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Kinetic studies on the effect of Pb(II), Ni(II) and Cd(II) ions on biosorption of Cr(III) ion from aqueous solutions by *Luffa cylindrica* fibre

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ABSTRACT

The biosorption of single metal system of Cr(III) and binary metal systems (Cr-Pb, Cr-Cd and Cr-Ni) from aqueous solutions using Luffa cylindrica fibre biomass was investigated as a function of biomass dose and contact time. Results showed that maximum adsorption of single Cr(III) ions was obtained at biomass dosage of 500 mg/L. In the binary solutions of Cr(III)-Cd(II), 63.45% of Cd(II) and 66.5% of Cr(III) were adsorbed at a biomass dosage of 1100 mg/L. At 300 mg/L dosage, 70.70% of Cr(III) and 94.27% of Pb(II) were obtained as the maximum metal-ion adsorbed in the binary metal systems of Cr-Pb. The optimum biomass dosage of Cr-Ni binary system was found to be 900 mg/L. All the optimum dosages obtained were used for kinetic experiment on both the single and binary mixtures. Studies on the effect of contact time on the adsorption of the metal ions were used to access the kinetics of the adsorption process. Both pseudo-first order and pseudo-second order kinetic models were applied to the experimental adsorption data and results showed that the biosorption process for the systems studied followed pseudo-second order kinetics.

Key words: Adsorption kinetics, biomass dose, biosorption, heavy metals, *Luffa cylindrica* fibre.

INTRODUCTION

Heavy metals occurring in our environment often pose serious health hazards. Ever-intensifying human technological activities have resulted in the generation of large quantities of aqueous effluents that contain high level of heavy metals and cause environment disposal problems [1-3]. Also, the use of industrial sludge as residential landfill is a major source of contamination, which can be avoided. Since these activities that can cause contamination are inevitable, it therefore becomes necessary to keep the concentrations of these heavy metal contaminants in the environments as low as possible and also by employing suitable methods of their removal from the aqueous environment. Conventional techniques for heavy metal removal include: chemical precipitation, ion exchange, adsorption on activated carbon, membrane separation processes (reverse osmosis) and so on [4-6]. Some of these techniques are either ineffective or are prohibitively expensive and inadequate especially when considering the vast wastewater quantities to be treated.

Ion exchange method can effectively remove dissolved metals. However, it is expensive and not widely applied particularly for large scale operations such as in mining effluent treatment. Precipitation has been the crude metal removal technology most widely applied. Metal species in solution are precipitated through increase in pH, usually aided by the addition of certain chemicals, based on metal binding capacities of various biological materials. Biosorption results as a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions [7]. When dealing with the removal of metals by biomass, a distinction however needs to be made between the two types of processes namely biosorption and bioaccumulation. Metal biosorption typically applies to the metabolically mediated passive process while bioaccumulation on the other hand refers to a metabolically active process [8].

Luffa cylindrica is an annual climbing crop which produces fruit containing fibrous vascular system. *Luffa* is derived from the cucumber and marrow family and originates from America. *Luffa* commonly called sponge gourd, *Luffa*, vegetable sponge, bath sponge or dish cloth gourd is a member of cucurbitaceous family. It is a lignocellulosic material composed mainly of cellulose, hemicelluloses and lignin. The fibres are composed of 60% cellulose, 30% hemicellulose and 10% lignin. One mature luffa sponge will produce at least 30 seeds. Some will produce many more [9]. It is well known that plant biomass have the ability for metal uptake from aqueous solutions and industrial waste water [10]. The current study assesses the effect of co-ions on the kinetics of bioremediation of Cr(III) from aqueous solutions using *luffa cylindrica* fibre.

MATERIALS AND METHODS

Preparation of biosorbent

The dried *Luffa cylindrica* fibre were collected from site located within Ibadan metropolis Nigeria. After removing the external dry coverage on the *Luffa cylindrica* fibre, the seeds inside the *Luffa cylindrica* fibre were removed. They were thereafter air-dried for six days. The dried samples were pulverized using an electric blender and thereafter sieved using a 150 μm size mesh screen. The prepared biosorbent was then stored in an air-tight polythene bag.

