown algae. The cellulose chains formed the structural and rigid network in which four other biopolymers (alginates, xylofucoglucans, xylofuco-glycuronans, and homofucans) are embedded. Similarity of fucose-containing polysaccharides of cell walls of several genera of brown algae as well as the variations of sugar constituents of algal polysaccharides were also described (Mabeau et al., 1990; Nishida et al., 1990). Although the brown algae polysaccharide used in this work for their sequestering ability differed taxonomically, their biomass featured two common moieties:

1) Sulfate esters in the cellular polysaccharides[Fucoidans (after removal of alginates) with $O\text{-}SO_3^-$ groups at the carbons C_2 or C_3 or containing disulfate esters at C_2 and C_3 in α-1,4-linked L-fucopyranosyl residues.

2) Polyuronides that are represented by galacturonic, glucuronic, mannuronic, and guluronic acids (alginates).

The carboxyl groups, present abundantly in the four mentioned uronic acids, together with sulfate groups, could be considered as ligands mainly responsible for the bulk of metal sorption (Crist et al., 1992). The content of sulfate groups as well as uronic acids in the algal biomass examined differs from not only between species but even seasonally and geographically within the same species (Percival and McDowell, 1967), the variations being responsible for potentially varying sorption capabilities.

Comparison of biosorbent lead removal performance

Fig. 1 compares the lead removal performance of the biosorbents of nonliving, dried marine brown algae, *U. pinnatifida, H. fusiformis, and S. fulvellum*. 0.2 g of each biosorbent was used in 500 ml solution of the 10 mg/L lead concentration at 20℃. The experimental results are expressed as the solution concentration divided by initial concentration (C/C_o) as a function of time. The data demonstrated that all biosorbents used in this study showed similar biosorption with above performance of 80%, and had relatively high biosorption capacity for lead. It was also found that the biosorbent-Pb^{2+} system attained the final equilibrium plateau within 90 min. Among the biosorbent materials investigated, the lead removal performance was in the order of *U. pinnatifida* ≥ *H. fusiformis* > *S. fulvellum*.

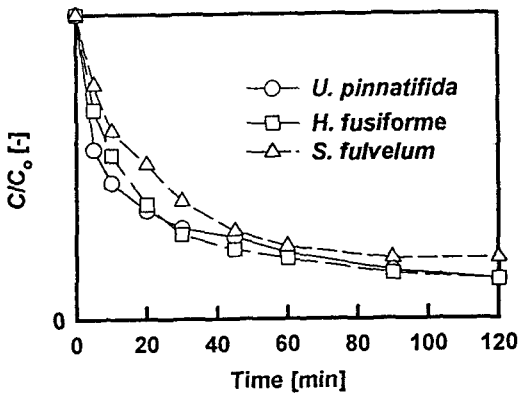

Fig. 1. The kinetics of lead biosorption by biosorbents of *U. pinnatifida, H. fusiformis,* and *S. fulvellum* (Initial lead concentration : 10 mg/L, Biosorbent weight : 0.2 g).

Effect of biosorbent amount

The effect of biosorbent amount on lead biosorption capacity was investigated. The 0.05g, 0.1g and 0.2g of biosorbent material, *U. pinnatifida,* and initial lead concentration of 10 mg/L were used. The result obtained is shown in Fig. 2. This figure shows better removal performance when biosorbent amount was increased. This result indicates that the increase of biosorbent amount contributes the increase of surface area available for adsorption. Among the biosorbent materials used, the decreasing order of the lead removal was *U. pinnatifida* ≥ *H. fusiformis* > *S. fulvellum*.

