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## **APPENDICE**



**APPENDIX A**  
**Properties of heavy metals**

### Properties of heavy metals

#### Copper (Cu)

Atomic number	29
Atomic mass	63.546 g.mol <sup>-1</sup>
Electronegativity according to Pauling	1.9
Density	8.09 g.cm <sup>3</sup> at 20°C
Melting point	1083°C
Boiling point	2595°C
Vanderwaals radius	0.128 nm
Ionic radius	0.096 nm (+1) ; 0.069 nm (+3)
Isotopes	6
Electronic shell	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
Energy of first ionisation	743.5 kJ.mol <sup>-1</sup>
Energy of second ionisation	1946 kJ.mol <sup>-1</sup>
Standard potential	+0.522 V (Cu <sup>+</sup> / Cu) ; +0.345 V (Cu <sup>2+</sup> / Cu)
Discovered by	The ancients

Copper is a reddish metal with a face-centered cubic crystalline structure. It reflects red and orange light and absorbs other frequencies in the visible spectrum, due to its band structure, so it has a nice reddish colour. It is malleable, ductile, and an extremely good conductor of both heat and electricity. It is softer than iron but harder than zinc and can be polished to a bright finish. It is found in group Ib of the periodic table, together with silver and gold. Copper has low chemical reactivity. In moist air it slowly forms a greenish surface film called patina; this coating protects the metal from further attack.

**Cadmium (Cd)**

Atomic number	48
Atomic mass	112.4 g.mol <sup>-1</sup>
Electronegativity according to Pauling	1.7
Density	8.7 g.cm <sup>-3</sup> at 20°C
Melting point	321 °C
Boiling point	767 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.097 nm (+2)
Isotopes	15
Electronic shell	[ Kr ] 4d <sup>10</sup> 5s <sup>2</sup>
Energy of first ionisation	866 kJ.mol <sup>-1</sup>
Energy of second ionisation	1622 kJ.mol <sup>-1</sup>
Standard potential	-0.402 V
Discovered	Fredrich Stromeyer in 1817

Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides.

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing.



Lead (Pb)

Atomic number	82
Atomic mass	207.2g.mol <sup>-1</sup>
Electronegativity according to Pauling	1.8
Density	11.34 g.cm <sup>3</sup> at 20°C
Melting point	327°C
Boiling point	1755°C
Vanderwaals radius	0.154 nm
Ionic radius	0.132 nm (+2) ; 0.084 nm (+4)
Isotopes	13
Electronic shell	[Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>
Energy of first ionisation	715.4kJ.mol <sup>-1</sup>
Energy of second ionisation	1450.0 kJ.mol <sup>-1</sup>
Energy of third ionisation	3080.7 kJ.mol <sup>-1</sup>
Energy of fourth ionisation	4082.3 kJ.mol <sup>-1</sup>
Energy of fifth ionisation	6608 kJ.mol <sup>-1</sup>
Discovered by	The ancients

Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements

## **APPENDIX B**

**Solubility of heavy metals and Elemental composition in  
*Caulerpa lentillifera***

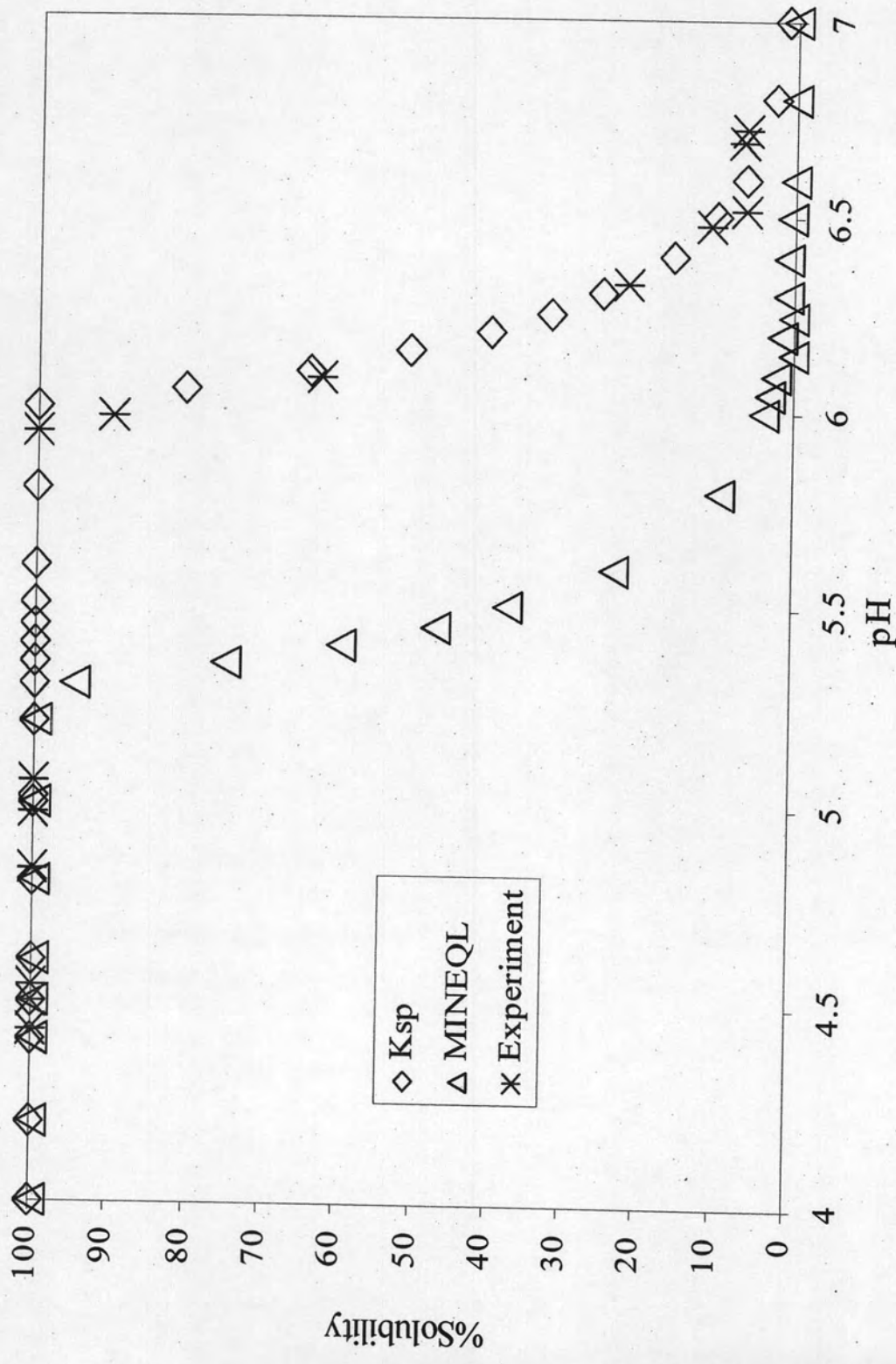


Figure A1 Solubility of copper (II) ion with initial concentration of 100 mg/l

Reference: Apiratikul, 2003

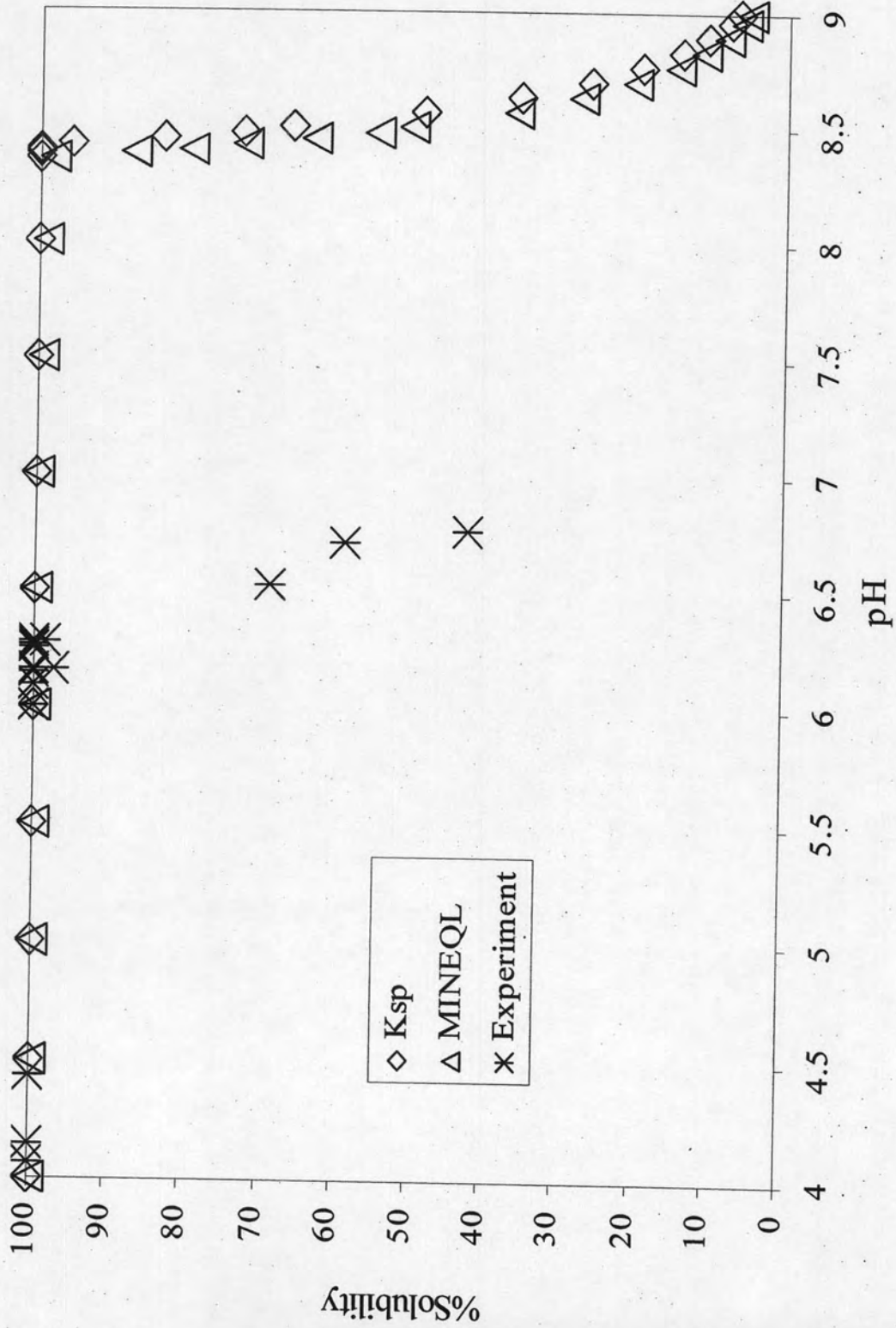


Figure A2 Solubility of cadmium (II) ion with initial concentration of 100 mg/l  
Reference: Apiratikul, 2003

