

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of buffer solution on biosorption

The solution pH was reported to be one of the most important variables governing the biosorption of metal ions (Pagnanelli et al., 2003). Previous work demonstrated that the optimum pH for the biosorption of heavy metals by *Caulerpa lentillifera* was 5 (Apiratikul and Pavasant, 2006). For the sake of experimental and operational simplification, the use of buffer solution to help control pH at 5 was considered in this work. Acetic/acetate buffer was selected to control the pH of the metal solution. The pH of metal solution was maintained by varying the acetate concentration between 10 and 200 mM (molar ratio of acetic:acetate ~ 1:2) at the metal concentration range of 0.1 and 3 mM. The results for the sorptions of Cu^{2+} , Cd^{2+} and Pb^{2+} are presented in Table 4.1, which shows that pH in these experiments was more stable with the presence of acetic/acetate buffer. Increasing the amount of buffer seemed to strengthen the stability of the pH in the system, however, the sorption capacities were found to decrease accordingly (Fig. 4.1). This was because the binding sites on the biosorbent were limited and the cations from buffer solution could compete with the metals for the free binding sites (Kuyucak and Volesky, 1989). The selection of buffer concentration was therefore a trade-off between the stability of the pH and the sorption capacity of the metals. In this work, the optimal point for the compensation between the two occurred at the buffer concentration of 15 mM. Thus, this optimal acetate concentration of 15 mM was selected as the test condition for the subsequent experiments.

4.2 Effect of initial heavy metal concentrations on biosorption

Initial metal concentration was found to have significant effects on the biosorption capacities of *Caulerpa lentillifera*. Fig. 4.2 illustrates the variation in the sorption capacity (q) as a function of initial heavy metal concentrations (from 0.1 and 10 mM) where it was found that a higher initial concentration provided a higher sorption capacity. As sorption is an equilibrium controlled process and therefore increasing the initial metal

concentration effectively shifted the equilibrium to the zone where the final metal concentration was higher. Therefore, although the sorption capacity increased, the removal percentage at the condition of higher initial concentration might be lower than that at lower initial concentration.

There have been several reports on the use of different kinetic models to adjust the experimental data of heavy metals sorption on biomass. For this work, the kinetics of Cu^{2+} , Cd^{2+} and Pb^{2+} biosorption by *Caulerpa lentillifera* were determined with two common kinetic models (Parab et al., 2005). The first model is the pseudo-first-order rate Lagergren model where the rate of occupation of sorption sites was assumed to be proportional to the number of unoccupied sites (Cruz, et al 2004), expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4.1)$$

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

$$\ln\left(1 - \frac{q}{q_e}\right) = -k_1 t \quad (4.2)$$

Should this first order kinetic model be applicable to the experimental results, a plot of $\ln(1-(q/q_e))$ against t must give a straight line

Alternatively, the observed kinetics might be described assuming that the rate of occupation of sorption sites was proportional to the square of the number of unoccupied sites. This second model is known as the pseudo-second-order kinetic model (Ho and McKay, 1999) which is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4.3)$$

where k_2 ($\text{g mmol}^{-1} \text{min}^{-1}$) is the rate constant of the second-order sorption model. Eq. (4.3) can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4.4)$$

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

For evaluating the biosorption kinetics of Cu^{2+} , Cd^{2+} and Pb^{2+} ions, both 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 non-linear regression are presented in Table 4.2 along with the corresponding correlation coefficients (R^2). The results revealed that, for the pseudo-first-order model, the correlation coefficient (R^2) could be as low as 0.87 within the range of initial concentration employed. On the other hand, by plotting t/q_t against t at different initial Cu^{2+} , Cd^{2+} and Pb^{2+} ion concentrations, straight lines were obtained for all cases and the second-order rate constant (k_2) and q_e values 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^{2+} , Cd^{2+} and Pb^{2+} ion concentrations compared well with the experiments. With this finding, the pseudo-second-order kinetic model was concluded to be a better model that described the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ions. The data demonstrated that the rate constant of the pseudo-second-order kinetic model decreased with an increase in the initial metal concentration, especially at the highest initial concentration. The reason for the decrease in the rate constant with increasing metal ion concentrations may be the competition among metal ions for the same binding sites on biosorbent surfaces.

4.3 Effect of biomass doses on biosorption

The effects of biomass dose on the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ions from aqueous solution were investigated by varying the quantity of biomass in the metal ions solutions. The results for the sorption of Cu^{2+} , Cd^{2+} and Pb^{2+} are presented in Figs. 4.3 and 4.4, which indicated that the sorption capacities for all metals decreased with increasing biomass doses for a given initial metal 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 sorbed for a certain unit surface area of sorbent decreased (Nuhoglu and

Oguz 2003). The removal efficiency of the metal also increased as there were higher surface and volume for the sorption at higher biosorbent dosage (Malkoc, 2006). Kinetics studies were carried out for the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} as a function of contact time at various biomass doses and the results are summarized in Table 4.3.

4.4 Effect of agitation rate on biosorption

The effects of agitation rate on the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} from aqueous solutions were investigated using four different agitation rates. The results for the sorptions of Cu^{2+} , Cd^{2+} and Pb^{2+} are shown in Fig. 4.5 where the sorption capacities of Cu^{2+} , Cd^{2+} and Pb^{2+} increased with agitation rates. This suggested that the transport of metal ions from the solution to the surface of sorbent increased with an increase in agitation rate (Malkoc, 2006). The sorption capacity reached a near constant level at 150 rpm where a further increase to 200 rpm did not show significant improvement on the sorption kinetic profile for all three metals.

The external mass transfer of heavy metals from the bulk solution to the surface of the biosorbent depended on two quantities, i.e. mass transfer coefficient (K) and the difference in the concentrations in the bulk liquid and at the surface, according to the following mass transfer equation:

$$\text{MASS TRANSFER RATE} = K(C_1 - C_2) \quad (4.5)$$

where K is convection mass transfer, C_1 is surface concentration and C_2 is concentration in the bulk fluid stream. As the mixture was shaken, the liquid film resistance became thinner, and biosorbent particles moved rapidly in the solution, and this increased the external mass transfer rate of K in Eq. (4.5). This led to a faster sorption rate as observed from the results in Fig. 4.5. This agreed with the results described by (Argun et al., 2006).

The results suggested that a shaking rate in the range from 150 to 200 rpm was sufficient to assure that all the binding sites were made readily available for metals uptake, so the effect of external film diffusion above this shaking rate on biosorption could be ignored in any engineering analysis (Cruz et al 2004). Kinetic studies were carried out for the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} at various agitation rates (0, 50, 150 and 200 rpm) and the results are shown in Table 4.4. However, an agitation rate of 150 rpm was chosen for subsequent experiment due to economical reasons.

4.5 Effect of temperature on biosorption

The effects of temperature on the biosorption of Cu^{2+} , Cd^{2+} and Pb^{2+} ions were investigated under three different conditions. These results are presented in Figs. 4.6 and 4.7. The data demonstrated that the sorption capacity of the microalgae for Cu^{2+} and Pb^{2+} ions did not significantly change with temperature. In other words, the biosorption of Cu^{2+} and Pb^{2+} on the algal biomass appeared to be temperature independent over the temperature range tested. The sorption capacity of the biomass for Cd^{2+} ions has been found to increase with an increase in temperature from 20 to 40°C. This result suggested that the sorption of heavy metal by this dried biomass was an endothermic process.

The kinetic factors of Cu^{2+} , Cd^{2+} and Pb^{2+} ions on biosorption are presented in Table 4.5. For Cd^{2+} , the rate constant of the pseudo-second-order kinetic model increased with an increase in temperature which may be due to an increase in the number of active surface sites available for biosorption and a decrease in the thickness of the boundary layer surrounding the biosorbent with temperature, so that the mass transfer resistance of sorbate in the boundary layer decreased (Meena et al., 2005). However, the rate constants of the pseudo-second-order kinetic models for Cu^{2+} and Pb^{2+} ions did not significantly change with temperature. The biosorption of Cu^{2+} and Pb^{2+} on the algal biomass appeared to be temperature independent over the temperature range tested.

4.6 Sorption equilibrium modeling

Equilibrium sorption isotherms are of fundamental important in the design of sorption systems since they indicate how metal ions are partitioned between the biosorbent and liquid phases at equilibrium as a function of metal concentration. To create the equilibrium data, experiments were performed with heavy metal ions concentration ranged from 0.1 to 1.0 mM at a fixed biosorbent dose and pH for each heavy metal. The two most widely accepted surface sorption models for single-solute systems are Langmuir and Freundlich models (Parab et al., 2005).