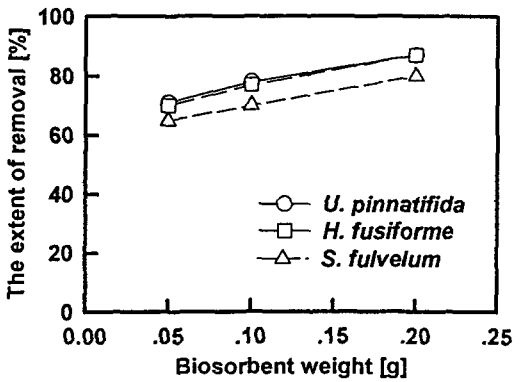

Fig. 2. Effect of biosorbent weight on lead removal (Initial lead concentration: 10 mg/L).

Fig. 3 illustrates the lead biosorption capacity at constant loading on the variation of biosorbent amount of *U. pinnatifida, H. fusiformis, and S. fulvellum.* This figure shows that the equilibrium lead biosorption capacity decreases as the amount of biosorbent added was increased. Among the biosorbent materials used, the decreasing order of the lead biosorption capacity was *U. pinnatifida* ≥ *H. fusiformis* > *S. fulvellum.*

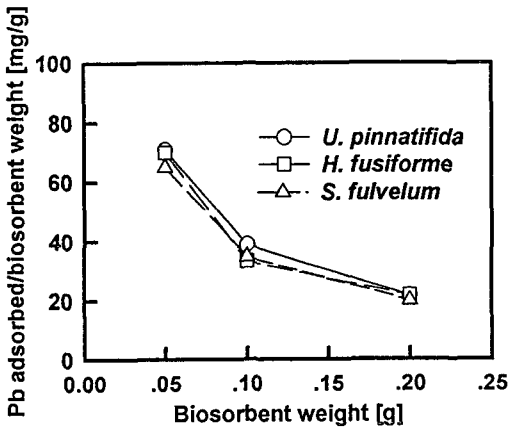

Fig. 3. Effect of biosorbent weight on lead biosorption (Initial lead concentration: 10 mg/L).

Effect of initial lead concentration

Fig. 4 shows how the variation of the initial lead concentration affects the biosorption performance. The initial concentrations of lead used were 10, 25, 50, and 100 mg/L. As shown in figure, the experimental results show the better lead biosorption capacity when initial concentration was higher. This feature is caused by the increase of driving force of mass transfer as the initial lead concentrations increase. Among the biosorbent materials used, the decreasing order of lead biosorption capacity was *U. pinnatifida* > *H. fusiformis* > *S. fulvellum.*

Effect of pH

It was investigated the effect of pH on the lead biosorption capacity and its removal by biosorbent materials. A constant pH for batch equilibrium sorption experiment was maintained at pH 2, 3, 4, 5 and 6, respectively. Each pH was controlled with Na_2CO_3 (10^{-4}N) and HNO_3 or NaOH. The amount of biosorbent was 0.2 g at 20℃ and initial lead concentration of 10 mg/L at each pH value was used. The natural pH of all lead solutions without pH adjustment was 5.4 and slightly increased to 5.6 as biosorbent was added.

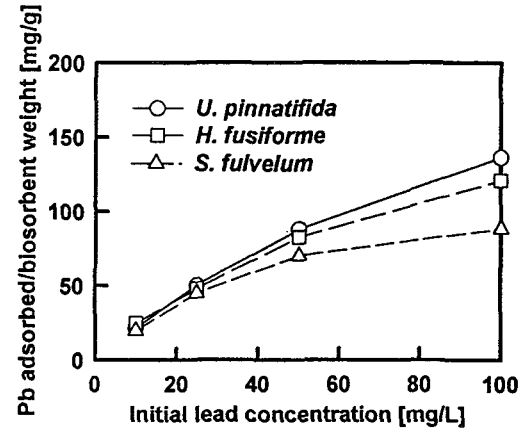

Fig. 4. Effect of initial lead concentration on lead biosorption (Biosorbent weight : 0.2 g).