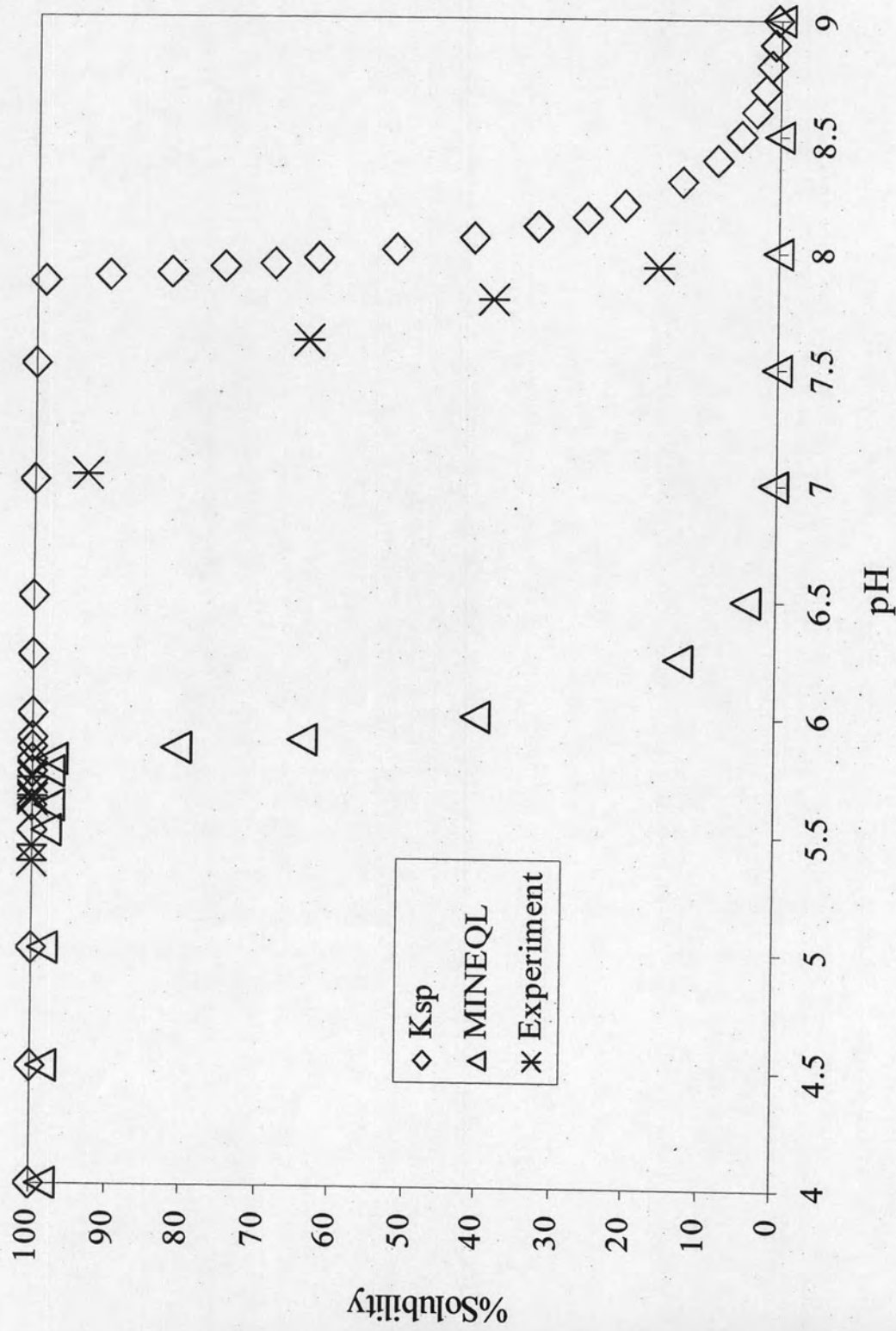


Figure A3 Solubility of lead (II) ion with initial concentration of 100 mg/l

Reference: Apiratikul, 2003



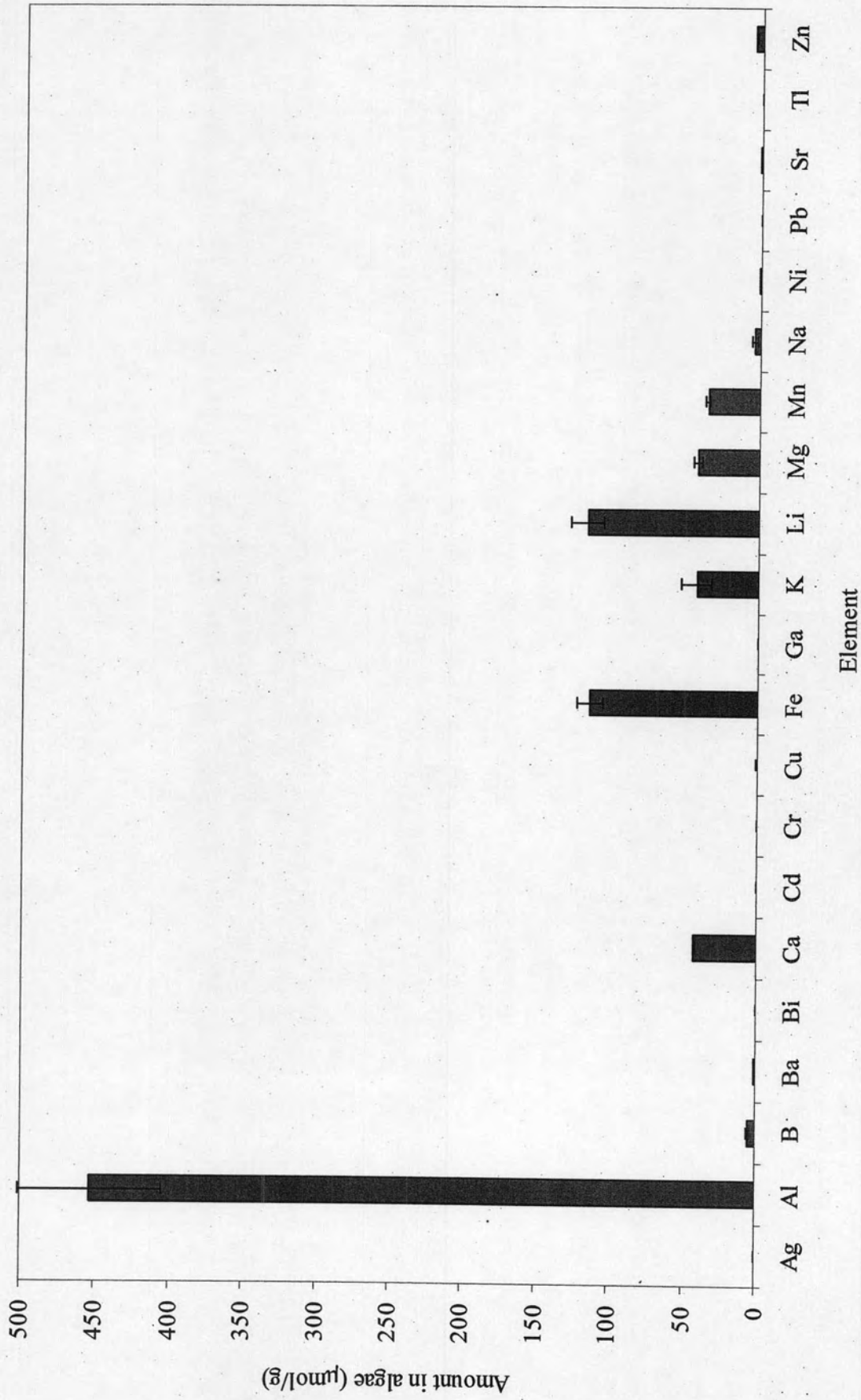


Figure A4 Elemental composition in *Caulerpa lentillifera*  
Reference: Apiratikul, 2003

## Heavy metals uptake by dried *Caulerpa lentillifera*

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**Abstract:** The adsorption of heavy metals onto biomaterial derived from the marine alga, *Caulerpa lentillifera*, was investigated. The biosorption equilibrium level was determined as a function of initial heavy metal concentration and sorbent concentrations. The metals uptake of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from aqueous solution increased with initial metals concentration and decreased with sorbent concentration. The biosorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on the biomass was correlated well ( $R^2 > 0.99$ ) with the Langmuir equation as compared to Freundlich isotherm equation under the concentration range studied. According to Langmuir isotherm, the maximum capacity ( $q_m$ ) is 0.19 and 0.18  $\text{mmol g}^{-1}$  for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions, respectively. The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data and the results were better described using the pseudo-second-order.