With the resulting sorption isotherms of Cu^{2+} , Cd^{2+} and Pb^{2+} as shown in Fig. 4.8, Freundlich and Langmuir sorption constants could be determined and presented in Table 4.6. For the Langmuir isotherm model, the maximum capacities (q_{max}) were found to be 0.19, 0.11 and 0.18 mmol g^{-1} for Cu^{2+} , Cd^{2+} and Pb^{2+} on the algal biomass. The

maximum sorption capacity slightly increased with an increase in sorption temperature. Similar trends were observed for sorption affinity (b), indicating that the affinity of the alga biomass for Cu^{2+} , Cd^{2+} and Pb^{2+} ions increased as the temperature of sorption increased. These results were due to an increase in kinetic energy of the biosorbent particles at high temperature, which in turn increased the frequency of collisions between the biosorbent and metal ions and, thus, enhanced biosorption of metals on the surface of the biosorbent (Nacèra and Aicha 2006)

In view of the results presented in Table 4.6, the isotherms appeared to follow the Langmuir model more closely than the Freundlich model at all temperatures studied. However, the Freundlich sorption model also seemed to agree well with the experimental data. K_f , one of Freundlich constants has been used as a relative measure of sorption capacity, n the other Freundlich constant is related to intensity of sorption. The values of K_f increased with the rise in temperature and the highest K_f values were determined as 0.05, 0.02 and 0.09 mmol g^{-1} at 40 °C for Cu^{2+} , Cd^{2+} and Pb^{2+} , respectively.

As metal concentrations increased, the removal efficiencies decreased from 69.91 to 27.40% for Cu^{2+} , 26.95 to 11.13% for Cd^{2+} and 90.90 to 29.47% for Pb^{2+} . the result are show in Table 4.2. Thus, increasing the initial heavy metal concentrations in the solutions decreased the removal efficiency. It is that a given mass of biosorbent material has a finite number of biosorption sites, and that as metal concentration increased, these sites became saturated. There is some metal concentration that produces the maximum sorption for a given biosorbent mass and thereafter adding more metal cannot increase sorption because no more sites are available all are occupied (Argun et al., 2006).

4.7 Determination of thermodynamic constants of biosorption

Changes in the Gibbs free energy of the biosorption process can be calculated using equilibrium constants (b) obtained from Langmuir model. The dependency of b with temperature can be used to estimate enthalpy (ΔH), entropy (ΔS) and (ΔG) associated with the biosorption process using the following expression:

$$\ln b = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4.6)$$

where R is the ideal gas constant ($1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K).

The plot of $\ln b$ with $1/T$ yielded a straight line from which ΔH equals 0.163, 3.732 and 3.409 kcal mol⁻¹ for Cu²⁺, Cd²⁺ and Pb²⁺, respectively, and ΔS of 7.60×10^{-4} , 1.30×10^{-2} and 1.23×10^{-2} cal mol⁻¹ K⁻¹, accordingly (Fig. 4.10). The positive value of ΔH confirmed the endothermic character of biosorption on Cu²⁺, Cd²⁺ and Pb²⁺ by *Caulerpa lentillifera* system. ΔS was positive indicating the redistribution of energy state between the sorbate and the biosorbent. In other words, before sorption, the heavy metal ions near the surface of the biosorbent could be more ordered than those in the subsequent sorption state. As a result, the distribution of rotational and translational energy among a small number of molecules increased as the biosorption process proceeded by producing a positive value of ΔS at the solid-solution interface during the process of biosorption. The Gibbs free energies of biosorption are presented in Table 4.6. The Gibbs free energy for all three metals shows that the biosorption process was thus likely to occur spontaneously at normal and high temperatures because $\Delta G > 0$ and the degree of spontaneity of the reaction increased with increasing temperature.

4.8 Ionic exchange mechanism

The existence of ion-exchange mechanism during the metal sorption by *Caulerpa lentillifera* was investigated in this work by measuring the releases of light metal ions (Li⁺, Ca²⁺, K⁺, Mg²⁺, and Al³⁺) from this sorbent after the sorption of the heavy metals. The net release of light metal ions due to the sorption process was calculated by subtracting the amount of these cations released under controlled experiments where the alga was washed with deionized water from the amount of cations measured in the solution after metal sorption. The results in Table 4.7 indicated a significant release of light metal ions from biosorbent due to the uptakes of Cu²⁺, Cd²⁺ and Pb²⁺. This could potentially indicate the displacement of these cations by the heavy metal ions. It should be noted here that these light metals were found to constitute the biomass from the work of Apiratikul (2003) (see quoted results in Figure A4 in Appendix B). It appears that there was more Ca²⁺ released than the other cations which was consistent with the fact that calcium was the major exchangeable cation in the composition of *Caulerpa lentillifera*.

To evaluate for the magnitude of ion exchange process, % ion exchange is proposed as an indicator where:

$$\% \text{ion exchange} = \frac{\text{Release of light metal}}{\text{Heavy metals sorption capacity}} \times 100 \quad (4.7)$$

The results of %ion exchange as summarized in Table 4.7 demonstrated that the percent of ion-exchange of Cu^{2+} , Cd^{2+} and Pb^{2+} were equal to 88.9, 85.7 and 1.62, respectively. Thus, ion-exchange was an important mechanism involved with the uptakes of Cu^{2+} and Cd^{2+} by *Caulerpa lentillifera* whereas the sorption of Pb^{2+} might be due to other mechanisms. However, Table 4.7 (Fig. 4.9) reveals that the level of ion exchange decreased with an increase in the initial metal concentration which meant that there must also be some other mechanisms responsible for the sorption of Cu^{2+} and Cd^{2+} . Ion exchange seemed to be limited by the number of light cations in the algal matrix and therefore, at high metal concentration, the number of ion exchange was limited by the availability of the light ion in the biomass. However, a lower %ion exchange suggested that, at high metal concentration, metal sorption still took place but at a lower extent and the biosorption due to other mechanisms such as adsorption-complexation emerged as a significant sorption process.

Table 4.1 Effect of acetic/acetate buffer solution on biosorption by *Caulerpa lentillifera*

[CH ₃ COONH ₄] (mM)	Cu ²⁺ 0.1 mM		Cd ²⁺ 0.1 mM		Pb ²⁺ 0.1 mM	
	pH (before)	pH (after)	pH (before)	pH (after)	pH (before)	pH (after)
0	5.05	7.12	5.13	7.03	5.11	6.86
15	4.54	4.93	4.51	4.98	4.47	4.98
10	4.67	4.87	4.56	4.80	4.64	4.91
30	4.64	4.72	4.65	4.71	4.67	4.74
40	4.67	4.67	4.67	4.63	4.69	4.74
50	4.70	4.71	4.71	4.70	4.71	4.71

[CH ₃ COONH ₄] (mM)	Cu ²⁺ 3 mM		Cd ²⁺ 3 mM		Pb ²⁺ 3 mM	
	pH (before)	pH (after)	pH (before)	pH (after)	pH (before)	pH (after)
0	5.03	5.30	5.16	6.60	5.02	5.51
10	4.55	4.96	4.84	5.30	4.66	4.93
15	4.64	4.83	4.87	5.17	4.75	4.91
50	4.86	4.78	4.92	4.94	4.87	4.85
100	4.97	4.87	5.00	4.96	4.99	4.91
200	5.05	4.93	5.08	5.00	5.06	4.96

* before = before sorption, after = after sorption

Table 4.2 Kinetic parameters for the sorption of metals by *Caulerpa lentillifera*: effects of initial metal concentrations

initial metals concentration (mM)	Experimental		First-order kinetic model			Second-order kinetic model		
	$q_{e,exp}$ (mmol g ⁻¹)	% removal	k_1 (min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2	k_2 (g mmol ⁻¹ min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
Cu²⁺								
0.1	3.15×10^{-3}	69.91	0.499	2.71×10^{-3}	0.8848	137.2	3.23×10^{-3}	0.9953
0.2	6.55×10^{-3}	65.97	0.418	5.58×10^{-3}	0.9016	55.52	6.70×10^{-3}	0.9959
0.3	1.05×10^{-2}	66.05	0.632	8.73×10^{-2}	0.8875	44.24	1.05×10^{-2}	0.9948
0.8	2.68×10^{-2}	69.95	0.504	2.33×10^{-2}	0.8941	17.27	2.75×10^{-2}	0.9985
1	3.30×10^{-2}	68.52	0.787	2.83×10^{-2}	0.8923	18.21	3.34×10^{-2}	0.9981
3	7.41×10^{-2}	46.20	0.501	6.85×10^{-2}	0.9617	8.630	7.60×10^{-2}	0.9995
5	1.04×10^{-1}	37.07	0.653	9.28×10^{-2}	0.8706	6.230	1.07×10^{-1}	0.9994
10	1.44×10^{-1}	27.40	0.795	1.38×10^{-1}	0.8954	3.800	1.48×10^{-1}	0.9993
Cd²⁺								
0.1	1.37×10^{-3}	26.95	0.932	1.22×10^{-3}	0.9170	662.9	1.39×10^{-3}	0.9998
0.2	2.81×10^{-3}	27.15	0.465	2.70×10^{-3}	0.9589	285.7	2.89×10^{-3}	0.9997
0.3	3.98×10^{-3}	24.28	0.608	3.40×10^{-3}	0.8984	124.3	4.04×10^{-3}	0.9980
0.8	9.43×10^{-3}	21.70	0.701	8.43×10^{-3}	0.9465	73.34	9.63×10^{-3}	0.9992
1	1.26×10^{-2}	22.00	0.586	1.12×10^{-2}	0.9197	45.80	1.29×10^{-2}	0.9992
3	2.71×10^{-2}	15.93	0.308	2.29×10^{-2}	0.8639	9.630	2.83×10^{-2}	0.9944
5	3.54×10^{-2}	12.26	0.251	3.20×10^{-2}	0.9489	7.542	3.73×10^{-2}	0.9985
10	6.67×10^{-2}	11.13	0.343	5.96×10^{-2}	0.9008	5.313	6.97×10^{-2}	0.9981
Pb²⁺								
0.1	3.57×10^{-3}	90.90	1.534	4.34×10^{-3}	0.9814	478.3	4.62×10^{-3}	0.9999
0.2	9.58×10^{-3}	94.82	1.973	8.69×10^{-3}	0.9784	142.1	9.58×10^{-3}	0.9999
0.3	1.26×10^{-2}	91.95	1.168	1.16×10^{-2}	0.9814	112.2	1.26×10^{-2}	0.9997
0.8	3.78×10^{-2}	94.67	1.212	3.41×10^{-2}	0.9599	28.55	3.81×10^{-2}	0.9994
1	4.91×10^{-2}	83.83	0.840	4.55×10^{-2}	0.9348	23.83	4.98×10^{-2}	0.9999
3	1.05×10^{-1}	62.55	0.676	9.76×10^{-2}	0.9634	8.690	1.07×10^{-1}	0.9999
5	1.38×10^{-1}	47.42	0.700	1.24×10^{-1}	0.9408	5.440	1.40×10^{-1}	0.9997
10	1.57×10^{-1}	29.47	0.761	1.38×10^{-1}	0.9243	4.100	1.60×10^{-1}	0.9998

