

# **Adsorption capacity of Lead (II) ( $Pb^{2+}$ ) in aqueous solution by brown seaweed (*Fucus spiralis*)**

## **ABSTRACT**

The sorption uptake of lead by marine brown alga *Fucus spiralis* was investigated in bimetallic solutions. The experimental data fitted very well to Langmuir model. In bimetallic systems, the affinity of biomass for lead and cadmium increased and the sorption uptake of these metals was not affected by increasing concentrations. However, in solutions with both metals there was a significant mutual decrease of their sorption levels at high concentrations of the other metal. There is practical removal up to  $100 \pm 4$  % for biomass dosage  $4.0 \pm 0.1$  g which correspond to lowest adsorbed amount of  $0.25 \pm 0.1$  mg/g. The highest adsorbed value was recorded with biomass dosage  $0.25 \pm 0.1$  g but with the lowest percentage removal of  $92.50 \pm 6$  %. In this study at initial metal concentration of 10 mg/L the highest metal removal of 96 % was achieved.

*Keywords: Fucus spiralis, lead, absorption, biomass, and brown seaweed.*

## **1.0 INTRODUCTION**

Both essential and non-essential metals have been shown to accumulate in algae. Since the 1970s, scientists have been studying the use of algae for environmental monitoring. 1 Excess metals in water bodies may have a substantial impact on microalgae, which are the primary food supply for other plants and animals during their developmental phases. 2 Microscopic photosynthetic algae can be found in both freshwater and seawater, and their photosynthetic activities are similar to those of land plants. However, because of their smaller cellular structure and the fact that they are submerged in an aquatic environment with abundant CO<sub>2</sub>, water, and other valuable nutrients, they can more quickly convert solar energy into biomass. 3 Microalgae are the first rung in the food chain in aquatic systems, and they collect extracellular polysaccharides such as sheaths, capsules, and envelopes (mass enclosing their cells). 3 Fatty acids and lipids make up the membranes of microalgae, which serve as sources of energy, metabolites, and storage products. 3 Both marine and freshwater microalgae are extraordinarily efficient at scavenging metals in world ecology, and they are taxonomically diverse, having evolved over 500 million years. Many microalgae species are valuable nutrients that can be utilised in microbial metabolic processes at low concentrations. 3 Many metal ions have potential affinity for macro algae such as green macroalgae, seaweed, and their alginates derivatives. 4

Bio sorbents materials especially marine macro algae-based species has been extensively researched as an alternative option to replace the conventional adsorbents. This is due to their potentiality in removing pollutants from wastewater and environment in a cost-effective way. The ability of macro algae in metals uptake from wastewater has been widely

recognised and based on chemical binding and electrostatic attractions involving ion-exchange.<sup>2</sup>

Brown macroalgae has been reported to be an excellent bio sorbent for heavy metals, in comparison to other macroalgae algae (red and green) and other types of commercially adsorbent<sup>2,3</sup>. In this work, lead has been exposed to *Fucus spiralis* for the uptake capacity. Lead was chosen as an adsorbate for this study due to its environmental impact. The method used in this study was adapted from the work of Filote *et, al.*<sup>4</sup>

A brown macro alga with prominent midrib, pairs of reproductive bodies on tips of fronds often twisted. The fronds are measured 20 cm long and 2 cm wide.<sup>5</sup> The fruiting bodies are inflated and round. Moreover, the spiral twist is noticed when this species is hanging down from the rocks. Like *F. vesiculosus*, the colouration ranges from olive – green to light brown.<sup>5</sup> The sexes appear in same individual for reproduction and these occurs at the branch apices.<sup>2</sup> The most common habitat of *F. spiralis* is rocky substrata in the upper shore of sheltered shores.<sup>5</sup>

There are many research publications on the determination of the levels of heavy metal contamination or pollution using various analytical methods. Inductively coupled plasma atomic emission spectrometry (ICP – AES) have been applied to investigate the levels of metals toxicity in some biological samples by using microcentric nebulization.<sup>15</sup>