**Keywords:** biosorption, *Caulerpa lentillifera*, heavy metal

### 1. INTRODUCTION

Heavy metals such as copper, lead, cadmium, etc., are hazardous to the environment, and therefore, it is necessary that they are appropriately removed from the waste stream before being discharged into the environment. In fact, a total recycle of heavy metals is an ultimate goal that all industries should be aiming at. However, this might not be achieved in the near future due primarily to the limitation in available recovery technologies. Meantime, it is of primary importance that contaminated wastewater be properly treated before discharge. Heavy metal bearing effluents can be treated effectively by several methods. Conventional techniques for removing dissolved heavy metals such as chemical precipitation, carbon adsorption, ion exchange, evaporation and membrane processes [1], are only practical and cost-effective when applied to high strength wastes with heavy metal ion concentrations greater than 100 ppm [2]. Low strength heavy metal containing wastewaters generally cannot be treated successfully with such methods. Sorbent materials (biosorbents) derived from suitable biomass, on the other hand, has been shown to be capable of effective removal and recovery of heavy metal ions from wastewater streams even at low concentrations. The choice of sorbents is often the main criteria and the use of unwanted agricultural waste as sorbent has lately been introduced as a promising alternative due to economical reasons. One of the most promising biosorbents is "algae" [3]. Different algal species often had different sorption characteristics, and external factors such as pH, metal ion concentration, temperature, other metal ions, etc., were always found to influence the sorption [1].