Table 4.3 Kinetic parameters for the sorption of metals by *Caulerpa lentillifera*: effect of sorbent doses

Sorbent dose (g)	Experimental		First-order kinetic model			Second-order kinetic model		
	$q_{e,exp}$ (mmol g ⁻¹)	% removal	k_1 (min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2	k_2 (g mmol ⁻¹ min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
Cu²⁺ [0.1mM]								
0.10	7.23×10^{-3}	34.86	0.134	6.78×10^{-3}	0.9586	137.2	8.00×10^{-3}	0.9951
0.25	3.86×10^{-3}	46.65	0.150	3.71×10^{-3}	0.9575	55.52	4.23×10^{-3}	0.9957
0.50	3.15×10^{-3}	69.91	0.499	2.71×10^{-3}	0.8848	44.24	3.23×10^{-3}	0.9982
1.00	3.15×10^{-3}	74.43	0.564	2.85×10^{-3}	0.9167	17.27	3.23×10^{-3}	0.9995
Cd²⁺ [0.1mM]								
0.10	3.20×10^{-3}	12.05	0.186	2.99×10^{-3}	0.9793	63.63	3.43×10^{-3}	0.9983
0.25	2.03×10^{-3}	18.92	0.335	1.79×10^{-3}	0.9144	156.2	2.13×10^{-3}	0.9965
0.50	1.37×10^{-3}	26.95	0.932	1.23×10^{-3}	0.9171	662.6	3.19×10^{-3}	0.9998
1.00	1.07×10^{-3}	39.96	0.473	9.80×10^{-4}	0.9176	560.5	1.10×10^{-3}	0.9996
Pb²⁺ [0.1mM]								
0.10	1.60×10^{-3}	66.31	0.178	1.54×10^{-2}	0.9583	13.55	1.73×10^{-3}	0.9999
0.25	8.10×10^{-3}	86.58	0.738	7.32×10^{-3}	0.9232	103.1	8.21×10^{-3}	0.9999
0.50	4.59×10^{-3}	90.90	1.534	4.34×10^{-3}	0.9814	478.3	4.63×10^{-3}	0.9997
1.00	2.35×10^{-3}	94.20	0.108	2.16×10^{-3}	0.9783	401.3	2.51×10^{-3}	0.9994
Cu²⁺ [3 mM]								
0.10	1.20×10^{-1}	15.25	0.506	1.80×10^{-1}	0.9033	4.149	1.24×10^{-1}	0.9989
0.25	8.81×10^{-2}	27.59	0.468	8.15×10^{-2}	0.9446	6.868	9.06×10^{-2}	0.9996
0.50	7.41×10^{-2}	46.20	0.501	6.85×10^{-2}	0.9617	8.630	7.60×10^{-2}	0.9995
1.00	4.22×10^{-2}	55.07	0.586	3.88×10^{-2}	0.9382	17.83	4.31×10^{-2}	0.9998
Cd²⁺ [3 mM]								
0.10	6.63×10^{-2}	7.884	0.131	6.45×10^{-2}	0.9809	1.740	7.59×10^{-2}	0.9908
0.25	3.33×10^{-2}	9.930	0.224	3.10×10^{-2}	0.9550	6.831	3.58×10^{-2}	0.9968
0.50	2.71×10^{-2}	15.93	0.309	2.29×10^{-2}	0.8639	9.630	2.83×10^{-2}	0.9944
1.00	1.76×10^{-2}	21.17	0.740	1.56×10^{-2}	0.9485	37.65	1.79×10^{-2}	0.9988
Pb²⁺ [3 mM]								
0.10	1.27×10^{-1}	14.37	0.378	1.17×10^{-1}	0.9374	3.758	1.31×10^{-1}	0.9995
0.25	1.11×10^{-1}	32.01	0.446	1.02×10^{-1}	0.9406	5.136	1.13×10^{-1}	0.9998
0.50	1.05×10^{-1}	62.35	0.676	0.98×10^{-1}	0.9634	8.690	1.07×10^{-1}	0.9999
1.00	7.07×10^{-2}	81.84	0.624	6.72×10^{-2}	0.9731	14.75	7.19×10^{-2}	0.9999

Table 4.4 Kinetic parameters for the sorption of metals by *Caulerpa lentillifera*: effect of agitation rates

Agitation rate (rpm)	Experimental		First-order kinetic model		Second-order kinetic model		
	$q_{e,exp}$ (mmol g ⁻¹)	k_1 (min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2	k_2 (g mmol ⁻¹ min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
Cu²⁺ [0.1mM]							
0	2.86×10^{-3}	0.068	2.78×10^{-3}	0.9457	26.84	3.27×10^{-3}	0.9986
50	2.94×10^{-3}	0.072	2.85×10^{-3}	0.9570	27.16	3.37×10^{-3}	0.9462
150	3.15×10^{-3}	0.444	2.74×10^{-3}	0.8816	134.1	3.23×10^{-3}	0.9626
200	3.17×10^{-3}	0.445	2.90×10^{-3}	0.8464	167.6	3.27×10^{-3}	0.9995
Cd²⁺ [0.1mM]							
0	1.31×10^{-3}	0.331	1.19×10^{-3}	0.8559	284.3	1.36×10^{-3}	0.9989
50	1.35×10^{-3}	0.485	1.22×10^{-3}	0.7352	395.4	1.39×10^{-3}	0.9998
150	1.37×10^{-3}	0.932	1.22×10^{-3}	0.6981	662.9	1.39×10^{-3}	0.9988
200	1.37×10^{-3}	1.576	1.29×10^{-3}	0.7668	1590	1.38×10^{-3}	0.9999
Pb²⁺ [0.1mM]							
0	4.39×10^{-3}	1.208	3.66×10^{-3}	0.5111	142.4	4.46×10^{-3}	0.9986
50	4.50×10^{-3}	0.993	3.98×10^{-3}	0.7107	190.1	4.57×10^{-3}	0.9995
150	4.59×10^{-3}	1.534	4.34×10^{-3}	0.8104	478.3	4.63×10^{-3}	0.9999
200	4.59×10^{-3}	1.770	4.39×10^{-3}	0.7298	708.8	4.62×10^{-3}	1.0000

Table 4.5 Kinetic parameters for the sorption of metals by *Caulerpa lentillifera*: effect of temperature

