

Comparative Study of Rates of Biosorption for Selected Single and Mixed Metal Ions using Natural Products

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Abstract
Heavy metals are usually found in low concentrations in natural aquatic ecosystem. In recent times, however, the occurrence of metal contaminants especially heavy metals in excess of natural loads has become a problem of increasing concern. The contributing factors are rapid growth of population, increased urbanization and expansion of industrial activities, exploration and exploitation of natural resources, extension of irrigation and other modern agricultural practices as well as lack of environmental regulations. This therefore, calls for efficient, cheap, available and non polluting method of controlling presence of heavy metals in water bodies. Use of natural biosorbents such as algae has demonstrated great potential to remove heavy metals from wastewater. An investigation of the effect of contact time, reaction kinetics, influence of ionic sizes and influence of presence of other metal ions in biosorption of heavy metals Cu, Zn and Pb using *Ascophyllum nodosum* has been done. Model wastewater solution containing a known concentration of the given heavy metal ions was prepared for both single and mixed at a fixed pH of 5. A 0.25g mass of dry algae was introduced for every 100 mL solution. Change in level of concentration was monitored at intervals of 10 minutes using AAS until the rate of biosorption was almost constant. The sorption process occurred in two stages; first being rapid adsorption and then gradual adsorption that was almost constant. Pb was most biosorbed while Zn was least for both systems, adopting the order Pb > Cu > Zn. The data obtained fitted both Langmuir isotherm and experimental parameters were determined. The order of reaction was found to follow pseudo second order after comparison of R^2 values that were deduced from first and second order linearized plots.
Key words: Biosorption, heavy metals, algae, wastewater, pollution

1. Introduction

Worldwide human population is increasing leading to prompt growth of industries with the sole purpose of satisfying their needs. Consequently, waste products are generated; some are renewable while others are unrenewable of which they are disposed to the environment via adjacent streams or public sewers. There is need therefore to monitor the levels of harmful contaminants prior to their discharge. Industries have applied several conventional techniques in order to comply with acceptable levels that are specified by governments and local authorities. The conventional techniques include chemical precipitation, chemical oxidation and reduction, ion-exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery and solvent extraction. These techniques give rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to dewater and require extreme caution in their disposal. Besides that, most of these methods also present some limitations whereby they are only economically viable at high or moderate concentrations of metals but not at low concentrations from 1 to 100 mg/L of dissolved metal ions (Cossich *et al*., 2001). Heavy metal removal by classical techniques involves expensive methodologies. These are due to high energy and reagent requirements (Xia and Liyuan, 2002). The current study aimed at evaluating the efficiency of *Ascophyllum nodosum* in removal of Cu, Zn and Pb from wastewater and investigating the effect of mixed metal ions in comparison to single metal ions.

2. Materials and Methods

2.1 Biomass preparation

The brown algae *Ascophyllum nodosum* was used as biosorbent for the biosorption of the metal ions. Samples of marine alga were collected from the coastal region, Kenya. The algae were washed several times with tap water then distilled water to remove impurities and salts. The biomass was sun-dried and then dried in an oven at 60 °C for 48 hours (Mohamad, 2008). The dried alga biomass was cut into small pieces, ground in a mortar and subsequently sieved and the particles with an average size of 0.5mm were used for biosorption.

1.2 Metal ion Solution Preparation

Model solution containing Cu, Pb and Zn were prepared at approximately 50 mg/L and pH adjusted to 5 using nitric acid or sodium hydroxide, 0.25g of dry algae was introduced for every 100 mL solution, stirred for seven minutes and the solution allowed to settle, after ten minutes 1 mL of solution was withdrawn ready for the concentration determination using AAS (Model A A-6200, Shimadzu, Corp., Kyoto, Japan). The same was repeated at the intervals of ten minutes until change in concentration was almost constant. The preliminaries showed that after 80 minutes the was no further change in concentration hence for uniformity reasons, the biosorption process for all cases were carried out for eighty minutes.

