Asian Journal of Chemistry Vol. 21, No. 3 (2009), 2032-2036

Chemical Modification of Some Functional Groups on Marine Algae (*Sargassum crasifolium*) Powder for the Evaluation of Lead(II) Uptake

RAHMIANA ZEIN, REFILDA SUHAILI, MAWARDI, EDISON MUNAF* and
GIORGIO BAVESTRELLO†
Laboratory of Analytical Environmental Chemistry, Department of Chemistry
Faculty of Mathematics and Natural Sciences, Andalas University, Padang 25163, Indonesia
E-mail: emunaf@fmipa.unand.ac.id

The functional group on marine algae (*Sargassum crasifolium*) has been modified using NaOH, formaldehyde and citric acid as a modifier. The modified of algae is used for the Pb(II) uptake. The experimental results showed that the modification of functional group on algae *Sargassum crasifolium* using NaOH much better than formaldehyde and citric acid, with the sorption capacity 1.25 mg Pb/g algae followed by 0.83 and 0.69 mg Pb/g algae powder for formaldehyde and citric acid modification, respectively.

Key Words: Chemical modification, Marine algae, Pb uptake.

INTRODUCTION

Stringent environmental regulations required the treatment of wastewater to remove toxic heavy metals. The conventional physical-chemical techniques such as reverse osmosis, chemical precipitation, ion-exchange and membrane separation process may present difficulties in the metal uptake from industrial wastewater as they proved to be costly for industries[1,2]. Biosorption process has been suggested as a potential alternative to the existing physico-chemical technologies for the detoxification and heavy metal uptake from wastewater[3,4]. Biosorption refers to different modes of non-active metal uptake by biological material or agricultural by-product where metal sequestration by cell wall can take place through adsorption, ion-exchange, complexation, *etc.* Numerous functional groups namely, amino, thiol, carboxyl, sulphydryl, carbonyl, hydroxide, imidazole and amide moieties have been suggested as the possible functionalities groups responsible for the binding of metal ions[5-7].

The contribution and characterization of the binding metal ions with the functional groups on the biomaterial have been reported elsewhere. The carboxyl and sulphonate metal has been checked by using potentiometric titration with the pH

---

†Dipartimento di Scienze del Mare, Universita Politecnica delle Marche, Ancona 60131, Italy.

dependent while the carboxylate and diamine functionalities using NMR spectrometry. The thiol and amino groups metal binding have been examined using N-malcimide and glutaraldehyde blocking agent[8-10].

Among the huge diversity of the biomaterial available, algae have already proved to be the most promising material for metal uptake and concentration[11-13]. Although the metal binding performance of algae biomass has been well described, but no report on the modification of their functional groups in order to increase sorption capacities has been cited. The aim of this study is to modify the functional groups on algae powder to enhance Pb(II) uptake from wastewater.

EXPERIMENTAL

The marine algae biomass used in this study was collected from Padang, Indonesia. Fresh samples were harvested, washed clean with deionized water and sun dried. The samples were then dried at 60 ºC in an oven and ground to powder within the particle size 180-250 µm.

All chemicals used were of analytical reagent grade or better and obtained from E. Merck (Darmstadt, Germany) unless otherwise noted. Standard solution of Pb(II) were prepared by dilution of a 1,000 mg Pb/L prepared from its nitrate salt. Sodium hydroxide, formaldehyde and citric acid were used for the modification of algal functional groups.

Modification procedures: Algae powder was treated in a different chemical modification on the following way: 3 g of materials were placed in 100 mL backer glass and 25 mL of each modification reagent at different concentration was added. The slurry was stirred at room temperature (*ca.* 28 ºC) for 4 h and the liquid was discarded. The treated algae powder then washed with deionized water to remove unbound modifier.

Biosorption procedure: All biosorption properties were studied in batch experiment. Each vial contained 0.3 g (dry weight) modified algae powder and 30 mL of 10 mg L^{-1} Pb solution. The vial is then were shaker at room temperature (*ca.* 28 ºC) for 4 h in a rotary shaker at 30 rpm. The solution of pH was kept constant at 5. The Pb(II) ion concentration which remained in the supernatant was determined by atomic absorption spectrometry (Analab, England). All experiments were carried out twice and the average value is reported.