Temperature (°C)	Experimental	First-order kinetic model			Second-order kinetic model		
	$q_{e,exp}$ (mmol g ⁻¹)	k_1 (min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2	k_2 (g mmol ⁻¹ min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
Cu ²⁺ [0.1mM]							
20	3.15×10^{-3}	0.067	2.79×10^{-3}	0.9769	137.2	3.32×10^{-3}	0.9982
30	3.22×10^{-3}	0.076	2.79×10^{-3}	0.9852	142.5	3.30×10^{-3}	0.9986
40	3.27×10^{-3}	0.070	2.83×10^{-3}	0.9253	151.9	3.34×10^{-3}	0.9984
Cd ²⁺ [0.1mM]							
20	1.37×10^{-3}	0.108	1.22×10^{-3}	0.9951	162.9	1.39×10^{-3}	0.9998
30	1.73×10^{-3}	0.073	1.62×10^{-3}	0.9748	123.0	1.74×10^{-3}	0.9999
40	2.42×10^{-3}	0.062	2.00×10^{-3}	0.9734	209.3	2.47×10^{-3}	0.9981
Pb ²⁺ [0.1mM]							
20	4.59×10^{-3}	0.175	4.34×10^{-3}	0.9402	422.6	4.63×10^{-3}	0.9999
30	4.67×10^{-3}	0.128	4.41×10^{-3}	0.9592	466.8	4.71×10^{-3}	0.9999
40	4.73×10^{-3}	0.099	4.42×10^{-3}	0.9718	478.3	4.76×10^{-3}	0.9999
Cu ²⁺ [3 mM]							
20	7.41×10^{-2}	0.143	6.85×10^{-2}	0.9508	8.630	7.60×10^{-2}	0.9995
30	7.35×10^{-2}	0.007	6.84×10^{-2}	0.6753	11.78	7.43×10^{-2}	0.9995
40	7.68×10^{-2}	0.203	7.34×10^{-2}	0.9422	12.33	7.83×10^{-2}	0.9998
Cd ²⁺ [3 mM]							
20	2.71×10^{-2}	0.065	2.29×10^{-2}	0.9830	9.629	2.83×10^{-2}	0.9944
30	4.86×10^{-2}	0.091	4.48×10^{-2}	0.7692	15.81	4.98×10^{-2}	0.9957
40	5.20×10^{-2}	0.105	4.82×10^{-2}	0.9619	11.41	5.30×10^{-2}	0.9998
Pb ²⁺ [3 mM]							
20	1.05×10^{-1}	0.097	9.76×10^{-1}	0.9165	8.690	1.07×10^{-1}	0.9999
30	1.12×10^{-1}	0.127	1.04×10^{-1}	0.9791	8.661	1.14×10^{-1}	0.9999
40	1.14×10^{-1}	0.027	1.06×10^{-1}	0.9742	9.402	1.16×10^{-1}	0.9999

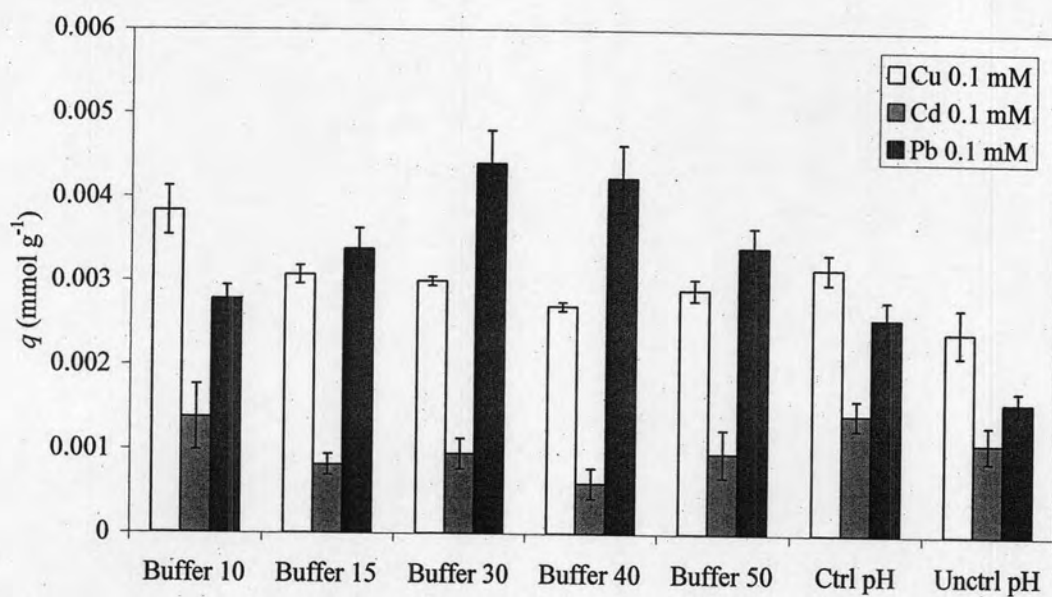
Table 4.6 Freundlich and Langmuir sorption constants associated with sorption isotherms of Cu²⁺, Cd and Pb²⁺ ions by *Caulerpa lentillifera* at different temperatures

Heavy metal ion	Temperature (°C)	Langmuir isotherm			Freundlich isotherm			
		q_m (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	ΔG (cal/mol)	K_F	$1/n$	R^2
Cu ²⁺	20	0.19	0.42	0.9901	-59.26	0.02	1.03	0.9953
	30	0.20	0.43	0.9740	-66.88	0.05	0.76	0.9495
	40	0.21	0.46	0.9521	-74.48	0.05	0.75	0.9267
Cd ²⁺	20	0.11	0.15	0.9967	-90.76	0.02	0.92	0.8883
	30	0.11	0.29	0.9543	-221.25	0.02	0.59	0.9611
	40	0.11	0.59	0.9941	-351.73	0.02	0.70	0.9477
Pb ²⁺	20	0.18	1.32	0.9931	-179.31	0.26	1.08	0.9005
	30	0.18	1.74	0.9973	-301.81	0.08	0.59	0.9611
	40	0.18	1.92	0.9945	-424.31	0.09	0.55	0.8020

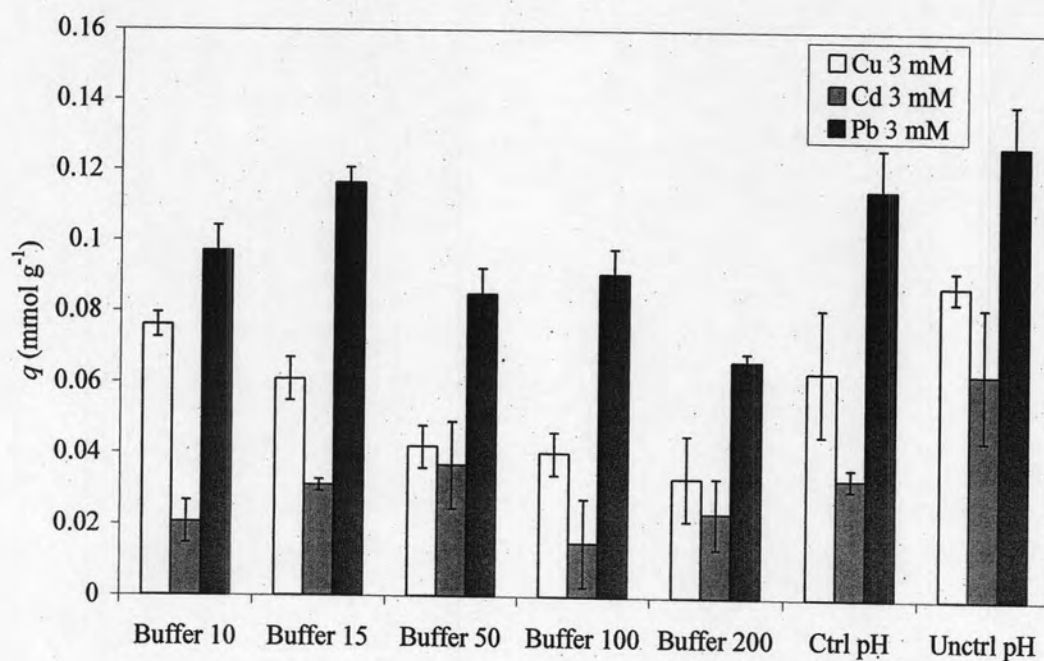
Table 4.7 Release of light metal ions after sorption on *Caulerpa lentillifera* at equilibrium