Preparation of stock solutions

Chromium, nickel, lead and cadmium solutions with same initial concentrations were prepared by dissolving known masses of $Cr(NO_3)_3 .9H_2O$, $Ni(NO_3)_2 .6H_2O$, $Pb(NO_3)_2$ and $Cd(NO_3)_2 .4H_2O$ respectively in de-ionized water in an appropriate standard volumetric flask and made up to the mark. Thereafter, 5 ml of the prepared solutions were taken and analyed for final concectration of the metal solutions using Buck scientific model of atomic absorption spectrophotometer (AAS). The working concentration was obtained from serial dilution of the stock solutions.

Biosorption Experiments

The influence of contact time on the biosorption process was investigated by adding 30 ml of 100 mg/L solution of each of the binary metal solutions (Cr–Pb, Cr-Ni and Cr-Cd) into 100 mL Erlenmeyer flask containing 0.5 g of the biosorbent at their respective optimum experimental pH. The flasks were agitated at different times (5, 10, 20, 30, 60 and120 min). After the agitation times, the mixtures were filtered and thereafter 5 ml of each of the filtrates was then determined for residual metal ion concentration using Atomic Absorption Spectrophotometer (AAS). Each experiment was carried out in duplicate. The influence of biomass mass was studied by introducing 30 ml of 100 mg/L solution of each of the binary metal solutions at the experimental pH of 4 for both single and binary systems into different Erlenmeyer flasks containing varying masses of 0.1 g, 0.3 g, 0.5 g, 0.7 g, 0.9 g and 1.1 g of samples of *Luffa cylindrica* fibre. The flasks were agitated for the predetermined optimum time for each of the systems on a shaker at 150 rpm and then filtered.

Data Analysis

Determination of total percentage metal removal

Residual concentration R (%) was calculated as:

$$R(\%) = \left[\frac{(C_i - C_f)}{C_i}\right] 100 \qquad \text{...(1)}$$

Where C_i and C_f are the initial and final concentrations in mg/L.

Metal uptake by biomass

Specific metal uptake was calculated as follows:

$$q_e = \frac{(C_i - C_f)V}{m} \qquad \text{…(2)}$$

Where C_i and C_f are the initial and final metal concentrations in mg/L respectively, V is the volume of the metal solution in L and m is dry weight of the biomas in g.

Kinetic models

Adsorption is a time dependent process. Kinetic sorption study was done by using two kinetic models (Pseudo-first order and Pseudo-second order).

Pseudo-first order Lagergren model

The Pseudo-first order rate expression is based on sorption capacity of the solid phase which is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad \ldots(3)$$

Where k_1 is the rate constant of first order adsorption process; q_e is the metal uptake in mg/g at equilibrium, q_t is the metal uptake in mg/g at time t. Integration of equation (3) yields

$$Log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad \ldots(4)$$

A plot of log (q_e–q_t) versus t was made and the model parameters q_e and k_1 were obtained from the intercept and slope of linear plots respectively.

Pseudo-second order model

This model is based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism. The model is represented by:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad \ldots(5)$$

Where k_2 is the rate constant for the second order biosorption.

On integrating between boundary conditions of t = 0, t = t and $q_t = 0$, $q_t = q_t$, *i.e*

$$\int_0^{q_1} \frac{dq_t}{d_t} = \int_0^{q_1} k_2\,(q_e - q_t)^2$$

We finally obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(6)$$

The values of q_e and k_2 are estimated from the slope and intercept of the linear plots of ${}^{t}/{}_{q_t}$ against t.

RESULTS AND DISCUSSION

Effect of biomass dosage on biosorption

One of the factors that accelerate the biomass application in effluent treatment is its economical and eco-friendly nature. The lesser the biomass dosage, the higher the possibility of its application. In order to determine the least biomass dosage for the maximum removal of Cr(III), Cr(III)-Pb(II) , Cr(III)-Cd(II) and Cr(III)-Ni(II) ions from both its single and in binary systems, considering chromium(III) as a priority metal-ion, the dosage effect of the biosorbent was studied using different biomass dosages in the range of 100 mg/L to 1100 mg/L and the results were presented in figs. 1 and 2. During the study an increase in the amount of metal ions adsorbed was observed in the

Cr(VI) ions with increase in the biomass loading up to 500 mg/L. In the binary solution of Cr(III)-Cd(II) , a steady increase of metal ions adsorbed with biomass dosage was observed with 63.45% for Cd(II) and 66.5% for Cr(III), at an optimal biomass dosage of 1100mg/L, which was used for further experiment on this binary mixture.