The Pb(II) uptake capacities by algae powder for the construction of sorption was determined with the following equation[12]:

$$Q = Vx(C_o - C_i)/1{,}000\ W$$

where V is the volume of solution in batch experiment, C_o is the initial concentration of Pb(II) in the solution (mg L^{-1}), C_i is the final concentration of Pb(II) in the solution (mg L^{-1}) and W is the mass weight of algae powder (g).

RESULTS AND DISCUSSION

Effect of NaOH pretreatment on Pb(II) uptake: Structurally, algae powder consist of lignin, cellulose, hemicellulose and protein which make them effective sorbent for divalent metal cations such as Pb(II). The extent of surface binding on algae cell surface may also be generalized by mass law equation, *e.g.*,

$$SH + Pb^{2+} \longleftrightarrow SPb^{+} + H^{+}$$

where S is designed a deprotonated bidentat surface group or chelating site such as: NH_2-R-COOH, R-$(COOH)_2$, OHR-COOH dan NH_2R-CH_2-SH.

Effect of NaOH pretreatment on Pb(II) uptake by algae powder is shown in Fig. 1. As seen in Fig. 1, treatment with 0.6 mol L^{-1} NaOH increasing Pb(II) uptake by algae surface from 0.28 to 1.25 mg Pb(II)/g algae. NaOH might increases the net negative charge on the algae surface by stabilizing surface lipid and or by removing base-solution tannins. At the same time, acetyl groups present in the surface of algae was hydrolyzed to amino groups. Which has electron pair available for coordination with Pb(II) ion.

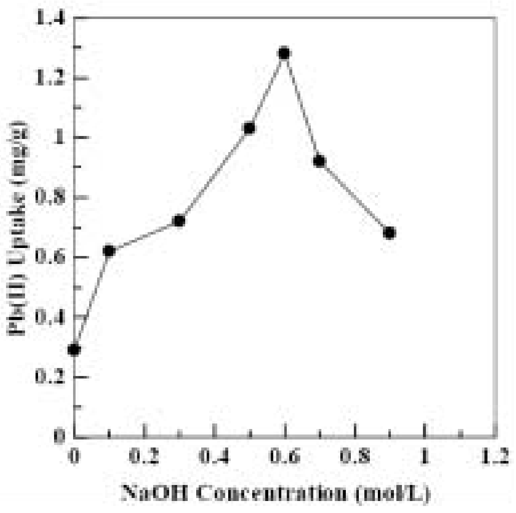

Fig. 1. Effect of concentration of NaOH on modification of functional group of algae *Sargassum crasifolium* for the Pb(II) uptake

Effect of formaldehyde pretreatment on Pb(II) uptake: General scheme of the type of chemistry occurring during the formaldehyde treatment is non-protonated amino groups on amino acid (*e.g.*, lysine) present in the algae surface to form hydroxylamine. The hydroxylamine combines slowly with amino, amide or imidazole groups of amino acids to form relatively stable intra or inter molecular cross-linked. Formaldehyde can also react with peptide groups to form acid stable compound.

$$\text{Algae-NH}_2 + \text{H-COOH} \rightarrow \text{Algae-NH}_3\text{OH} \rightarrow \text{Algae-NH=CH}_2$$

The results are shown in Fig. 2. As seen in Fig. 2, the Pb(II) uptake are increases with increasing formaldehyde concentration up to 10%, with the sorption capacity 0.83 mg Pb(II)/g algae powder, compared without formaldehyde pretreatment, where the Pb(II) uptake is 0.27 mg g^{-1}.

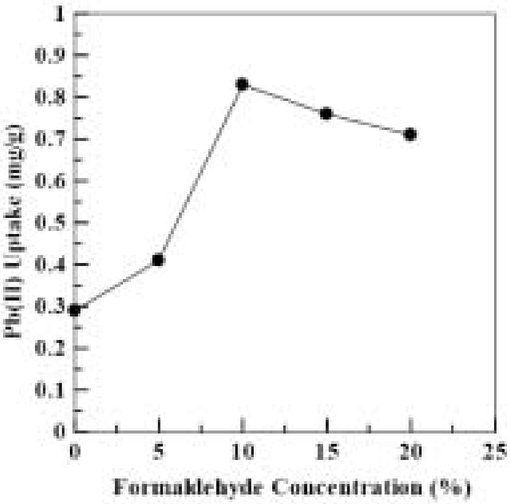

Fig. 2. Effect of Concentration of formaldehyde on modification of functional group of algae *Sargassum crasifolium* for the Pb(II) uptake