Heavy metal concentration (mM)	Equilibrium sorption capacity (meq g ⁻¹)	Equilibrium ionic exchange of light metal ions released (meq g ⁻¹) ^a					
		Li ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	% Ion-exchange
[Cu²⁺]							
0.1	5.00 × 10 ⁻³	0	8.80 × 10 ⁻⁴	1.80 × 10 ⁻³	1.61 × 10 ⁻³	0	85.71
0.2	1.15 × 10 ⁻²	0	8.72 × 10 ⁻⁴	1.80 × 10 ⁻³	7.18 × 10 ⁻³	0	85.15
0.3	2.00 × 10 ⁻²	0	8.69 × 10 ⁻⁴	1.80 × 10 ⁻³	1.38 × 10 ⁻²	0	82.19
0.8	6.06 × 10 ⁻²	0	8.65 × 10 ⁻⁴	1.02 × 10 ⁻³	4.22 × 10 ⁻²	0	72.74
1	7.12 × 10 ⁻²	0	8.90 × 10 ⁻⁴	1.71 × 10 ⁻³	4.42 × 10 ⁻²	0	65.64
3	1.54 × 10 ⁻²	0	8.77 × 10 ⁻⁴	1.72 × 10 ⁻³	9.68 × 10 ⁻²	0	64.60
5	2.01 × 10 ⁻¹	0	8.67 × 10 ⁻⁴	1.70 × 10 ⁻³	9.83 × 10 ⁻²	0	50.16
10	2.82 × 10 ⁻¹	0	8.92 × 10 ⁻⁴	1.70 × 10 ⁻³	1.10 × 10 ⁻¹	0	56.72
[Cd²⁺]							
0.1	2.74 × 10 ⁻³	3.16 × 10 ⁻⁴	1.78 × 10 ⁻⁴	1.79 × 10 ⁻³	0	3.29 × 10 ⁻⁴	95.73
0.2	5.06 × 10 ⁻³	3.13 × 10 ⁻⁴	1.70 × 10 ⁻⁴	2.78 × 10 ⁻³	0	1.53 × 10 ⁻³	94.84
0.3	7.24 × 10 ⁻³	3.11 × 10 ⁻⁴	1.70 × 10 ⁻⁴	3.20 × 10 ⁻³	0	2.95 × 10 ⁻³	91.53
0.8	1.89 × 10 ⁻²	3.22 × 10 ⁻⁴	1.74 × 10 ⁻⁴	5.29 × 10 ⁻³	0	8.53 × 10 ⁻³	75.84
1	2.63 × 10 ⁻²	2.15 × 10 ⁻⁴	1.76 × 10 ⁻⁴	1.82 × 10 ⁻³	0	1.74 × 10 ⁻²	74.65
3	5.74 × 10 ⁻²	4.91 × 10 ⁻⁴	2.03 × 10 ⁻⁴	3.66 × 10 ⁻³	0	3.12 × 10 ⁻²	61.97
5	7.71 × 10 ⁻²	5.29 × 10 ⁻⁴	2.92 × 10 ⁻⁴	3.66 × 10 ⁻³	0	3.80 × 10 ⁻²	55.12
10	1.31 × 10 ⁻¹	8.45 × 10 ⁻⁴	2.98 × 10 ⁻⁴	3.79 × 10 ⁻³	0	4.89 × 10 ⁻²	41.23
[Pb²⁺]							
0.1	9.78 × 10 ⁻³	0	0	6.18 × 10 ⁻³	0	0	63.14
0.2	1.97 × 10 ⁻²	0	0	1.18 × 10 ⁻²	0	0	59.85
0.3	2.44 × 10 ⁻²	0	0	1.42 × 10 ⁻²	0	0	58.08
0.8	7.66 × 10 ⁻²	0	0	4.44 × 10 ⁻²	0	0	57.95
1	1.04 × 10 ⁻¹	0	0	5.60 × 10 ⁻²	0	0	53.99
3	1.91 × 10 ⁻¹	0	0	6.74 × 10 ⁻²	0	0	35.26
5	2.79 × 10 ⁻¹	0	0	6.71 × 10 ⁻²	0	0	24.07
10	3.16 × 10 ⁻¹	0	0	7.18 × 10 ⁻²	0	0	22.73





(a)



(b)

*Ctrl pH = Manual control using NaOH (1N.)+HNO₃ (1N.).

Fig. 4.1 Effect of acetic/acetate buffer solution on biosorption by *Caulerpa lentillifera* (agitation speed: 150 rpm, temperature 20°C, sorbent dose 0.5 g/30 mL) (a) initial metals concentration = 0.1 mM (b) initial metals concentration = 3 mM

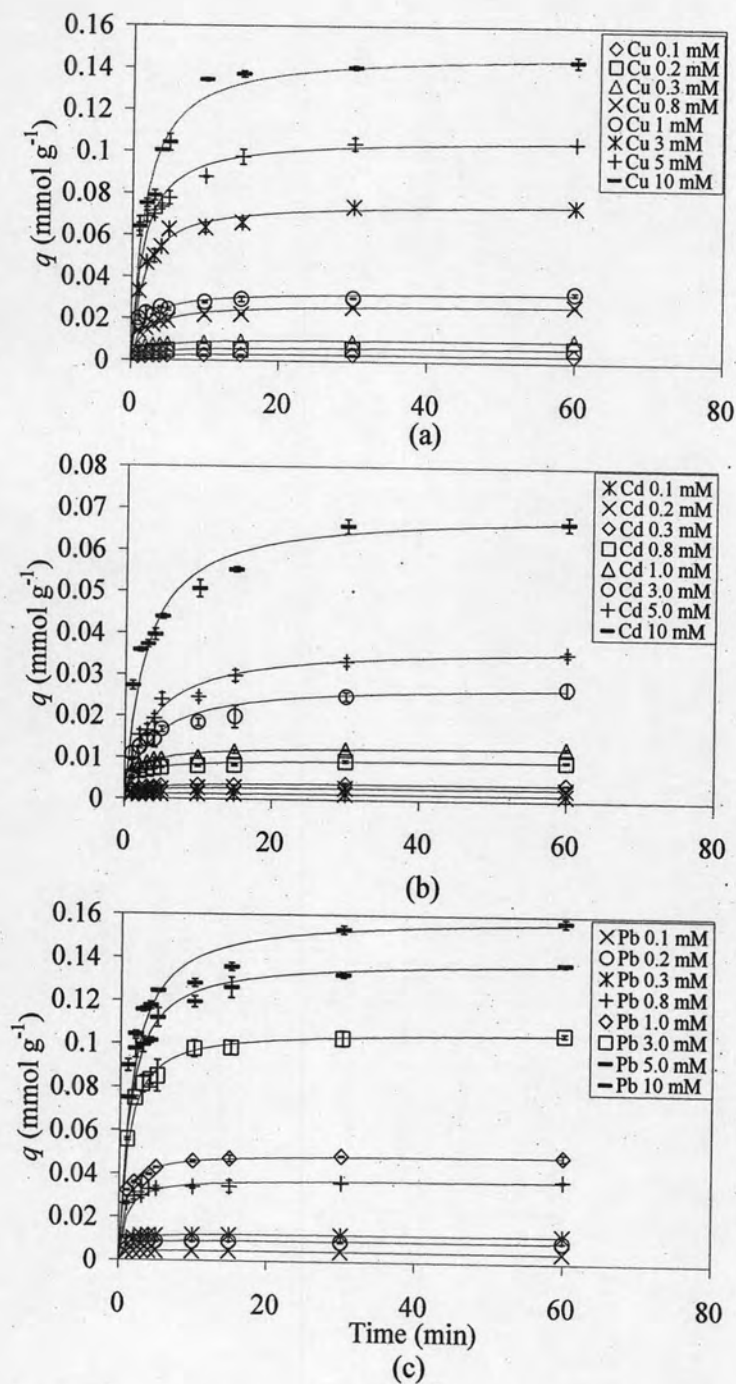


Fig. 4.2 Effect of initial metal ions concentration on biosorption by *Caulerpa lentillifera* (pH = 5, agitation speed = 150 rpm, temperature = 20°C, sorbent dose = 0.5 g/30 mL) (a) Initial Cu²⁺ ions concentration. (b) Initial Cd²⁺ ions concentration. (c) Initial Pb²⁺ ions concentration.

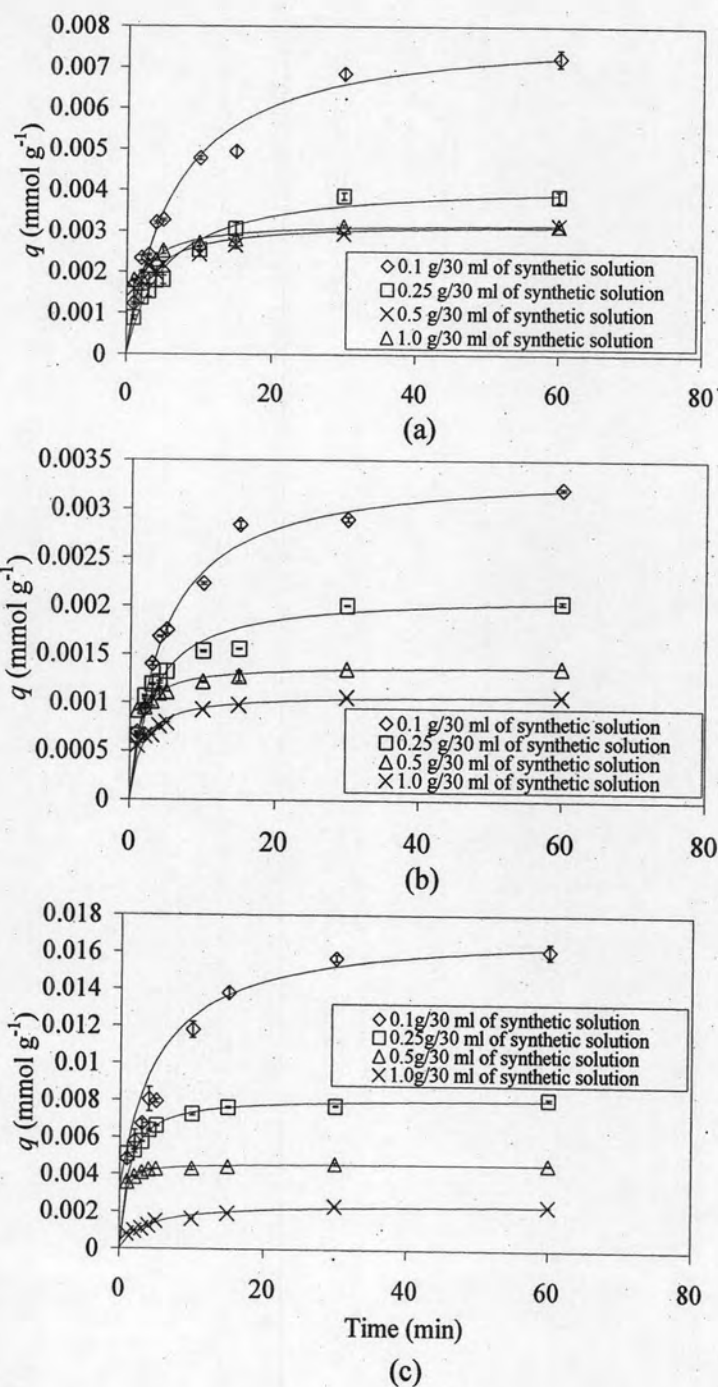


Fig. 4.3 Effect of sorbent dose on metals biosorption by *Caulerpa lentillifera* (pH = 5, agitation speed = 150 rpm, temperature = 20°C, initial metals concentration = 0.1 mM) (a) Cu^{2+} (b) Cd^{2+} and (c) Pb^{2+}