## 2.0 MATERIAL AND METHODS

### 2.1 Instrumentation

Unknown concentrations of lead (II) were determined by flame atomic absorption spectroscopy (Agilent technologies). The metal was analysed at a wavelength of 283.3nm, lamp current of 5.0 mA, slit width of 0.5 nm, using air-acetylene as oxidant gas and triplicate readings. Lead standard metal solution of 1000 mg/L (99.8% purity, analytical grade, Fisher Scientific). was purchased and used to prepare an accurate standard solution of 2.0, 4.0, 6.0, 8.0 and 10 mg/L. 50 mL volumetric flasks were used and make up to the mark for dilution.

Calibration curves were determined in each analysis in the working range of 1.0 - 25 mg/L and accepted for a determination coefficient  $R^2 > 0.994$  (fig 1). A limit of detection (LoD and limit of quantification (LoQ) was established at 0.005 and 0.015 mg/L respectively.

### 2.2 Sample preparation

*Fucus spiralis* (figure 1 below) used in this study was obtained from a west show beach near Llandudno in north Wales, U.K (53°19'17.9" N 3°51'01.3" W). The harvested *F. spiralis* biomass was washed severally with tap water to remove sand particles, impurities, and epiphytes before been washed with distilled water. The biomass was initially air dried at room temperature for 72 hrs before been chopped by scissor and crushed by hand prior to 24 hrs oven dried at 105°C using petri drying dishes. The dried algae were later grounded into powder using an electrical Retsch cyclone mill twister D -42781 and sieved to uniform particles size (0.5 mm) and kept in storing bottle.

In order to study the absorption of lead on *F. spiralis*, 0.5 g of the grounded sample were digested in triplicate, in glass tubes at 150°C for 2 hrs, 5.0 ml of distilled water, 12.0 ml of HCl and 4.0 ml HNO<sub>3</sub>. After digestion the solution was then filtered using cellulose acetate membrane (0.45 µm) porosity, diluted to 100.0 mL prior to analysis using flame atomic absorption spectroscopy (Agilent technologies).<sup>6</sup>

### 2.3. Batch biosorption procedure

Biosorption experiments were carried out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 100mL stoppered conical flask containing 25mL of test solution. Initial solutions with different concentration of Pb (II) were prepared by proper dilution from stock 1000 mg/L Pb (II) standards. Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8.



Figure 1. *Fucus spiralis* (present study)

### 3.0 RESULTS AND DISCUSSION

#### 3.1 effects of pH and adsorbent dosage

Lead (II) ( $\text{Pb}^{2+}$ ) Stock solution was prepared by dissolving 1.598 g of  $\text{Pb}(\text{NO}_3)_2$  analytical grade (Fisher Scientific U.K) in one litre of distilled water to achieve a concentration of 1000 mg/L. Initial metal concentration used in biosorption tests were then prepared by dilution of the stock solution.

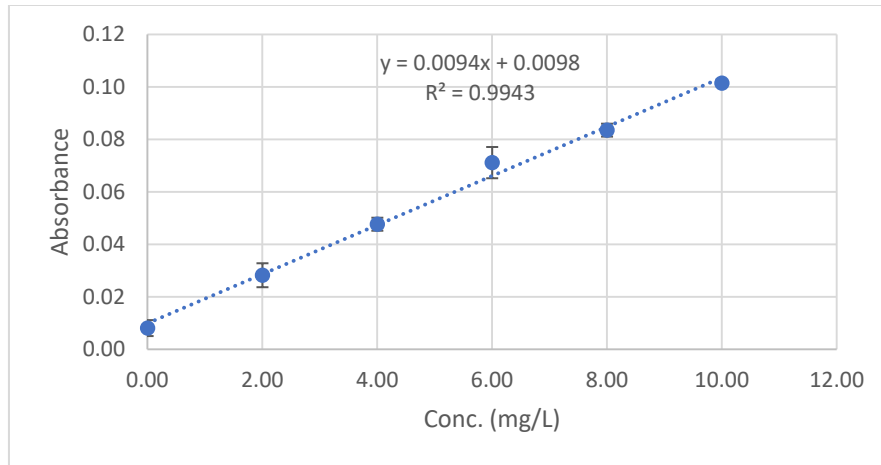


Figure 2. Lead standards showing linear relationship between absorbance and concentration using AAS.