*Caulerpa lentillifera* is a marine green macroalga cultivated as food for animals and humans, and also commonly used to treat wastewater from shrimp farms. Due to its rapid growth rate, farmers often have trouble with the over populated biomass. Turning excess *Caulerpa lentillifera* into biosorbent could be viable answer to this problem. Our previous works had focused on the biosorption of heavy metals by *Caulerpa, lentillifera* where various factors such as pH, particle size, concentration of algae and heavy metals were investigated [4]. The efficiency of various treatment techniques on the enhancement of the adsorption capacities of *Caulerpa, lentillifera* was also examined [5]. In addition, the competitive adsorption using *Caulerpa lentillifera* with multi-component heavy metal mixture aqueous solution (i.e. copper(II), cadmium(II), lead (II), and zinc(II)) was also analyzed [4]. However, all the previous works have not given details regarding the effect of initial heavy metal concentrations and also biomass doses on kinetics and equilibrium of the sorption processes. Therefore these become the main objectives of this present work. Copper and lead are selected as modeled heavy metals employed in this study.

### 2. METHODOLOGY

#### 2.1 Algal collection and preparation

*Caulerpa lentillifera* biomass was collected from Banjong Farm, Chachoengsao province. The biomass was washed with water until being fairly clean and then dried at 80°C for 12 hours and stored in dessicator.

#### 2.2 Batch biosorption studies

The biosorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions on the dried *Caulerpa lentillifera* was investigated in batch biosorption equilibrium experiments. The experiment was performed by mixing 0.5 g dried algae in 30 ml of the synthetic metal ion solutions. Analytical grade heavy metal reagents in nitrate form (UNIVAR) were used in all cases. The pH of solution was controlled by buffer (acetic acid / ammonium acetate system) at pH 5. The mixtures were mixed slowly with a rotary shaker at a rate of 150 rpm for 60 minutes at 20°C. The solid biomass was separated from the liquid phase with filter paper (Whatman No. 93 and GF/C). The initial heavy metal concentrations in the solution was varied from 0.1 to 10 mM and biomass dose was varied from 0.1 to 1.0 g. Heavy metal ion concentrations were then measured in the filtrate by atomic absorption spectrophotometer (AAS) (ZEE nit 700).

### 2.3 Determination of the adsorption capacity

The metal uptake can be calculated from:

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

where  $q$  is amount of metal uptake per unit mass of biomass ( $\text{mmol g}^{-1}$ ),  $C_i$  is initial concentration of heavy metal (mM),  $C_f$  is final concentration of heavy metal (mM),  $V$  is volume of the solution ( $\text{m}^3$ ),  $m$  is dry mass of the algae (g).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of initial metal concentration on biosorption

Initial metal concentration was found to have significant effect on the biosorption capacities of *Caulerpa lentillifera*. Figs 1 and 2 illustrate the variation in the sorption capacity ( $q$ ) as a function of initial heavy metal concentrations between 0.1 and 10 mM where it was found that a higher initial concentration provided a higher sorption capacity. This was because the initial metal ion concentration provides an important driving force to overcome all mass transfer resistances of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  between the aqueous and solid phases [6]. This is the fundamental of the equilibrium between the sorption capacity and the final heavy metal concentration in the liquid phase, and this equilibrium is a very important factor that limits the sorption process.

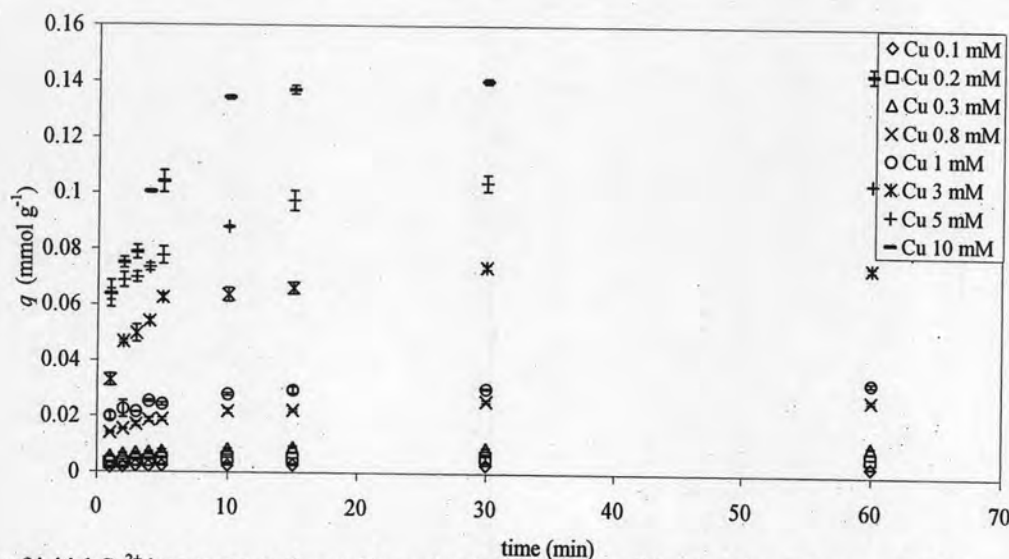


Fig.1 Effect of initial  $\text{Cu}^{2+}$  ions concentration on biosorption by *caulerpa lentillifera* (pH 5, agitation speed: 150 rpm, temperature 20°C sorbent dose 0.5 g)