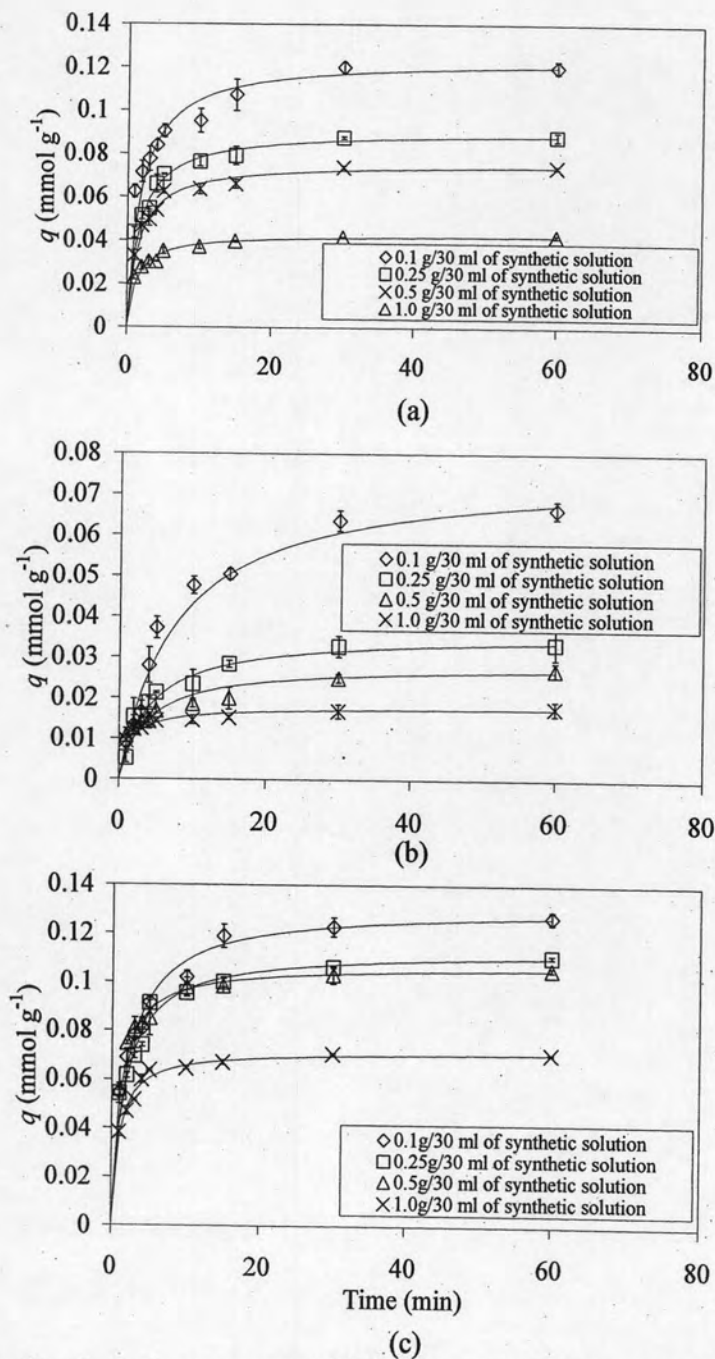


Fig. 4.4 Effect of sorbent dose on metals biosorption by *Caulerpa lentillifera* (pH = 5, agitation speed = 150 rpm, temperature = 20°C, initial metals concentration = 3 mM) (a) Cu^{2+} (b) Cd^{2+} and (c) Pb^{2+}

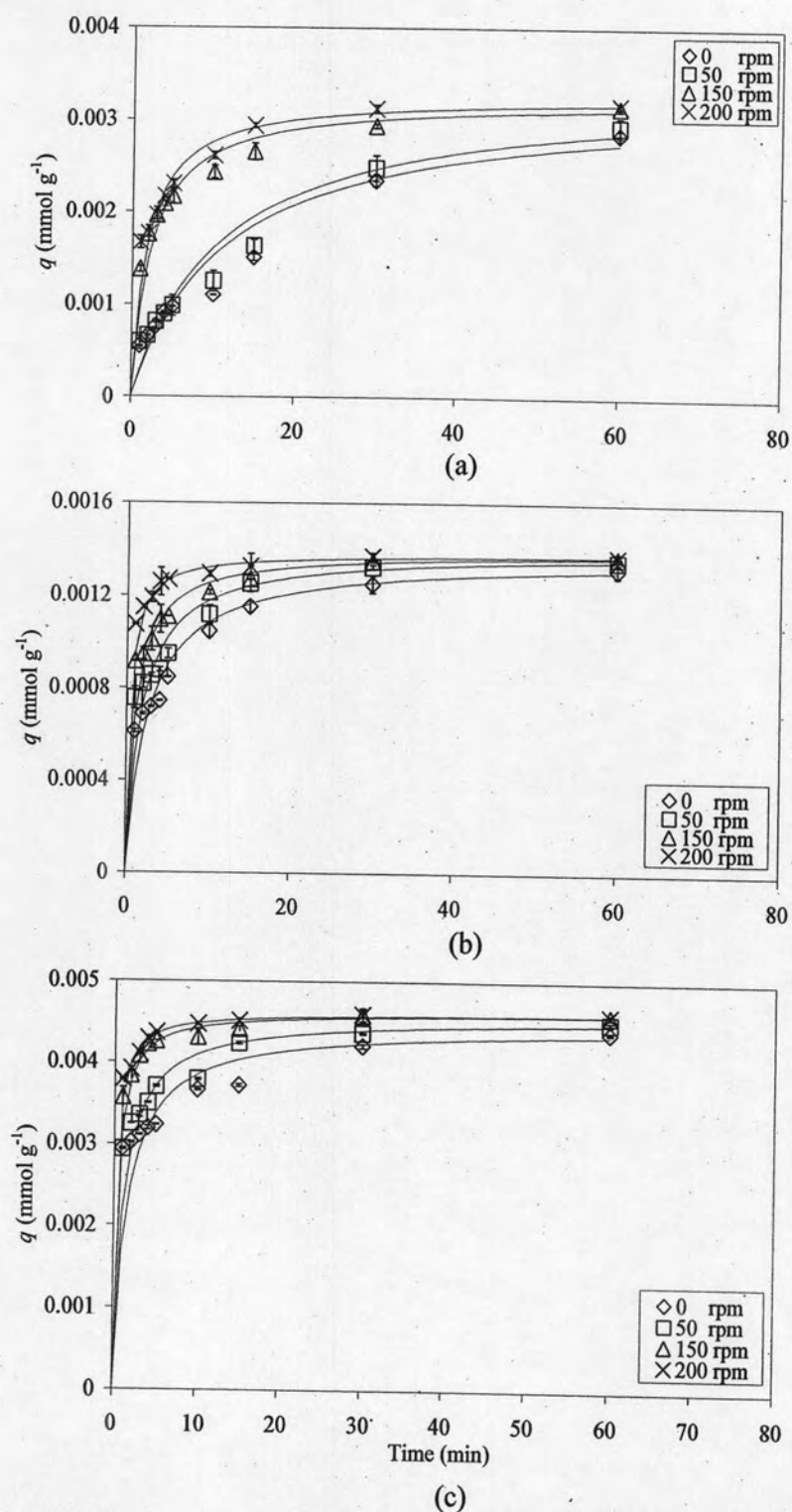


Fig. 4.5 Effect of agitation rate on metals biosorption by *Caulerpa lentillifera* (pH = 5, sorbent dose = 0.5 g/30 mL, temperature = 20°C, initial metals concentration = 0.1 mM) (a) Cu²⁺ (b) Cd²⁺ and (c) Pb²⁺