In order to determine the optimum biomass dosage, the mass of the adsorbent (*F. spiralis*) was varied (0.25 - 4.0 ± 0.2 g) and an experiment were carried out in 250 mL Erlenmeyer flasks capacity containing 50 mL of Pb (II) metal solution of 20 mg/L initial metal concentration, at 25°C. and pH value was adjusted to 4.5± 0.3 with conc. HNO<sub>3</sub> or HCl. The suspended solutions were then stirred in an orbital shaker operating at 180 rpm agitating for 4 hours. The samples solutions were then filtered using cellulose ester membrane filters (0.45 µm). The filtered solutions were centrifuge and analysed for adsorption of lead. Moreover, pH effect was also tested under same conditions as above (25°C, 180 rpm, 20 mg/L, 4 hrs etc). The adsorbent dosage was fixed at 0.50 ± 0.02 g and pH varied between 2.50 and 5.50. The initial pH metal solutions were adjusted using 0.02 M HNO<sub>3</sub> or 0.5 M NaOH. During the contact time, the maximum pH variation allowed was ± 0.3. It was observed that lead precipitation occurs at pH value greater than 6.0 this is even high with concentrated solutions.<sup>4</sup> Therefore, pH effect studies was only considered below the reported precipitation value of 5.50. The amount of lead adsorbed per gram of *F. spiralis* ( $Q_e$ , mg/g) was calculated by mass balance (Equation (1)) and removal efficiency by Equation (2), where  $C_o$  is the initial concentration (mg/L),  $C_e$  is the final or equilibrium concentration (mg/L),  $m$  is the bio sorbent mass used (g) and  $V$  is the solution volume (L).

$$Q_e = (C_o - C_e)V/m \quad (1)$$

$$\% \text{ removal} = (C_o - C_e) / C_o \cdot 100 \quad (2)$$

In order to evaluate the rate at which the biosorption process takes place, kinetic experiments were carried out at different initial Pb (II) concentrations: 5.0, 10, 15, 20, 50, 70 mg/L. Metal solutions (100 mL) were mixed with adsorbent 0.50 ± 0.02 g and stirred at 25 °C for 7 h. The pH was initially adjusted and readjusted when necessary to pH 4.5 ± 0.3. For each analysed concentration, samples were filtered, and centrifuge and lead concentration analysed in the liquid phase by AAS. The calculated adsorbed amount was recorded as a function of the contact time and metal concentration.

### 3.2 effect of biomass dosage

The effect of *F. Spiralis* dosage was studied and result presented fig (3). There is practical removal up to  $100 \pm 4$  % for biomass dosage  $4.0 \pm 0.1$  g which correspond to lowest adsorbed amount of  $0.25 \pm 0.1$  mg/g. The highest adsorbed value was recorded with biomass dosage  $0.25 \pm 0.1$  g but with the lowest percentage removal of  $92.50 \pm 6$  %. A study conducted to investigate the effect of biomass dosage on Pb (II) and Cd (II) ions on the *Ulva lactuca* biomass,<sup>8</sup> the results shows that the bio sorption efficiency of the metals is highly dependent on the increase in adsorbent dosage of the solution.<sup>7</sup> Therefore, based on these results, an optimum biomass dosage of  $0.50 \pm 0.1$  g was chosen to be used in further experiments.