The adsorption of metal ions onto the *Luffa cylindrica* fibre from a binary solution of Cr(III)-Pb(II) increased to 70.70% for Cr(III) and 94.27% for Pb(II), when the dosage changed from 100 mg/L to 300 mg/L. The maximum biosorption 66.31% for Cr(III) and 36.13 for Ni(II) of the binary Cr(III)-Ni(II) metal system were attained at a biomass dosage of about 900 mg/L. Generally, in all the binary and single metal ion systems studied, an increase in the biomass dose increased the amount of biosorbed metal ions. This is because an increase in surface area of the biomass increases the number of binding sites [11]. Comparatively, the amount of Cr(III) ions adsorbed in the binary system is higher than the amount of Cr(III) ions adsorbed in single Cr(III) ion solution and this shows that the adsorption of Cr(III) onto *Luffa cylindrica* fibre is greatly enhanced by the presence of other metal ions competing for the sorbent surface. This also indicates that the metals may be adsorbed through different mechanisms or are adsorbed onto diferent sites on the adsorbent surface. From the analysis of experimental data obtained for both single and binary systems, it was observed that the biosorption capacity became nearly constant above their optimum dosage value in some binary systems. This leveling effect may have resulted from interference between binding sites at higher biomass dosages or insufficient metal ions in the solution with respect to the available binding sites [12].

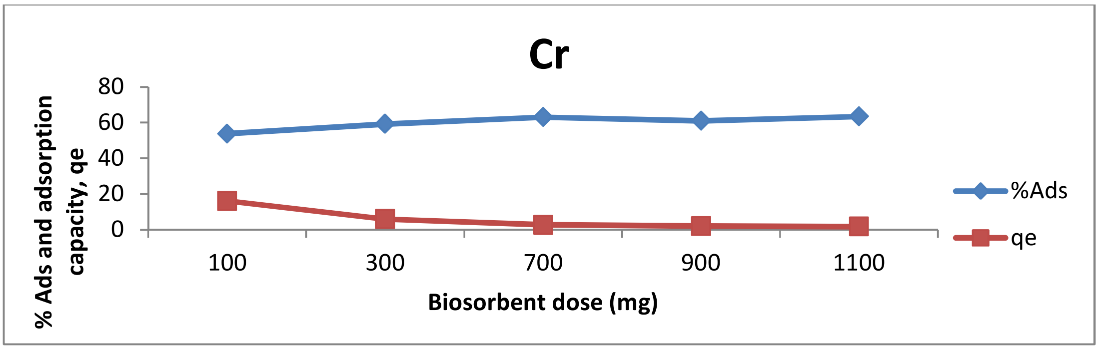

Figure1. Effect of biosorbent dose on the biosorption of Cr(III) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 10 min; Temperature 27^{o}C)

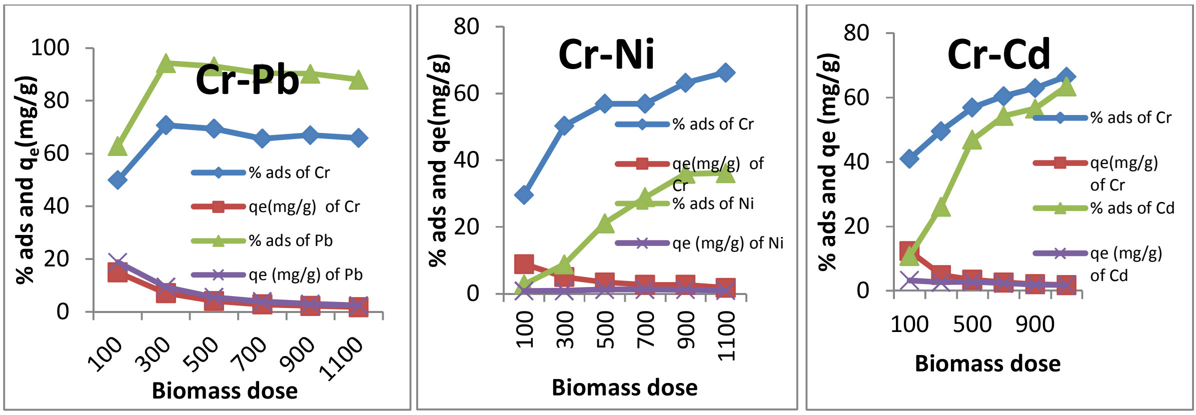

Figure 2. Effect of biosorbent dose on the binary biosorption of Cr(III)-Pb(II), Cr(III)-Ni(II) and Cr(III)-Cd(II) metal ions by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 5 min; Temp. 27^{o}C)