Effect of citric acid pretreatment: The algae contain 25-37 % of alginic acid on a dry-weight basis. Alginic acid, a linear polysaccharide of β-D-mannuronic acid and a-L-guluronic acid, is a main cell boundary constituent of *Sargassum crasifolium* algae. The interaction of a metal with an algae cell will thus normally involve the following steps: diffusion of the metal from the bulk solution to the biological surface; sorption surface complexation of the metal at passive binding sites within the protective layer or at sites on the outer surface of the plasma membrane; uptake or internalization of the metal (transport across the plasma membrane). The biological end points that are normally considered as indicators of bioavailability for phytoplankton include metal bioaccumulation (sorption, uptake), as well as metal effects on such processes as photosynthesis, respiration, motility and growth, much depend on the solution of pH on the suspension. Thus, the acidic conditions play role in the metal uptake by algae.

The effect of citric acid pretreatment of algae on lead uptake is shown in Fig. 3. From the Fig. 3, it seen that when citric acid concentration was changed from 0 to 20 %, the lead uptake was increased with increasing citric acid concentration up to 10 %. Where Pb(II) uptake by algae powder was increased from 0.27 to 0.69 mg g^{-1}.

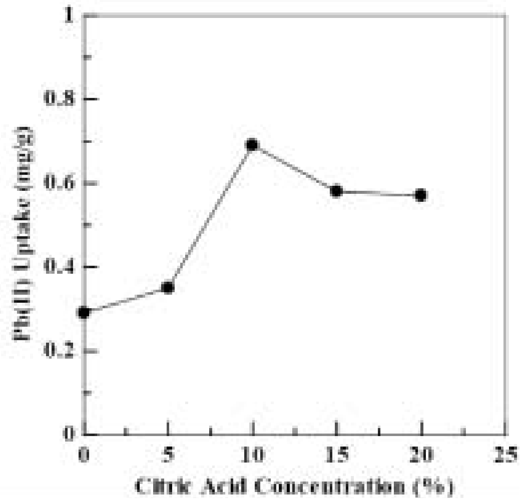

Fig. 3. Effect of Concentration of citric acid on modification of functional group of algae Sargassum crasifolium for the Pb(II) uptake

In conclusion, the present study showed that the chemical modifications can affect metal sorption capacity on the marine algae *Sargassum crasifolium*.

REFERENCES

1. B. Volesky, *FEMS Microbiol. Rev.*, **14**, 291 (1994).
2. H. Eccles, *Trends Biotechnol.*, **17**, 462 (1999).
3. A.D. Andradea, M.C.E. Rollemberga and J.A. Nobrega, *Process Biochem.*, **40**, 1931 (2005).
4. T.A. Davis, B. Volesky and A. Mucci, *Water Res.*, **37**, 4311 (2003).
5. B.P. Skowronska, *Aquatic Toxicol.*, **50**, 221 (2000).
6. H.B. Xue, W. Stumm and L. Sigg, *Water Res.*, **22**, 917 (1988).
7. B. Volesky and Z.R. Holant, *Biotechnol. Prog*, **11**, 235 (1995).
8. T. Saitoh, N. Nagaki, Y. Uchida and M. Hiraide, *Anal. Sci.*, **17**, 793 (2001).
9. R. Herrero, B. Cordero, P. Lodeiro, C. Rey-Castro and M.E. Sastre de Vicente, *Marine Chem.*, **99**, 106 (2006).
10. P. Lodeiro, C. Rey-Castro, J.L. Barriada, M.E. Sastre de Vicente and R. Herrero, *J. Coll. Interface Sci.*, **289**, 352 (2005).
11. A.J. Miao and W.X. Wang, *Aquatic Toxicol.*, **78**, 114 (2006).
12. K. Vijayaraghavan, J. Jegan, K. Palanivelu and M. Velan, *Chemosphere*, **60**, 419 (2005).
13. J.T. Matheickal and Q. Qiming Yu, *Bioresour. Technol.*, **69**, 223 (1999).

(*Received*: 19 March 2008; *Accepted*: 12 November 2008) AJC-7024