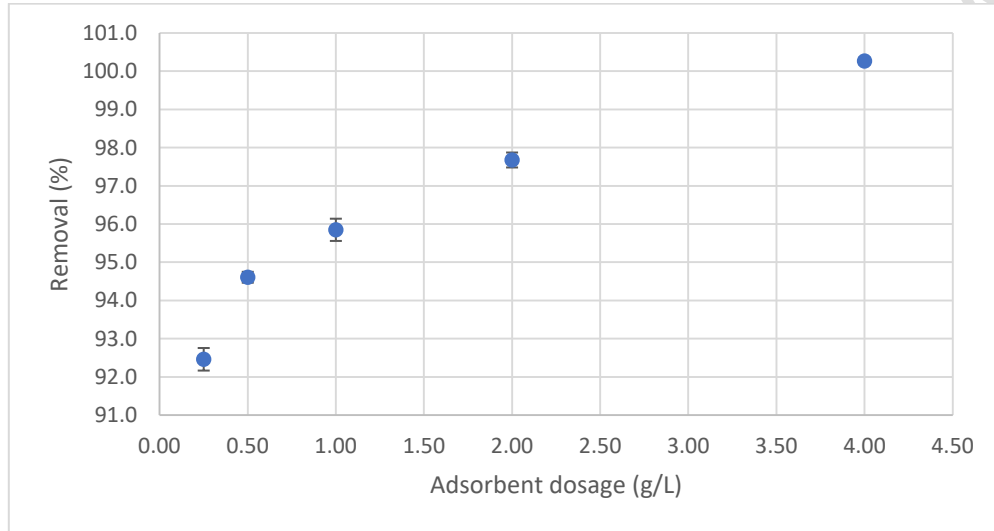


Fig 3. Bio sorption removal efficiency ( $\pm$  global uncertainty) of Pb (II) by *F. spiralis* at different adsorbent dosages, using 20 mg/L of metal solution, pH  $4.5 \pm 0.5$  and a temperature of 25 °C.

Further studies show that *Fucus spiralis* biomass dosage ranged 0.50 to 4.0 g can remove up to 100 % of Pb (II).<sup>4</sup> This study further revealed that the high the amount of adsorbent dosage the lower the adsorbed value (mg/g) and vice versa.

### 3.3 Effect of varying pH

The pH is an important factor influencing the biosorption process. From the point of view of the solid surface, pH affects protonation/de- protonation of the functional groups and their availability to establish bonds with adsorbates, chemical species (oxidation state, complexes, charge) being also pH dependent.<sup>4</sup> In this work, pH influence was studied in the acidic range, using initial pH values of 2.5, 3.0, 4.0, 4.5 and 5.5 as shown in figure 4.

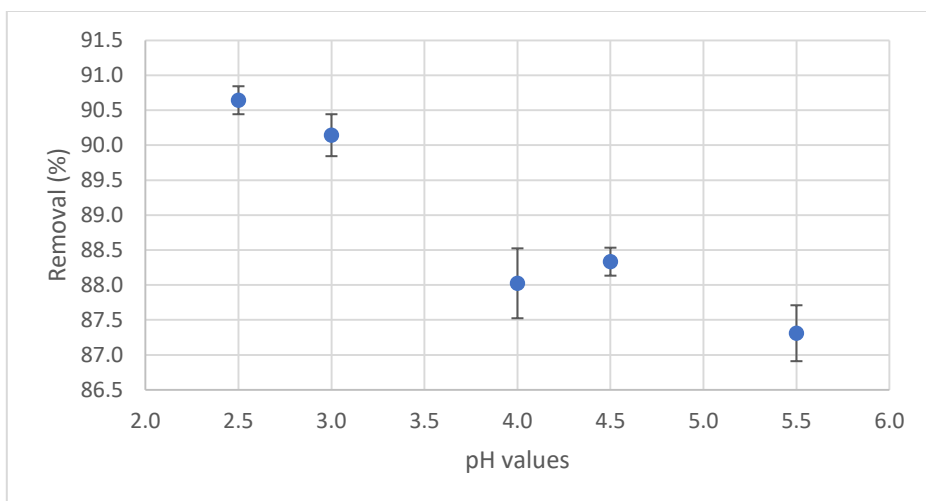


Fig 4. Removal efficiency of Pb (II) by *F. spiralis* at different pH values (2.5 – 5.5  $\pm$  0.5), using 20 mg/L of metal solution, 0.50 g of adsorbent dosage and a temperature of 25 °C