Effect of contact time on biosorption

The duration of the batch experiment was varied from 5 to 120 min while all other parameters such as metal ion concentration, temperature, biosorbent mass and pH were kept constant for all systems (Cr, Cr-Ni, Cr-Pb, Cr-Cd) considered. Figure 3 showed that the rate of metal uptake (single metal ion solution of Cr(III)) increased rapidly in the first part within 5 min of contact, then slowly increased till it reach a constant value of metal concentration after

10 min. This short time required for biosorption is in accordance with the result given in a similar research [13]. Both binary metal ion solutions of Cr-Pb and Cr-Ni showed a very fast adsorption for *Luffa Cylindrica* fibre biomass with an optimum contact time of 10 min, during which period the fraction removed were 75.67% for Cr(III) and 92.34% for Pb(II) in the binary system of Cr(III)-Pb(II), 90.56% for Cr(III) and 71.2% for Ni(II) in the binary system of Cr(III)-Ni(II). Figure 5 showed that the rate of metal uptake in the equimolar mixture of Cr(III) and Cd(II) is faster in the first 5 min and equilibrium was established in the range of 60-120 min for the adsorption process. It can be seen that metal biosorption consists of two phases: a very rapid initial sorption, followed by a long period of much slower uptake. The two-stage kinetics of biosorption was also reported for immobilized biomass as well as some conventional sorbents [13]. During the initial stage of sorption, a large number of vacant surface sites are available for biosorption. After lapse of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase. Besides, the metal ions are adsorbed into the mesopores that get almost saturated with metal ions during the initial stage of biosorption. Thereafter, the metal ions have to traverse farther and deeper into the pores encountering much larger resistance, which resulted in the slowing down of the biosorption during the later period of the process.

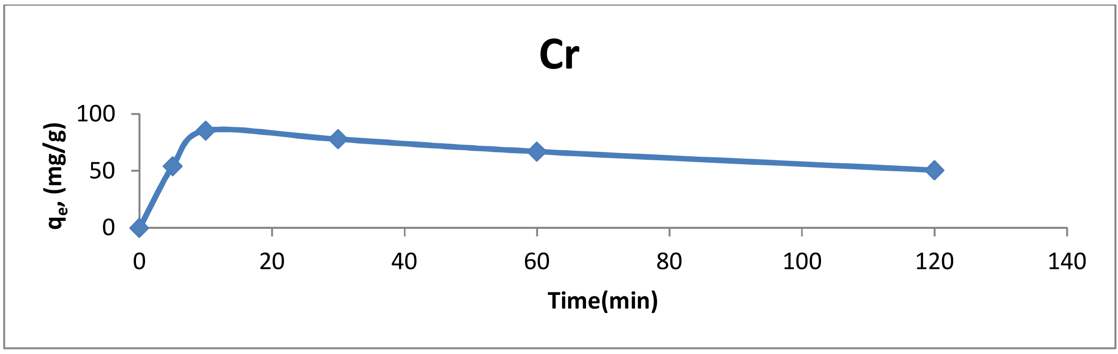

Figure 3: Effect of contact time on the biosorption of Cr(III) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

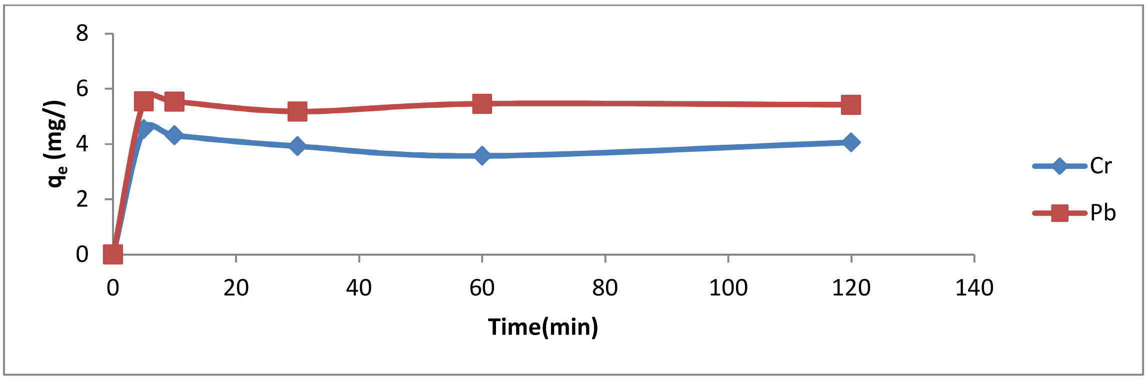

Figure 4 : Effect of contact time on the competitive biosorption of Pb(II) and Cr(III) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