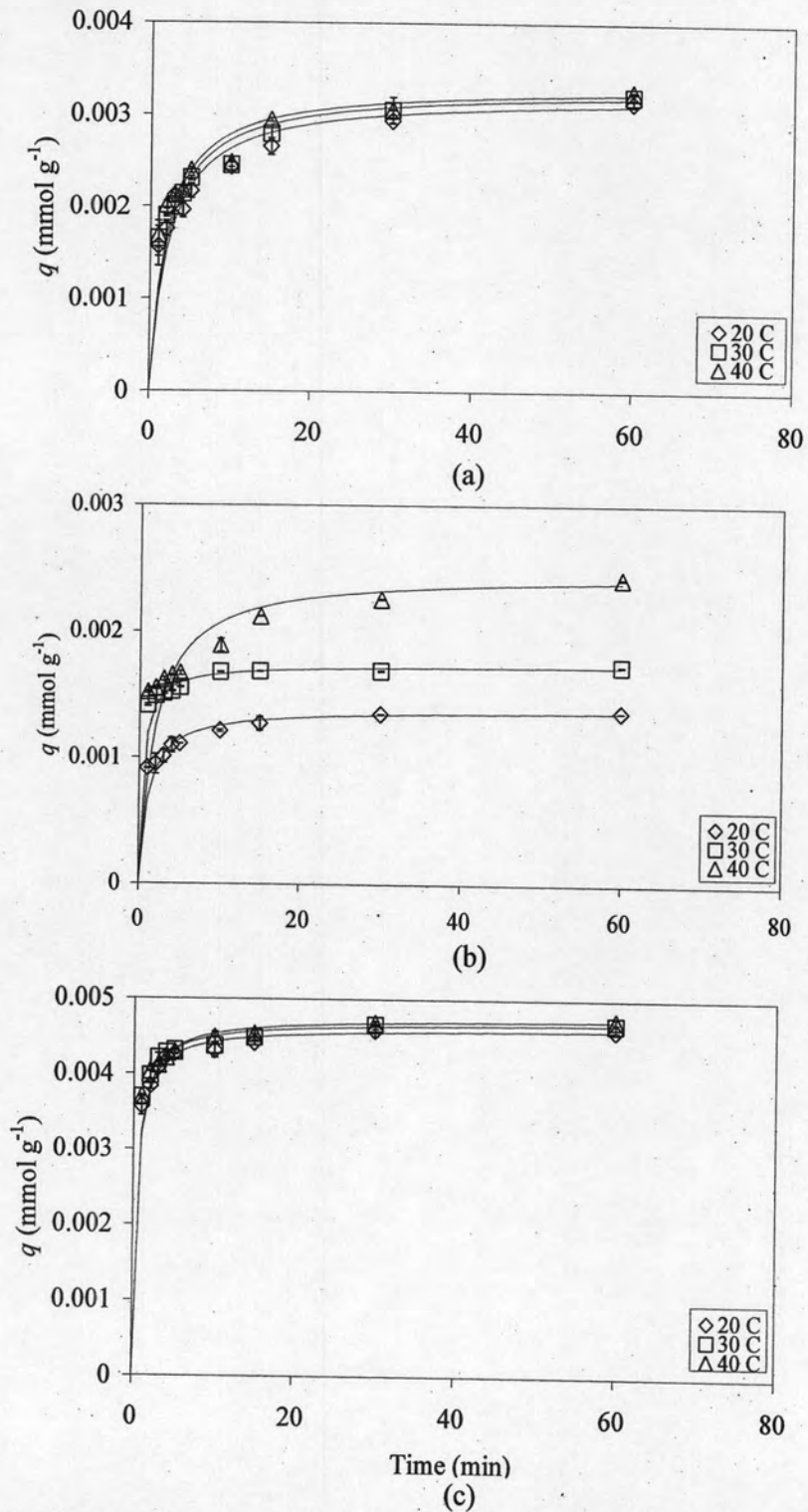


Fig. 4.6 Effect of temperature on metals biosorption by *Caulerpa lentillifera* (pH = 5, sorbent dose = 0.5 g/30 mL, agitation speed = 150 rpm, initial metals concentration = 0.1 mM) (a) Cu^{2+} (b) Cd^{2+} and (c) Pb^{2+}

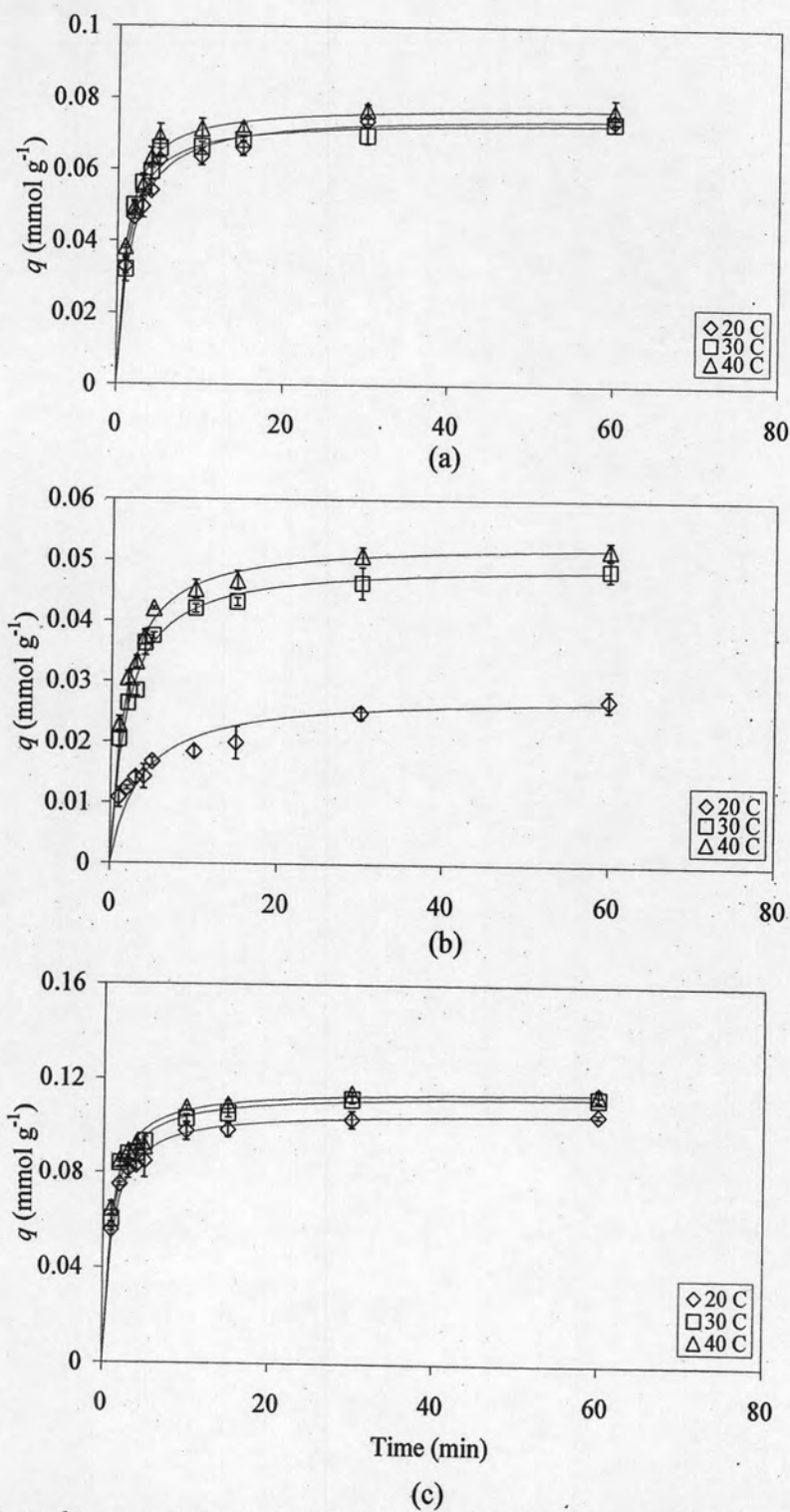


Fig. 4.7 Effect of temperature on metals biosorption by *Caulerpa lentillifera* (pH = 5, sorbent dose = 0.5 g/30 mL, agitation speed = 150 rpm, initial metals concentration = 3 mM) (a) Cu^{2+} (b) Cd^{2+} and (c) Pb^{2+}