During the stirring time, pH was controlled, and maximum variations observed for each one of the studied pH were 2.5  $\pm$  0.4, 3.0  $\pm$  0.5, 4.0  $\pm$  0.2, 4.5  $\pm$  0.5 and 5.5  $\pm$  0.3. Initial pH levels above 5.5 were avoided to eliminate the interference of metal hydroxide precipitation, which easily occurs at higher pH values.<sup>9,10</sup> where the authors mentioned pH levels between 1.2 and 3.0 was good. Results on the varying pH effect presented in Fig. 4 shows an increase in pH from 2.50 to 4.50 favoured the uptake of Pb (II) from solution with an increase in removal efficiency from 87.30  $\pm$  0.4 % to 90.60  $\pm$  0.2 %. In the pH range studied, lead is mostly present in water as a free cation (Pb<sup>2+</sup>) under strong acidic conditions.<sup>4</sup> Protons (H<sup>+</sup>) compete with lead for the active sites of the bio sorbent and the removal efficiency is limited.<sup>4</sup> As the pH rises, the number of deprotonated active sites increases, a negative charge is developed and a significant enhancement in the amount of Pb<sup>2+</sup> adsorbed was observed.<sup>4</sup> Maximum uptake values of cationic heavy metals by algae and algal-derived materials have been reported near pH 5.<sup>4,11,12,13,8</sup> close to the pK of carboxylic acids dissociation as it was also observed in this work. Carboxylic groups are the most abundant in brown algae and are known to establish bridging or bidentate complexes with heavy metals.<sup>2</sup> Adsorption studies and infrared spectra from *F. spiralis* biomass suggest that these functional groups are present in an effective way. At the optimum pH, the adsorbed amount of Pb (II) was 36  $\pm$  3 mg/g. Though the experimental conditions are different our value agree with adsorption value of 45.3 mg/g at pH 5 reported by Freitas *et al.*,<sup>12</sup> obtained for lead uptake unto raw *F. spiralis* biomass (2.0 g). Based on this result and available literature it was decided to fix the biosorption test at pH 4.5.

### 3.4 Biosorption kinetics

In order to determine the rate at which the Pb (II) biosorption takes place on adsorbent, the effect of contact time was evaluated in experiments conducted at different initial adsorbate concentrations and results presented in Fig 5. For an initial metal concentration of 5.0 mg/L, 93.8 % removal occurred with equilibrium being achieved with 10 mg/L. The time necessary to reach equilibrium seems to increase with increasing initial adsorbate concentrations. In this study at initial metal concentration of 10 mg/L the highest metal removal of 96 % was achieved. For the studied conditions, very high removal was found,  $\approx$  99 % for 10 mg/L initial lead concentration and lowest 93 % for 5.0 mg/L. Equilibrium times of 1–3 h have been reported in literature for the uptake of Pb(II) by different bio sorbents.<sup>14,15</sup> Biosorption as a

passive and a metabolism-independent process is relatively fast, which is an important advantage from an operational point of view.