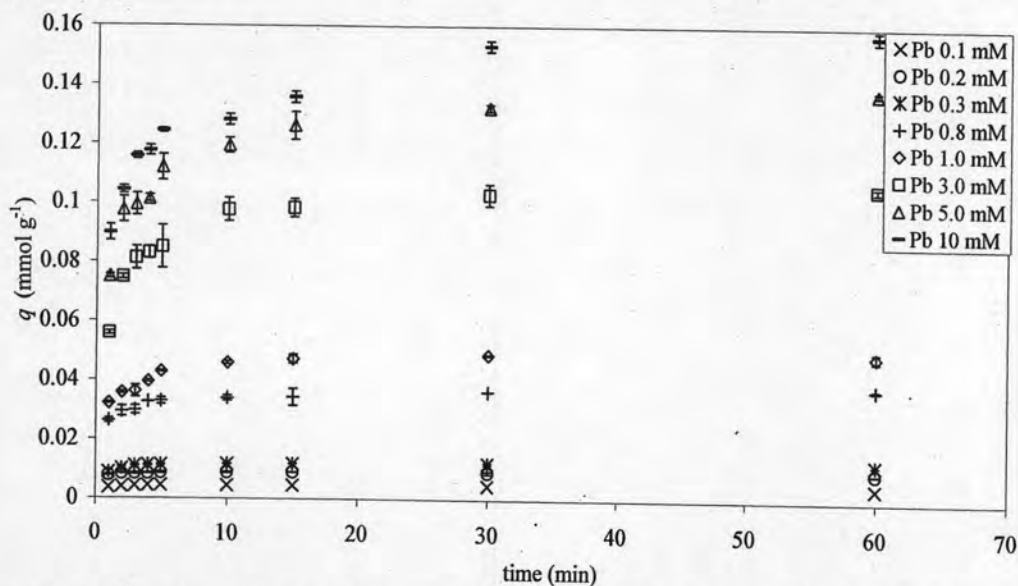


Fig.2 Effect of initial  $\text{Pb}^{2+}$  ions concentration on biosorption by *caulerpa lentillifera* (pH 5, agitation speed: 150 rpm, temperature 20°C sorbent dose 0.5 g)

E043-(P)

### 3.2 Effect of sorbent dose on biosorption

The effects of sorbent concentration on the removal of heavy metal ions from aqueous were investigated using three different sorbent concentrations. The extent of biosorption is proportional of specific area which is defined as the portion of the area available for biosorption to the total area on the sorbent [6]. Sorbent concentration was varied from 0.1 to 1g/30 mL of synthetic waste water. The effect of biomass on the sorption kinetics of heavy metal ion was studied at pH of 5.0 and 0.1 mM initial  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentrations. The results for the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  are presented in Figs. 3 and 4, respectively, which indicated that the equilibrium concentrations for both metals decreased with increasing biomass doses for a given initial  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  concentration. This result was anticipated because increasing sorbent doses provided a greater surface area which could accommodate a higher quantity of heavy metals, and due to the equilibrium limitation, the quantity of metals being adsorbed for a certain unit surface area of sorbent decreased [7,8].

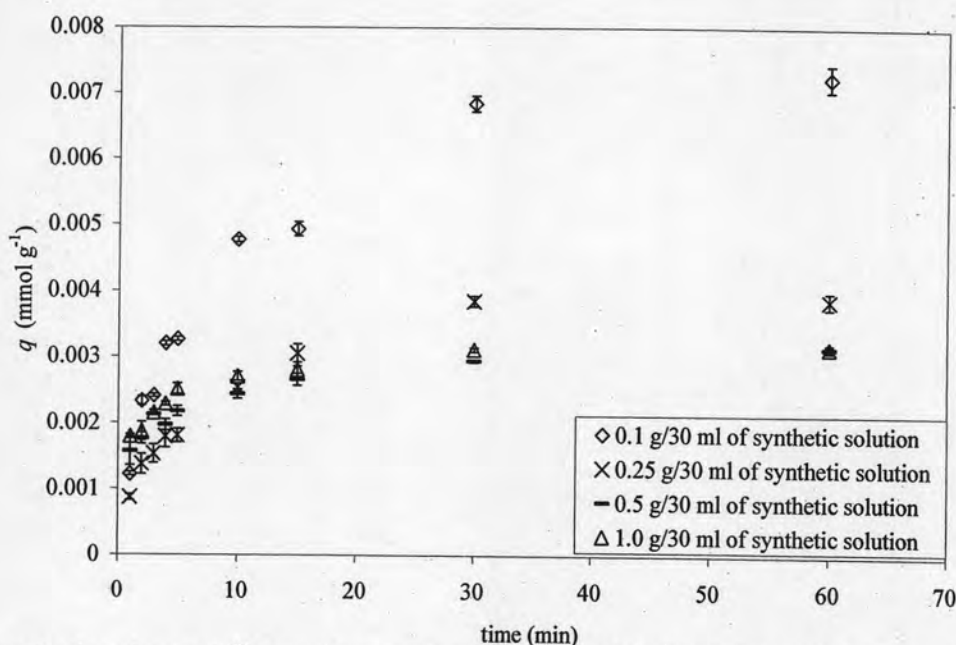


Fig.3 Effect of sorbent dose on  $\text{Cu}^{2+}$  biosorption by *caulerpa lentillifera* (pH 5, agitation speed: 150 rpm, temperature 20°C initial  $\text{Cu}^{2+}$  concentration 0.1 mM)