Fig. 5 shows the lead biosorption capacity of marine algae at different constant pH values. As shown in figure, a low pH of 2 resulted in a markedly lower lead biosorption and higher lead biosorption capacity was obtained in the range of pH 3.0~6.0. The reason for this can be expected due to the higher hydrogen ion concentration with decreasing pH, which in turn prevents the biosorbent-lead binding the more. The experimental results demonstrate that the pH of the solution is a very important factor in lead biosorptive capacity by marine algae. Metal ions could not only displace protons, both other already bound molecules. For instance, in studies with the alga *Vaucheria* (Crist et. al., 1981), strontium could displace zinc even though it was securely bound to the wall, suggesting that electrostatic attraction plays an important role in the metal biosorption process. Tobin et al. (1984) found that the biosorption capacity of metal ions by non-living biomass of fungus, *Rhizopus arrhizus* was strongly pH dependent and they proposed that the biosorption mechanism involves electrostatic attraction of metal ions to positively charged functional groups. In this study, the solutions of lead salts used for sorption tests should not exceed pH 7 because insoluble lead hydroxides tend to precipitate from the solutions at higher pH values, which makes the true sorption tests impossible as shown in Table 1.

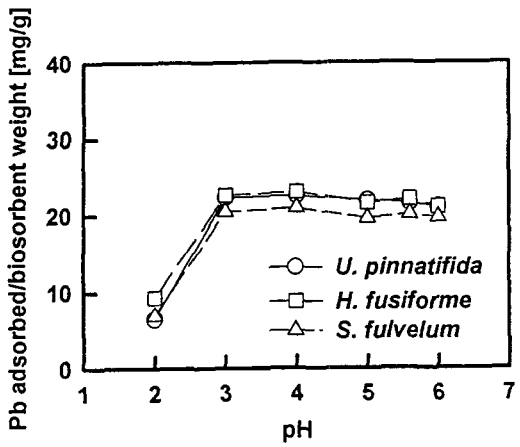

Fig. 5. Effect of pH on lead biosorption (Initial lead concentration: 10 mg/L, Biosorbent weight : 0.2 g).

Table 1. Effect of pH on probable solution percent composition of lead ion species (Lee, 1995) (Unit : %)

Ion species	pH 4	pH 5	pH 6	pH 7	pH 8
Pb^{2-}	100	100	98	83	33
$Pb(OH)^{-}$	–	–	2	17	66
$Pb(OH)_2$	–	–	–	–	1

Fig. 6 shows lead isotherms for *H. fusiformis* at various pH values, together with those for *U. pinnatifida*, and *S. fulvellum* at nonadjusted pH, in the range of C_o of 10~500 mg/L. The starting pH of lead solutions with no pH adjustment was in the range of 5.4~4.9. And, it was in the range of 5.6~4.8 immediately after adding biosorbent and in the range of 5.9~4.5 after 2 hours of contact. The data demonstrated that biosorbent material had relatively high biosorption capacity for lead, exhibiting an observed maximum biosorption capacity of 244 mgPb/g of biomass *U. pinnatifida*. The lead biosorption capacity by *S. fulvellum* were very low, compared to those by *U. pinnatifida* and *H. fusiformis*. The lead biosorption capacity by each biosorbent decreased in the following sequence: *U. pinnatifida* > *H. fusiformis* > *S. fulvellum*.

Fig. 7 represents the Langmuir isotherm plot of lead. The values of q_{max}, b, and correlation coefficient (r^2) for biosorption systems are summarized in Table 2. It was also found that the data fitted reasonably well to the Langmuir model and the calculated maximum biosorption capacity for *U. pinnatifida* was found to be 258 mgPb/g

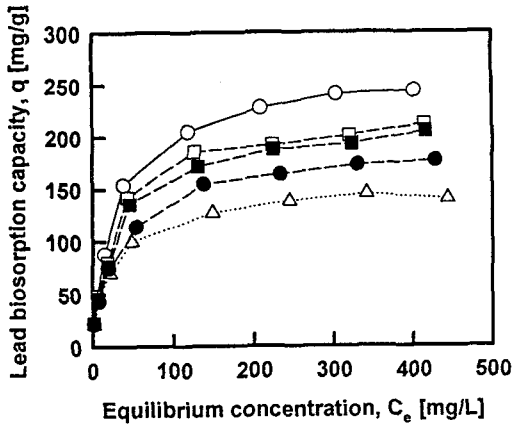

Fig. 6. Lead biosorption isotherms for biosorbents of *H. fusiformis* at different pH values (● pH=3, ■ pH=4, □ Nonadjusted), *U. pinnatifida* (○), and *S. fulvellum* (△) at nonadjusted pH.