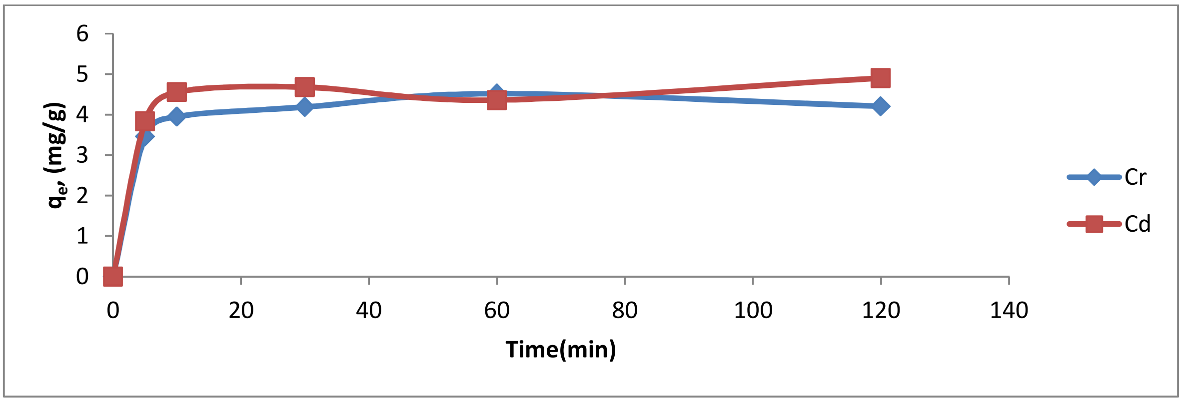

Figure 5. Effect of contact time on the competitive biosorption of Cd(II) and Cr(III) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27 °C)

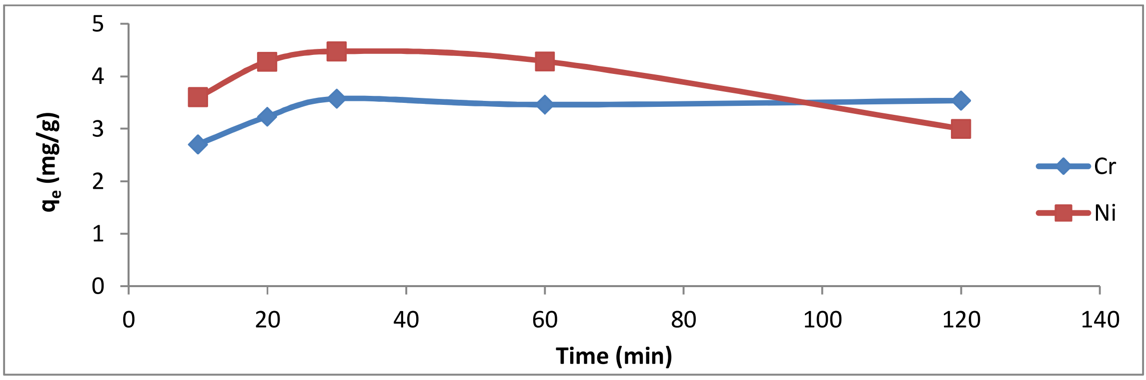

Figure 6, Effect of contact time on the competitive biosorption of Ni(II) and Cr(III) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L ; contact time 120 min; Temperature 27°C)

Kinetic modeling

The biosorption kinetics was investigated for better understanding of the dynamics of adsorption of the metal ions onto *Luffa cylindrica* fibre and to obtain predictive models that allow estimations of the amount adsorbed with the treatment time. This information could be used for the scale-up to a larger system. The pseudo-first and pseudo-second order kinetics were thus applied to the experimental data obtained. The pseudo-first order model assumes that a metal ion only adsorbs on one sorption site of the sorbent surface and is represented by the following scheme [14].