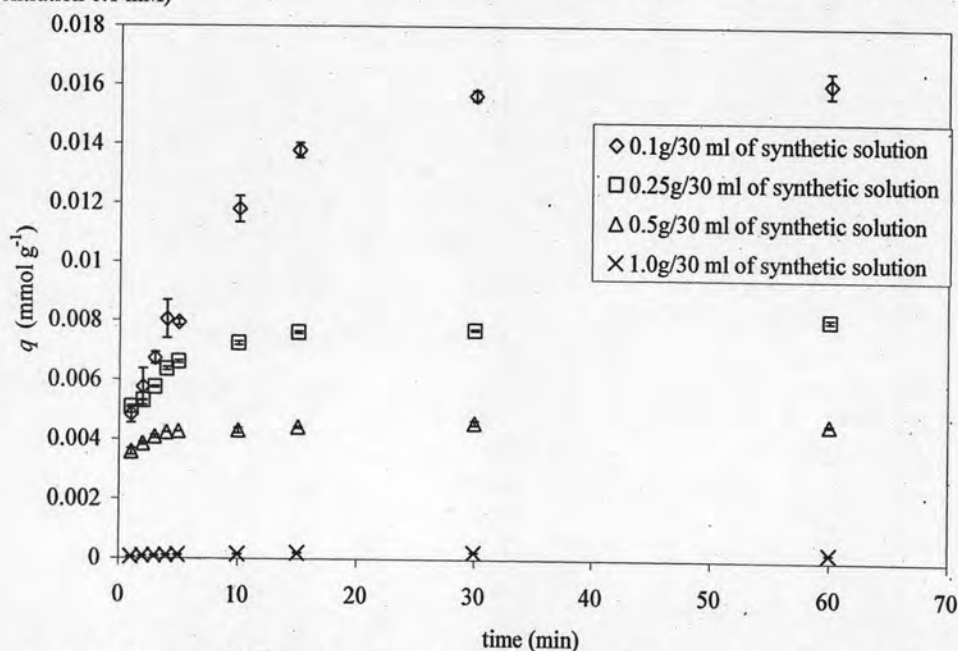


Fig.4 Effect of sorbent dose on  $\text{Pb}^{2+}$  biosorption by *caulerpa lentillifera* (pH 5, agitation speed: 150 rpm, temperature 20°C initial  $\text{Pb}^{2+}$  concentration 0.1 mM)



### 3.3 Adsorption kinetic

The kinetics of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> biosorption on the algal biomass were determined with two different kinetics models [9,10]. The first model is the pseudo-first-order rate Lagergren model, expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where  $k_1$  is the rate constant of first-order biosorption ( $\text{min}^{-1}$ ) and  $q_e$  and  $q_t$  denote the amounts of the biosorption at equilibrium and at time  $t$  ( $\text{mmol g}^{-1}$ ), respectively. Integration by applying the boundary condition  $q=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$ , gives:

$$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t \quad (3)$$

A plot of  $\ln(1 - (q/q_e))$  against  $t$  should give a straight line to confirm the applicability of the first-order kinetic model. The second model is the pseudo-second-order kinetic model [10] which is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where  $k_2$  ( $\text{g mmol min}^{-1}$ ) is the rate constant of second-order adsorption. Eq. (4) can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

The plot  $t/q_t$  versus  $t$  should give a straight line if second-order kinetics are applicable and  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot, respectively.

For evaluating the biosorption kinetics of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions, the pseudo-first-order and pseudo-second-order were used to fit the experimental data. The Lagergren first-order rate constant ( $k_1$ ) and  $q_{e,cal}$  determined from the model are presented in Table 1 along with the corresponding correlation coefficients ( $R^2$ ). However, the first-order model data did not produce a straight line indicating that this model was less appropriate. It is important to note that for a pseudo-first-order model, the correlation coefficient ( $R^2$ ) could be as low as 0.78 within the range of initial concentration employed.

By plotting  $t/q_t$  against  $t$  at different initial Cu<sup>2+</sup> and Pb<sup>2+</sup> ions concentrations, a straight line was obtained in all cases and the second-order rate constant ( $k_2$ ) and  $q_e$  values (in Eq. 5) could well be determined from the plots. The values of correlation coefficient were very high ( $R^2 > 0.995$ ) and the theoretical  $q_{e,cal}$  values at different initial Cu<sup>2+</sup> and Pb<sup>2+</sup> ions concentrations compared well with the experiments. With this finding, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions.