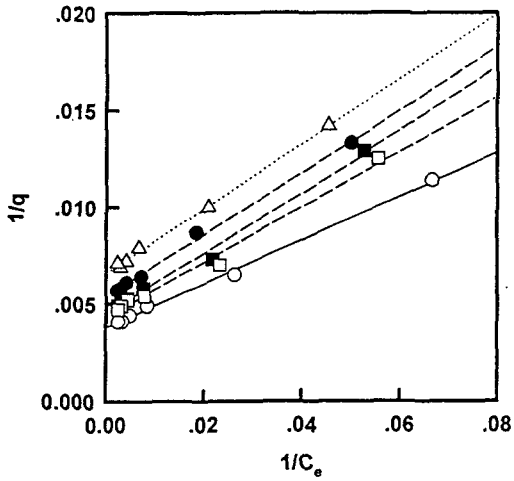

Fig. 7. Langmuir isotherm plot for biosorbents of *H. fusiformis* at different pH values (● pH=3, ■ pH=4, □ Nonadjusted), *U. pinnatifida* (○), and *S. fulvellum* (△) at nonadjusted pH.

of biosorbent.

The Freundlich isotherms for lead was plotted in Fig. 8. For the Freundlich model, reasonable straight-line correlations (r^2) was also achieved. Calculated values of r^2, K, and n are given in Table 3. The values of n obtained in this experiment were in the range of 3.453~4.726. These n values indicate that the marine brown algae used in this study are very favourable biosorbent materials. The values of K giving a measure of adsorbent capacity for no pH adjustment decreased in the follo-

wing sequences: *U. pinnatifida* >*H. fusiformis* >*S. fulvellum*. And, it can be known that the lead biosorption capacity increases with increasing pH from the values of q_{max} and K obtained for *H. fusiformis* at various pH values (see Table 2 and 3).

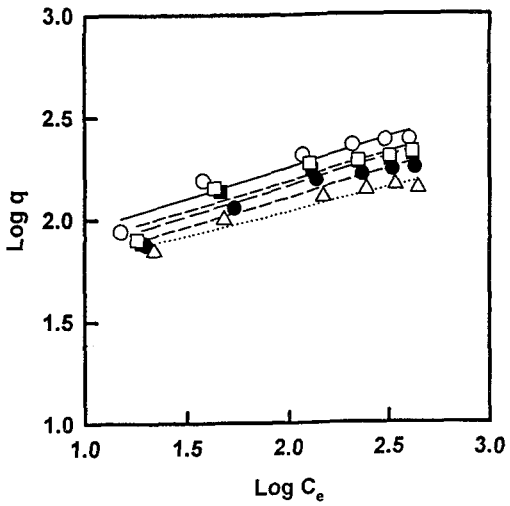

Fig. 8. Freundlich isotherm plot for biosorbents of *H. fusiformis* at different pH values (● pH=3, ■ pH=4, □ Nonadjusted), *U. pinnatifida* (○), and *S. fulvellum* (△) at nonadjusted pH.

Fig. 9 illustrates the comparison of calculated values by Langmuir and Freundlich correlation with experimental data of lead biosorption. The adsorption of metals by microorganisms was observed to be a reversible phenomenon and could be represented by the Langmuir adsorption isotherm (Kuyucak and Volesky, 1987; Khummongkol et al., 1982; Morel and Morgan, 1972; Tsezos and Volesky, 1981). Experimental data obtained in this study agree with both correlated values. Comparing the values of r^2 obtained by Langmuir and Freundlich isotherm, it was found that the experimental data of the lead biosorption by biosorbent materials are expressed better by the Langmuir isotherm than by the Freundlich isotherm.