$$S_{(solid)} + M^{2+}_{(aqueous)} \longrightarrow SM^{2+}_{(adsorbed\ phase)}$$

Where S is the biosorption site. On the other hand, the essential assumption of the pseudo-second order model is that one metal ion is adsorbed onto two surface sites. As indicated by the following equation.

$$2S_{(solid)} + M^{2+}_{(aqueous)} \longrightarrow S_2M^{2+}_{(adsorbed\ phase)}$$

Results obtained showed that the experimental data fitted better into pseudo-second order kinetic model. Table 1 lists results of rate constants studied for the single chromium metal ion system and the Cr-Cd, Cr-Pb and Cr-Ni binary systems by the pseudo-second order model. The values of correlation coefficient, R^2 for the pseudo-second order adsorption model is relatively high. However, the correlation coefficient, R^2 for the biosortion of the metal ions onto *Luffa cylindrica* fibre does not fit a pseudo-first order kinetic model. Therefore, it can been concluded that the pseudo-second order adsorption model is more suitable to describe the adsorption kinetics of all the binary systems and single metal ions system studied over *Luffa cylindrica* fibre biomass. This suggests that the rate-limiting step in this sorption process may be chemisorption involving valency forces through the sharing or exchange of electrons between sorbent and sorbate.

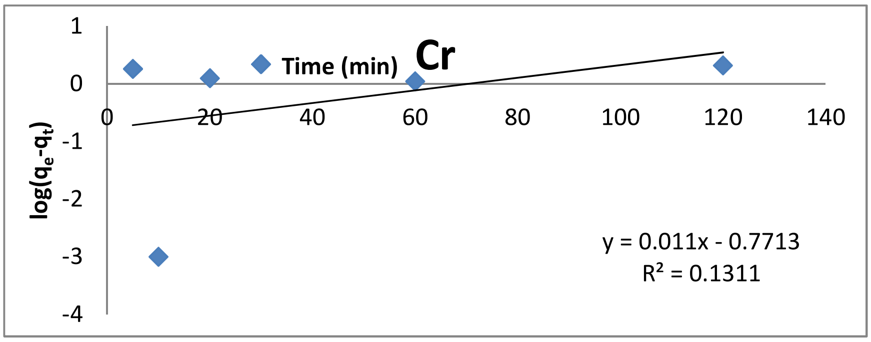

Figure 7. The pseudo-first order plot for the kinetic study of Cr(III) biosorption by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

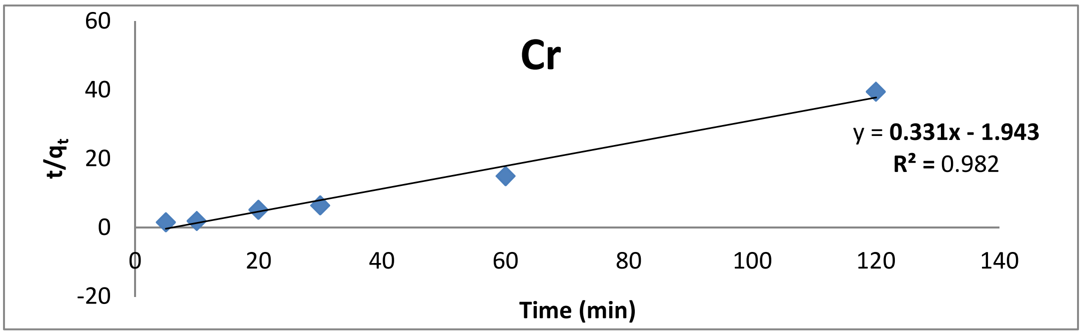

Figure 8. The pseudo-second order plot for the kinetic study of single Cr(III) biosorption by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C).