3. Results and Discussion

3.1 Reaction Kinetics

The dependence of a chemical reaction on initial reactant concentration can be shown by a rate equation. The rate equation gives an expression of the variation in concentration with time. The order of reaction was deduced from the integrated rate equation by appropriate plot of variables to give a linearized plot. A reaction can either be pseudo first order or pseudo second order. The first order rate equation for metal adsorption on algae is;

$$\frac{\partial q_t}{\partial t} = k_1(q_e - q_t)$$

where q_t and q_e are the masses of metal adsorbed by the algae in (mg/g) at any time t and at equilibrium respectively, k_1 is the rate constant for the adsorption. On integration, equation (i) gives the solution;

$$k_1 t = \ln q_e - \ln(q_e - q_t) \text{ .... (ii)}$$

Plot of time t against $ln(q_e - q_t)$ gave a straight line. The following figures (a - d) shows the plots 1st and 2nd order kinetics for Cu when single and when in mix with Zn and Pb.

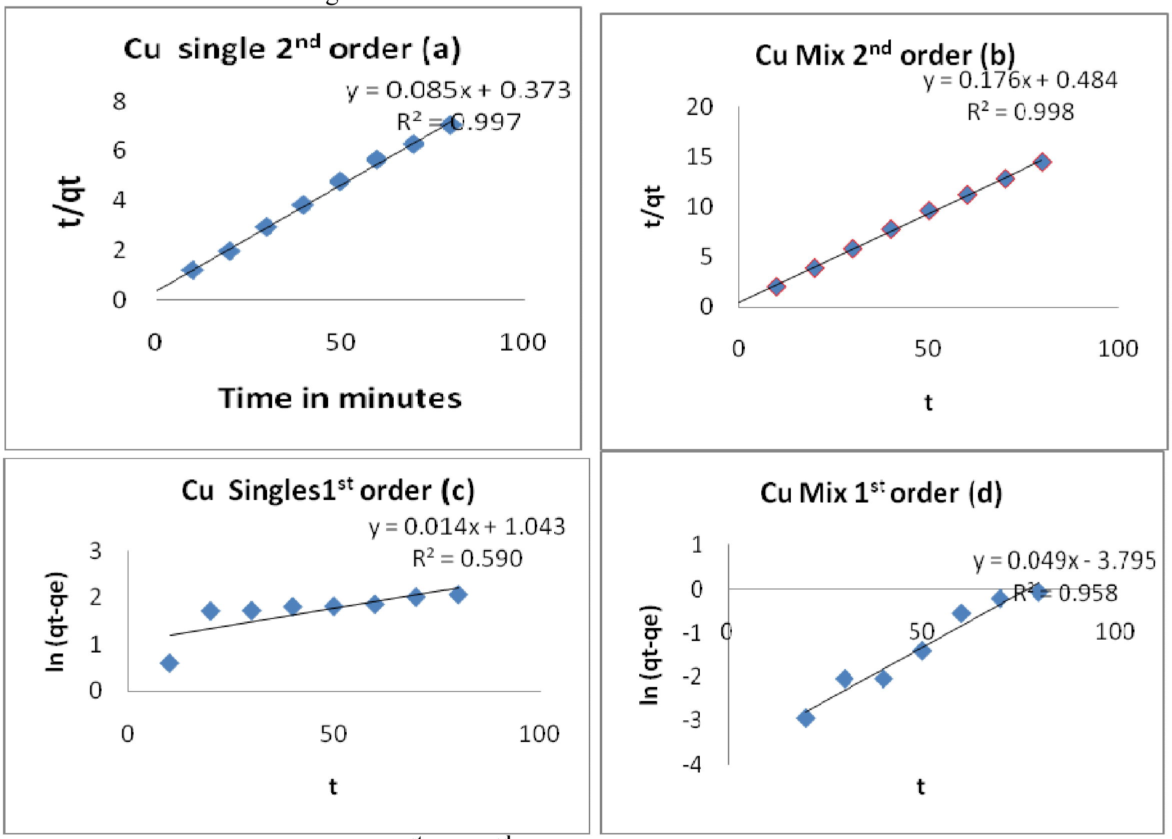

Figure 1: Graphs (a-d) comparing 1st and 2nd order for single and mixed metal ions

The second order rate equation can be represented as;

$$\frac{\partial q_t}{\partial t} = k_2(q_e - q_t)^2 \text{ .... (iii)}$$

Where k_2 is the second order rate constant, q_e and q_t have same meanings as before. Upon integration, equation (iii) gives the solution;

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^{\,2}} \text{ .... (iv)}$$

The plot of t/q_t against t gave a straight line as shown in figure 1 (a) and (b) from which the rate constant k_2 and q_e were calculated.