Table 1 Kinetic parameters for the sorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> by *Caulerpa lentillifera*

initial metals concentration (mM)	First-order kinetic model			Second-order kinetic model				
	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mmol g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mmol}^{-1} \text{min}^{-1}$ )	$q_{e,exp}$ ( $\text{mmol g}^{-1}$ )	$q_{e,cal}$ ( $\text{mmol g}^{-1}$ )	$R^2$	
Cu <sup>2+</sup>	0.1	0.046	0.7623	137.2	0.003	0.003	0.9953	
	0.2	0.053	0.9043	55.52	0.007	0.007	0.9959	
	0.3	0.041	0.8022	44.24	0.014	0.011	0.9948	
	0.8	0.080	0.9805	17.27	0.027	0.028	0.9985	
	1	0.042	0.8329	18.21	0.034	0.033	0.9981	
	3	0.143	0.9508	8.630	0.074	0.076	0.9995	
	5	0.147	0.9888	6.230	0.104	0.107	0.9994	
	10	0.012	0.8643	3.800	0.144	0.148	0.9993	
	Pb <sup>2+</sup>	0.1	0.175	0.9402	478.3	0.005	0.005	0.9999
		0.2	0.036	0.8172	142.1	0.010	0.010	0.9999
0.3		0.072	0.7801	112.2	0.126	0.013	0.9997	
0.8		0.060	0.8814	28.55	0.038	0.038	0.9994	
1		0.147	0.9874	23.83	0.049	0.050	0.9999	
3		0.097	0.9165	8.690	0.105	0.107	0.9999	
5		0.147	0.9345	5.440	0.138	0.140	0.9997	
10		0.052	0.9640	4.100	0.157	0.160	0.9998	



### 3.4 Adsorption isotherm

The two most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models [8].

Langmuir isotherm:

The Langmuir equation [12] was derived based on the assumption of monolayer sorption onto a surface a finite number of identical sites and is given by Eq. (6):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (6)$$

Eq. (6) is usually linearized to obtain the following form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \quad (7)$$

where  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $q_e$  the maximum amount of the  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions per unit weight of the biomass to form a complete monolayer on the surface bound at high  $C_e$  and  $b$  is a constant related to the affinity of binding sites.  $q_m$  represents a practical limiting biosorption capacity when the surface is fully covered  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions and assists in the comparison of biosorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments.  $q_m$  and  $b$  can be determined from the linear plot of  $C_e/q_e$  versus  $C_e$  [10]. The values of  $q_m$  and  $b$  constants and the correlation coefficient for the Langmuir isotherm are presented in Table 2.

Freundlich isotherm:

The Freundlich model has been widely adopted to characterize the adsorption experiments [13,14]. This model assumed that the uptake to metal ions occur on a heterogeneous sorbent surface [15]. The Freundlich equation is given by Eq. (8)

$$q_e = K_F C_e^{1/n} \quad (8)$$

where the parameters  $K_F$  and  $n$  can be obtained using the linear form of Eq.(8);

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where  $C_e$  is the amount of the residual metals concentration in the solution. The values of  $K_F$  and  $n$  constants, and the correlation coefficient for the Freundlich isotherm are presented in Table 2.

Table 2 Isotherm constants for the sorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  by *Caulerpa, lentillifera*

Heavy metal ion	Langmuir isotherm			Freundlich isotherm		
	$q_m$	$b$	$R^2$	$K_F$	$1/n$	$R^2$
	( $\text{mmol g}^{-1}$ )	( $\text{L mmol}^{-1}$ )				
$\text{Cu}^{2+}$	0.19	0.42	0.9901	0.02	1.03	0.9953
$\text{Pb}^{2+}$	0.18	1.32	0.9931	0.26	1.08	0.9005

The biosorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  on the biomass was correlated well ( $R^2 > 0.99$ ) with the Langmuir equation as compared to Freundlich isotherm equation under the concentration range studied.

### 4. CONCLUSION

*Caulerpa lentillifera* is a marine green macroalga cultivated as food for animals and humans, and also commonly used to treat wastewater from shrimp farms. The rapid growth of this alga requires that the excess quantity be frequently removed. Turning excess *Caulerpa lentillifera* into biosorbent could be a viable answer to this problem. For this reason, the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  removal from aqueous solutions through biomass of *Caulerpa lentillifera* may be evaluated as an environmentally friendly and extra economic treatment.

The present investigation shows that the biomass of *Caulerpa lentillifera* is an effective and inexpensive sorbent for the removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions from aqueous solution. The maximum  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  biosorption capacity has been found to be 0.19 and 0.18  $\text{mmol g}^{-1}$  of dry weight of biomass. However, adsorption capacity provided by *Caulerpa lentillifera* was still relatively low compared with other biosorbents e.g, *Chlamydomonas reinhardtii* (1.5  $\text{mmol Pb}^{2+} \text{g}^{-1}$ ) [16], *Ecklonia maxima* (1.48  $\text{mmol Cu}^{2+} \text{g}^{-1}$ , 1.17  $\text{mmol Pb}^{2+} \text{g}^{-1}$ ) [17], *Spirogyra* species (2.10  $\text{mmol Cu}^{2+} \text{g}^{-1}$ ) [18]. Further work is still needed the applicability of this biosorbent.

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