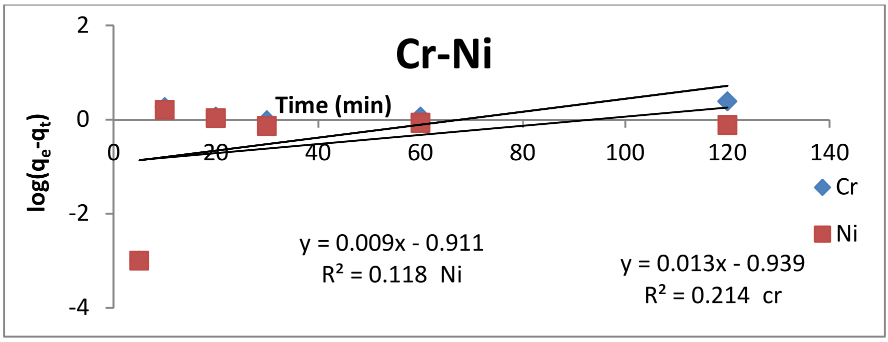

Figure 9. The pseudo-first order plot on the kinetic study for the binary biosorption of Cr(III) and Ni(II) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

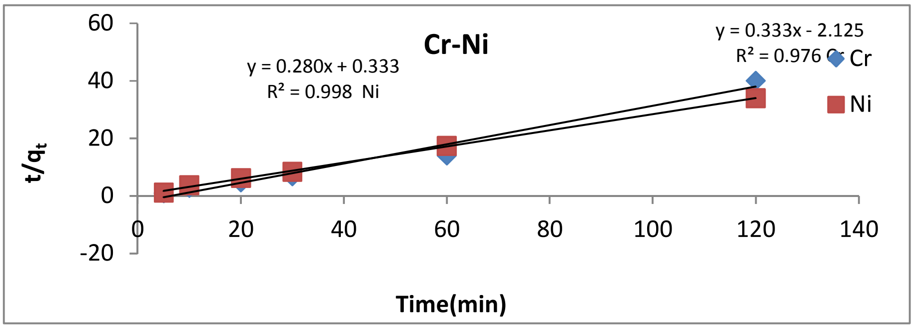

Figure 10. The pseudo-second order plot on the kinetic study for the binary biosorption of Cr(III) and Ni(II) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

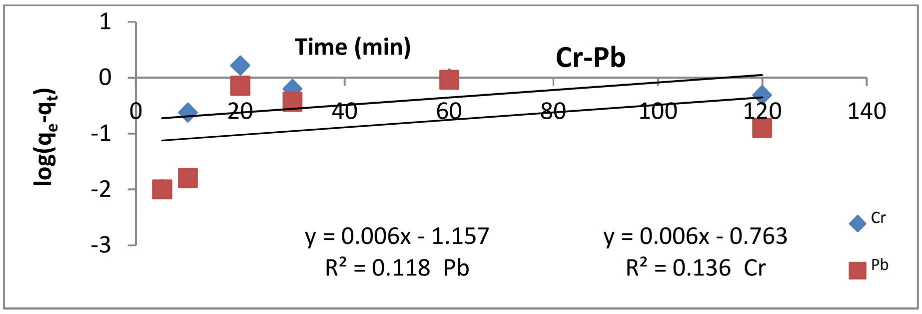

Figure 11. The pseudo-first order plot on the kinetic study for the binary biosorption of Cr(III) and Pb(II) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L ; contact time 120 min; Temperature 27°C)

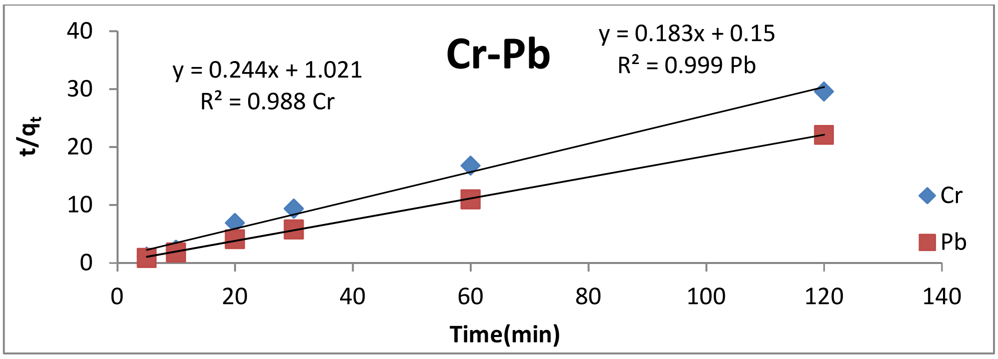

Figure 12. The pseudo-second order plot on the kinetic study for the binary biosorption of Cr(III) and Pb(II) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L ; contact time 120 min; Temperature 27°C)