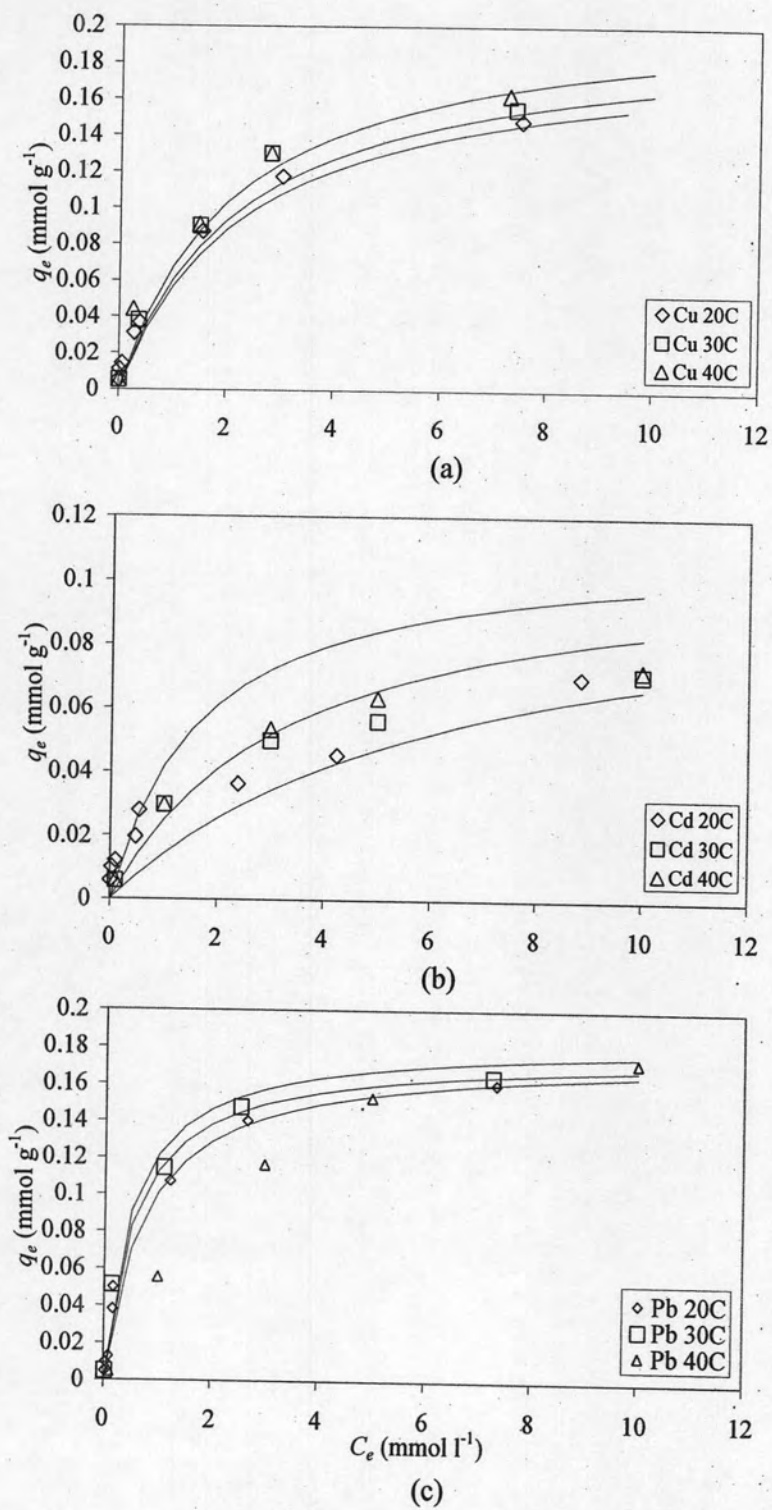


Fig. 4.8 Isotherm of metal biosorption by *Caulerpa lentillifera* (a) Cu^{2+} (b) Cd^{2+} and (c) Pb^{2+}

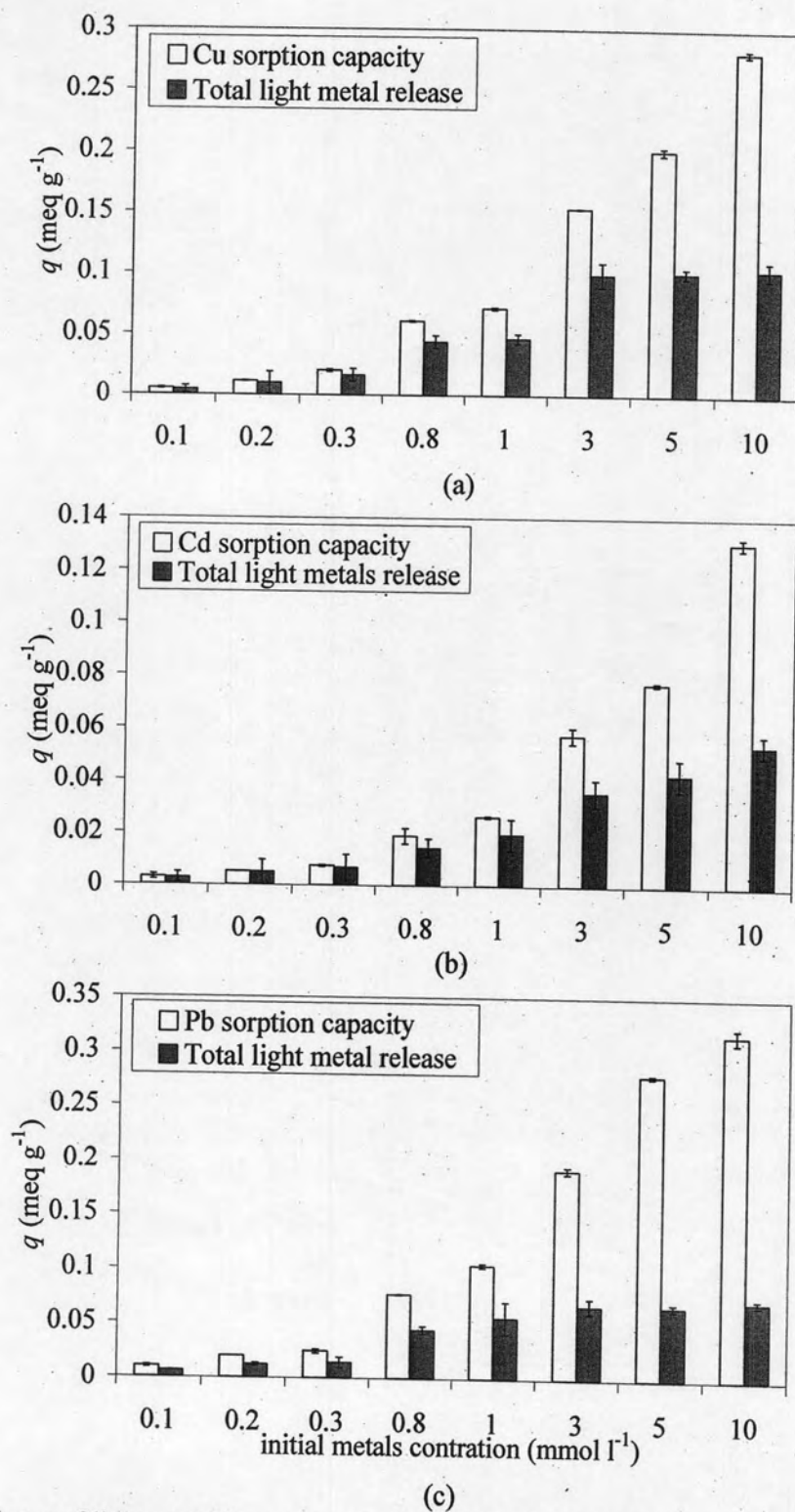


Fig. 4.9 Release of light metal ions after sorption on *Caulerpa lentillifera* at equilibrium (a) Cu²⁺ (b) Cd²⁺ and (c) Pb²⁺

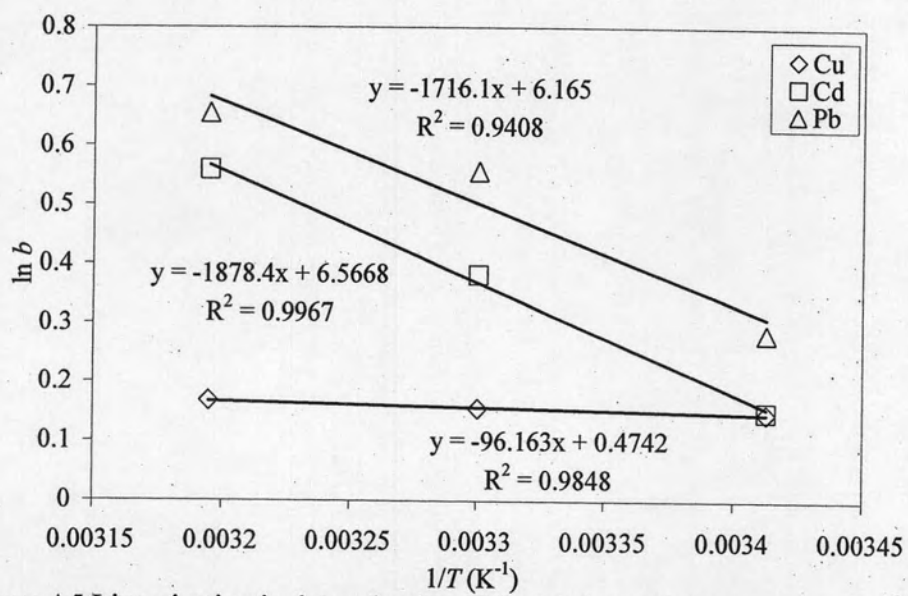


Figure A5 Linearization in determination of thermodynamic parameters of Cu^{2+} , Cd^{2+} and Pb^{2+} (Eq. 4.6)