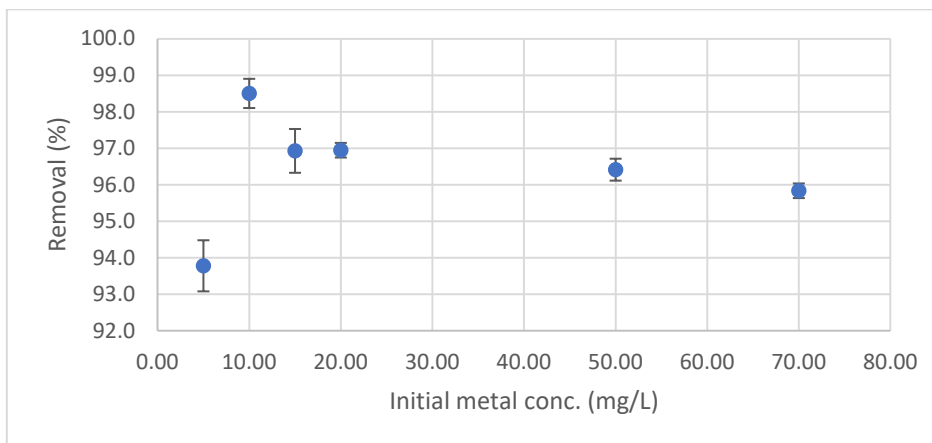


Fig. 5 Effect of initial metal concentrations on Pb (II) biosorption on *F. spiralis* (pH  $4.5 \pm 0.5$ , 0.50 g/ of adsorbent, 25 °C): experimental data (values  $\pm$  global uncertainty).

### 3.5 Equilibrium Isotherm Modelling

Equilibrium is established when the concentration of a metal ion in the solution is in balance with that of the bio sorbent surface. In such cases, an equilibrium isotherm model is employed to describe the experimental data in order to give useful information about the bio sorbent. Three of the most common and most successful isotherm models in describing biosorption equilibrium data are Langmuir and Freundlich (equations 3 and 4 respectively). Metal sorption on a homogeneous surface, as a monolayer, without interaction between adsorbed molecules is the basis of the Langmuir model.

The experimental results were modelled using pseudo-first order Langmuir model;

$$q_e = q_{\max} \frac{C_e}{1+bC_e} \quad (3)$$

$$q_e = k_f C_e^{1/n} \quad (4)$$

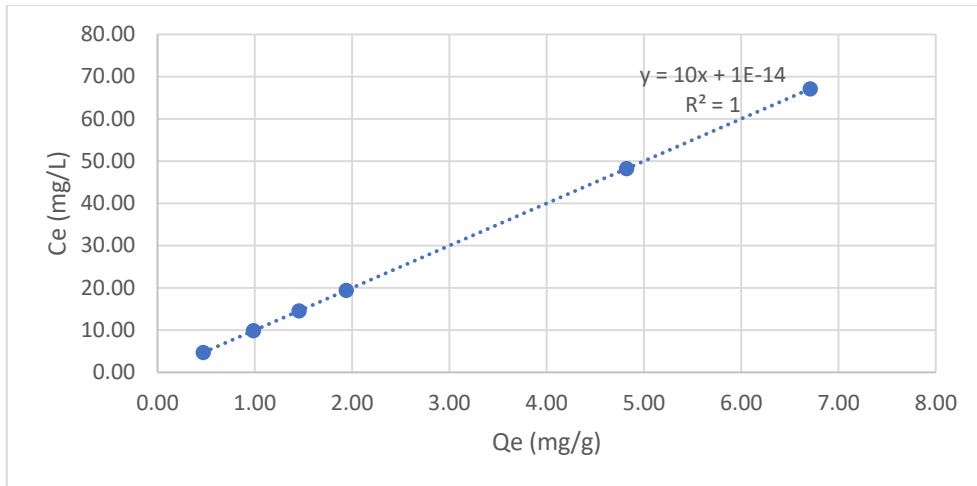


Figure 6. Relationship between sorption capacity and the concentration at equilibrium for lead (II)