The linearity of the graphs reveals that the reaction kinetics is best described by 2nd order kinetics hence deduced constants can be summarized in the table below;

Table 1: Summary of constants for pseudo second order for the mixed and single metal ions

Metal	Pseudo second order					
	Singles			Mixed		
	K_2	q_e	R^2	K_2	q_e	R^2
Cu^{2+}	0.01937	11.7647	0.997	0.064	5.6818	0.998
Pb^{2+}	0.041886	12.6582	0.999	0.023876	16.1290	0.998
Zn^{2+}	0.005628	9.9000	0.959	0.06723	3.8020	0.999

The quantity of metal uptake at equilibrium (q_e) was paramount in prediction of order of preference on biosorption of metal ions to the surface especially when the metal ions were mixed. The analysis revealed that the order of preference to the active sites present in the algae was Pb >Cu> Zn, the order was the same even for single metal uptake. It should be noticed also that when the metals were mixed q_e for Pb was high due to its large ionic size hence occupying large number of active sites consequently q_e for Cu and Zn were small compared to when they were single.

1.2 Effect of Contact Time

Among my research questions was" for how long should the biosorbent be in contact with the metal ions?" therefore, estimation of the time required for quantitative amount of uptake of the metal ions from the solution was essential. As outlined in the methodology, the initial concentration of any given metal ion was predetermined prior to introduction of the biosorbent and change in concentration monitored until change in concentration was almost constant. To determine the average time required for maximum biosorption onto the surface, a graph of time in minutes against quantity of the metal uptake was plotted has shown below.

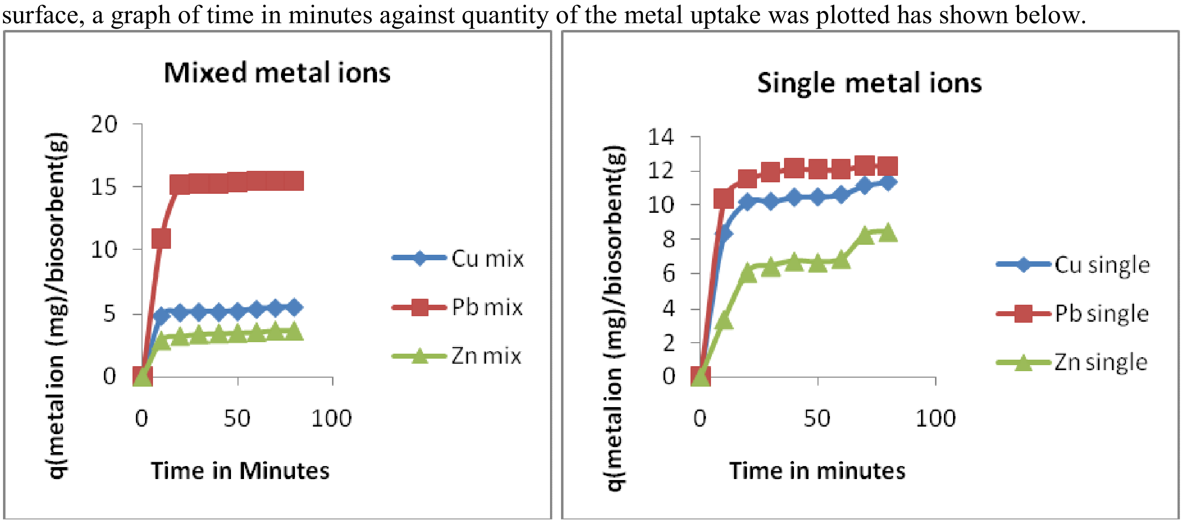

Figure 2: Graphs showing effect of contact time on the amount of metal uptake

It was deduced from the plots that the adorption process ocurred in two stages; the first stage being rapid and the later being gradual. The first stage occurred within the first 20- 30 minutes and this was due to infinite number of active sites, the second stage occurred when most of the active sites had been occupied and hence involved diffusion of the metal ions into the cells of the algae.