Conclusions

Using the biosorbent material of nonliving, dried marine brown algae including *U. pinnatifida, H. fusiformis,* and S. fulvellum harvested, their sorption performance

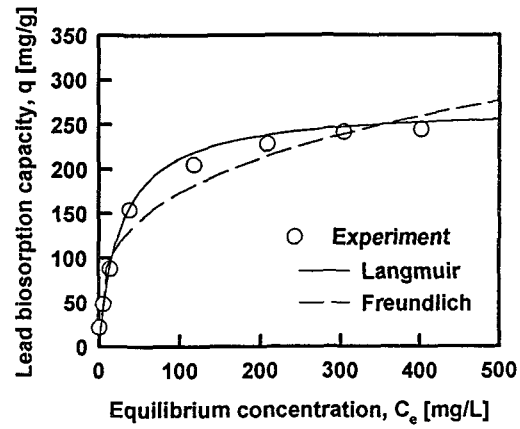

Fig. 9. Comparison of calculated values by Langmuir and Freundlich model with experimental data for *H. fusiformis*.

Table 2. Langmuir isotherm parameters for lead biosorption by biosorbent materials

Biosorbent materials	Langmuir parameters		
	q_{max} (mg/g)	b	r^2
U. pinnatifida			
Nonadjusted pH*	258	0.037	0.992
H. fusiformis			
pH 3.0	185	0.033	0.996
pH 4.0	208	0.030	0.989
Nonadjusted pH*	233	0.030	0.989
S. fulvellum			
Nonadjusted pH*	153	0.042	0.974

*The starting and final pH of the solution with no pH adjustments was in the range of 5.6~4.8 and 5.9~4.5, respectively.

Table 3. Freundlich isotherm parameters for lead biosorption by biosorbent materials

Biosorbent materials	Freundlich parameters		
	K	n	r^2
U. pinnatifida			
Nonadjusted pH*	45.67	3.453	0.938
H. fusiformis			
pH 3.0	34.89	3.563	0.948
pH 4.0	38.27	3.546	0.906
Nonadjusted pH*	41.49	3.532	0.899
S. fulvellum			
Nonadjusted pH*	39.36	4.726	0.940

*The starting and final pH of the solution with no pH adjustments was in the range of 5.6~4.8 and 5.9~4.5, respectively.

of lead was investigated. Batch reactor experiments had been performed to investigate the effects of initial solution concentration, the biosorbent amount and pH. The following results were obtained.

All biosorbents used in this study showed similar performance of more than 80% and had relatively high biosorption capacity for lead. The experimental result showed better lead removal performance but less lead biosorption capacity as the biosorbent amount was increased. However, the lead biosorption capacity by the biosorbent materials increased with increasing initial lead concentration and pH in the range of C_o of 10~500 mg/L. Among the biosorbent materials used, the decreasing order of lead biosorption capacity was as follows: *U. pinnatifida* > *H. fusiformis* > *S. fulvellum.*

The values of Freundlich constant n obtained in this study were in the range of 3.453~4.726. These n values indicated that the marine brown algae used in this study are very favourable biosorbent materials. The experimental data of the lead biosorption by biosorbent materials are better expressed by the Langmuir isotherm than the Freundlich isotherm.

Nomenclature

- b Langmuir constant (energy constants) [−]
- C concentration of lead in the solution [mg/L]
- C_e equilibrium concentration of lead in the solution [mg/L]
- C_o initial concentration of lead in the solution [mg/L]
- K Freundlich constant (adsorbent capacity) [−]
- M biosorbent weight [g]
- n Freundlich constant (adsorption intensity) [−]
- q lead biosorption capacity [mg of lead/g of dry biosorbent]
- q_{max} maximum biosorption capacity [mg of lead/g of dry biosorbent]
- V volume of the solution [mℓ]

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