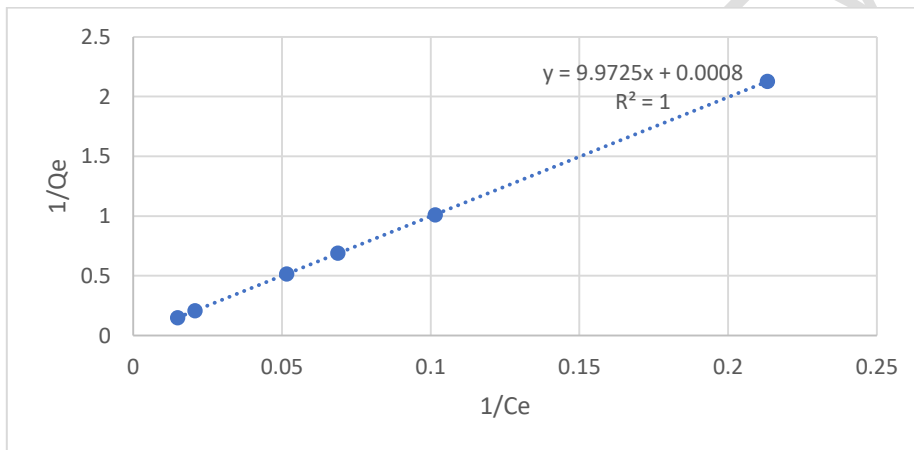


Figure 7. Langmuir isotherm plot for lead ions

#### 4.0 CONCLUSION

The brown algae represent an especially efficient and resilient class of biosorbents relative to other biomass types. Fortunately, due to their economic value in many industrial applications, there is much information about their basic structure and biochemical constitution. This in turn makes the interpretation of the sorption behaviors and elucidation of metal binding mechanisms more rigorous. The order Laminariales and Fucales of the brown algae (division Phaeophyta) are the most important groups of algae to the field of biosorption because of the abundance of their cell wall matrix polysaccharides and extracellular polymers. The alginate polysaccharide is mainly responsible for the natural ion-exchange capacity of the brown algae. Its unique macromolecular structure gives rise to selective metal binding whose mechanism is commonly represented by the “egg-box” model.

## COMPETING INTERESTS DISCLAIMER:

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## REFERENCES

- 1 T. A. Davis, F. Llanes, B. Volesky and A. Mucci, *Environ. Sci. Technol.*, 2003, **37**, 261–267.
- 2 T. A. Davis, B. Volesky and A. Mucci, *Water Res.*, 2003, **37**, 4311–4330.
- 3 E. Romera, F. González, A. Ballester, M. L. Blázquez and J. A. Muñoz, *Bioresour. Technol.*, 2008, **99**, 4684–4693.
- 4 C. Filote, I. Volf, S. C. R. Santos and C. M. S. Botelho, *Sci. Total Environ.*, 2019, **648**, 1201–1209.
- 5 R. . Francis.D.B, Juliet. A.B, Christine. A.M and Anne, *Seaweeds of Britain and Ireland*, Wild Nature Press Winson House, Church Road Plympton St.Maurice, Plymouth, Second Edi., 2017.
- 6 M. Development, *FLAME ATOMIC ABSORPTION Method Development ePrimer*, .
- 7 A. Sari and M. Tuzen, *J. Hazard. Mater.*, 2008, **152**, 302–308.
- 8 M. M. Ghoneim, H. S. El-Desoky, K. M. El-Moselhy, A. Amer, E. H. Abou El-Naga, L. I. Mohamedein and A. E. Al-Prol, *Egypt. J. Aquat. Res.*, 2014, **40**, 235–242.
- 9 K. Dermentzis, E. Valsamidou and D. Marmanis, *J. Eng. Sci. Technol. Rev.*, 2012, **5**, 1–5.
- 10 H. J. Mansoorian, A. H. Mahvi and A. J. Jafari, *Sep. Purif. Technol.*, 2014, **135**, 165–175.
- 11 F. Luo, Y. Liu, X. Li, Z. Xuan and J. Ma, *Chemosphere*, 2006, **64**, 1122–1127.
- 12 O. M. M. Freitas, R. J. E. Martins, C. M. Delerue-Matos and R. A. R. Boaventura, *J. Hazard. Mater.*, 2008, **153**, 493–501.
- 13 M. M. Areco, S. Hanela, J. Duran and M. dos Santos Afonso, *J. Hazard. Mater.*, 2012, **213–214**, 123–132.
- 14 W. M. Ibrahim, A. F. Hassan and Y. A. Azab, *Egypt. J. Basic Appl. Sci.*, 2016, **3**, 241–249.
- 15 I. Volf, N. G. Rakoto and L. Bulgariu, *Sep. Sci. Technol.*, 2015, **50**, 1577–1586.

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