3.3 Influence of Ionic Sizes

Biosorption rates for different metal ions were compared to establish whether the algae biosorbed Cu^{2+}, Pb^{2+}, and Zn^{2+} in the same manner or differently. Investigation was done for both single and metal ions. One way ANOVA at 95% confidence level was used to test whether there was significant difference or not. The results of the test are summarized in figures 3 and 4 below.

ANOVA singles (Cu, Pb and Zn)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1721.519	2	860.7593	11.63477	0.000293	3.402826
Within Groups	1775.559	24	73.98161			
Total	3497.077	26				

Figure 3: One way ANOVA results for comparison of biosorption rates Cu, Pb and Zn for single metal ions.

ANOVA Mix (Cu, Pb and Zn)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	2106.461	2	1053.23	16.43357	3.19E-05	3.402826
Within Groups	1538.164	24	64.09018			
Total	3644.625	26				

Figure 4: One way ANOVA results for comparison of biosorption rates Cu, Pb and Zn for single metal ions.

From the ANOVA results it can be seen that p- value for both mixed and single metal ions is less that 0.05 implying that the biosorption of the three metal ions whether they appear in the wastewater alone or in mix with others they are biosorbed differently, this is attributed to differences in ionic radiuses.

3.4 Influence of Presence of other Metal ions

Industrial effluents can be contaminated by one or more metal ions; in this research it was considered important to compare the biosorption rates in each metal ion whether it occupied the wastewater alone or in company of other metal ions. The ANOVA results are summarized in the table 2 below.

Table 2: Summary of one way ANOVA results comparing influence of mixing metal ions on biosorption rates

Parameter	***P-value***	**$F_{calculated}$**	**$F_{critical}$**
Cu^{2+}	0.915033	0.011749	4.4940
Pb^{2+}	0.146008	2.335175	4.4940
Zn^{2+}	0.261049	1.357498	4.4940

The test revealed that whether the metal ions are mixed or in presence of others they were biosorbed in the same way since the p-value was greater than 0.05. Most probably ionic size plays a greater role than presence of other metal ions.

3.5 Adsorption isotherms

Langmuir and Freundlich isotherms were used to describe the adsorption process and to reveal the nature of biosorbent surface. The Langmuir isotherm model assumes that the sorption process forms a monolayer at the surface and that the surface has a finite number of identical sites. This isotherm can be defined according to the following equation:

$$q = q_{\max}\left(\frac{bC_e}{1+bC_e}\right)$$

where q is the amount of adsorbed metal per unit weight biomass at equilibrium (mg/g), C_e is the residual metal concentration in solution at equilibrium (mg/l), q_{max} is the maximum amount of metal per unit of biomass (mg/g) and b is a constant related to the affinity of the binding sites (l/mg). A graph of Langmuir isotherm for Cu when single and in mix with other metal ions is shown below:

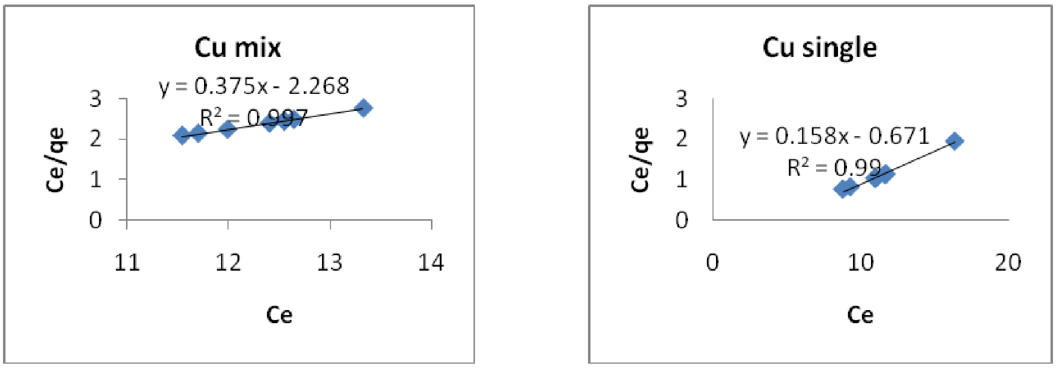

Figure 5: Graphs of Langmuir isotherms model for Cu in single and when in mix with other metal ions.