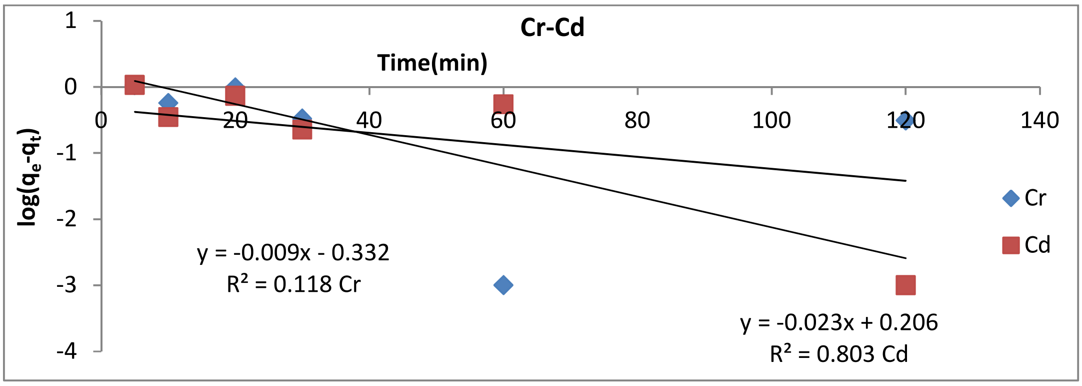

Figure 13. The pseudo-first order plot on the kinetic study for the binary biosorption of Cr(III) and Cd(II) by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

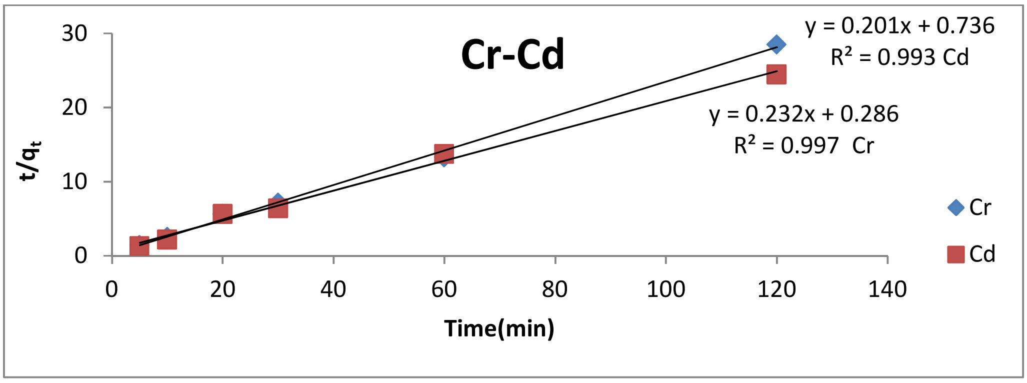

Figure 14. The pseudo-second order plot for the kinetic study for the binary biosorption of Cr(III) and Pb(II) metal ions by *Luffa cylindrica* fibre (pH 4; biosorption concentration 100 mg/L; contact time 120 min; Temperature 27°C)

Table1. The pseudo-second order parameters for the kinetic study of Cr, Cr-Pb, Cr-Ni, and Cr- Cd single and binary systems biosorption by *Luffa cylindrica* fibre biomass (LCFB)

Metal System	Metal ion	R^2 (g/mg min)	q_e (calc.)	q_e (expt.)
Cr	Cr	0.982	3.0212	5.123
Cr-Ni	Cr	0.978	3.0030	5.431
	Ni	0.998	3.5714	4.304
Cr-Pb	Cr	0.988	4.0984	4.550
	Pb	0.999	5.4645	5.550
Cr-Cd	Cr	0.976	3.0303	4.517
	Cd	0.976	3.0030	4.903

CONCLUSION

This work demonstrated the biosorption of a heavy metal solution by *Luffa cylindrica* fibre. This biomass was selected for studying biosorption due to its availability as well as to access the possibility of utilizing a waste biomass to eradicate heavy metal pollution. The obtained result for the biomass dose showed that a little quantity of biosorbent will be effective in adsorbing the metal ions from aqueous solution. The suitability of the pseudo-first order and pseudo-second order kinetic models for sorption of the metal systems onto *Luffa cylindrica* fibre was discussed and the results showed that pseudo-second order kinetic model was found to be in good agreement with the experimental data.

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