On the other hand, Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be described as follows:

$q_e = K_f (C_e)1/n$

where K_f and n are the Freundlich constants related to the adsorption capacity and intensity of the sorbent, respectively. For the linearized forms of equation were used to draw the linearized plots as shown in the figure below for Cu.

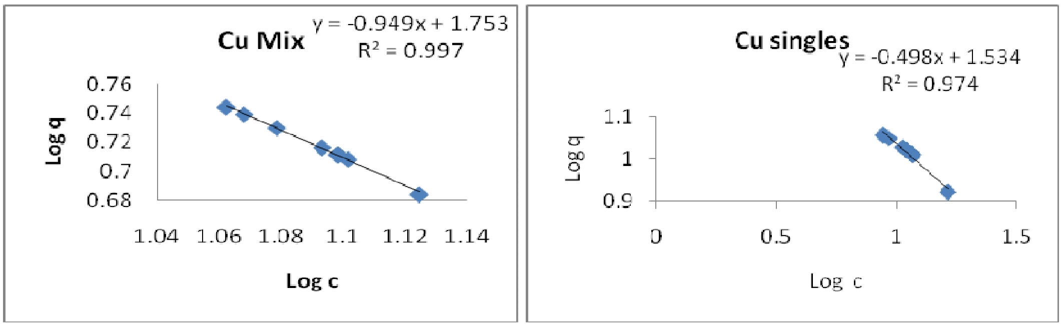

Figure 6: Graph of Freundlich isotherm model for Cu in single and when in mix with other metal ions.

The linearized graphs aided calculation of the contants q_{max} and b for langmuir that used predict the amount of metal uptake to the surface and the affinity of metal ions to the active sites present at the surface of the biosorbent, respectively. The constants of Freundlich isotherm were ignored since the data did not fit the model and hence could not be used to predict amount biosorbed nor affinity of the metal ions to the surface. The constants for Langmuir model are summarized in the table below;

Table 3: Summary of Langmuir constants

Metal	Single			Mixed		
	q_{max}	B	R^2	q_{max}	b	R^2
Cu	6.3291	0.2355	0.990	2.6667	0.1653	0.997
Pb	9.900	2.886	0.998	10.5263	2.1589	0.999
Zn	1.7990	0.0611	0.918	0.7369	0.0470	0.994

The data fitted Langmuir for both Pb and Zn just like Cu as demonstrated in figure 5 and 6. This, therefore, means that the surface of brown algae has homogenious a surface with finite number of identical sites. q_{max} predicted that the order of decreasing quantity of metal ion biosorbed was Pb> Cu> Zn, b also predicted that the order of decreasing affinity to the active sites present in the algae were Pb> Cu> Zn. This was in agreement with the order predicted by q_e of pseudo second order. It also agrees with finding of other researches (Mata *el al.*, 2008, Volesky and Chong, 1995, Volesky *et al.*, 1995).

4. Conclusion

The affinity to functional groups present in the algae depends on the type of the metal ion. When metal ions appear singly or when mixed with other metal ions it does not affect the rate of biosorption. The data obtained fitted Langmuir more than Freundlich isotherm suggesting that the surface of biosorbent in homogeneous and characterized with finite number of identical active sites based on assumptions of Langmuir isotherm. The order of the reaction was deduced to follow pseudo second order meaning that the biosorption process is dependent on both concentration of metal ion and biosorbent. The order of reaction was obtained by appropriate plots for first and second order; the correlation coefficient (R^2) from the linearized graphs showed that the linearized graphs of second order had higher values. The *Ascophyllum nodosum* proved to be efficient reaching over 50% for Cu, Pb, and Zn.

5. Recommendation

Industries whose effluents are contaminated with heavy metals especially Cu, Pb and Zn whether singly or mixed can employ brown algae as the biosorbent. A 0.25g of the brown algae should be used for every 100 mL of wastewater at pH of 5 and at room temperature (20- 24^oC). The industry should monitor the concentration of the individual heavy metals and apply the algae sequentially until all the metal ions are removed completely or to acceptable level.

6. Acknowledgements

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