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Der Chemica Sinica, 2015, 6(4): 114-124

ISSN: 0976-8505
CODEN (USA) CSHIA5

Effect of co-ions on the biosorption of Cr(III) from aqueous solutions using *Luffa cylindrical* fibre: Equilibrium consideration

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ABSTRACT

The biosorption of single metal system of chromium(III) and binary metal systems (Cr-Pb, Cr-Cd, and Cr-Ni) from aqueous solutions using Luffa cylindrica fibre biomass was investigated as function of pH and initial metal concentration. An optimum pH of 4 was obtained for all the metal systems investigated. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models were applied to describe the biosorption isotherm of the metal ions by Luffa cylindrica fibre biomass. The equilibrium adsorption data for the four single and binary metal ion systems were best described by Langmuir adsorption isotherm. The adsorption of binary mixture of heavy metal solutions onto the surface of Luffa cylindrica fibre was found to be a competitive type. In the binary system under study, chromium (III) was the priority metal and its uptake was greatly promoted in the presence of lead or Nickel cations, while the presence of cadmium inhibited chromium uptake by the Luffa cylindrica fibre biomass.

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

INTRODUCTION

The presence of heavy metals in aquatic environment has been identified as damaging to aquatic life. Apart from the fact that these metals kill microorganisms during biological treatment of waste-water with a consequent delay of the process of water purification, most of the heavy metal salts are soluble in water, form aqueous solutions and consequently cannot be separated by ordinary physical means of separation. The health risk of heavy metal ingestion deserves urgent attention. Chromium causes irritation, nausea and vomiting at low level exposure and kidney, liver, circulatory and nerve tissue damages on long term exposure. Lead causes damage to nervous, circulatory, blood forming and reproductive systems. Cadmium causes renal dysfunction, hypertension, hepatic injury, lung damage and is a potential carcinogen [1]. Long term exposure to nickel causes decrease in body weight, heart and liver damages.

The wastewaters from electroplating, mining, refining, printing and dyeing have constituted serious menace to our ecological security because of presence of various toxic and non-biodegradable heavy metals present in them [2]. Conventional approaches to removal of these heavy metal-containing wastewaters mainly include: precipitation, oxidation-reduction, evaporation, ion-exchange, electrochemical treatment and membrane separation technique. The major drawbacks with these methods lie in their relatively low treatment efficiency, complicated operation, high cost and possible generation of secondary pollutants that require further treatment [3].

Adsorption of heavy metals by activated carbon has proven a powerful technique for treating domestic and industrial wastewater [4, 5]. However, the high cost of activated carbon and its loss during the regeneration restricts its application. The adsorption of heavy metal ions by low cost renewable organic materials has gained proper intensity in recent times [6-8]. The utilization of sea-weeds, moulds, yeasts and other dead microbial biomass and agricultural waste materials for heavy metal removal has been explored [6, 9-11]. The major advantages of biosorption over conventional techniques for treatment of heavy metal-contaminated water include: Low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery.

Agricultural materials, particularly, those containing cellulose have shown potential metal biosorption capacity. The basic components of the agricultural waste biomass include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch containing variety of functional groups that facilitate metal complexation and consequently aid in sequestering of heavy metals [6, 12]. It has also been observed that appropriate functionalization of biosorbents [13] with crown ethers [14, 15], amines [16] and sulphur bearing groups like thiols, dithiocarbamates, dithiophosphates and xanthates [17] can further improve biosorption performance.

The present study investigates the ability of an agro-based materials, *Luffa cylindrica* fibre in removing Cr(III) from aqueous solutions. The presence of Pb(II), Ni(II) and Cd(II) in combination with the Cr(III) as binary mixtures was investigated and overall synergistic and antagonistic effects of these co-ions were assessed using different equilibrium isotherm models.

MATERIALS AND METHODS

Preparation of biosorbent

The dried *Luffa cylindrica* fibre used as biosorbent were collected from site located within Ibadan metropolis Nigeria. The *Luffa cylindrica* fibre were obtained after removing the external dry coverage on the fibre. 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 and then stored in an air-tight polythene bag.

Preparation of stock solutions

Stock solutions of chromium, nickel, lead and cadmium ions were prepared from their salts $Cr(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ respectively by dissolving known masses of the salts in de-ionized water. The concentrations of the metal solutions were analyzed using atomic absorption spectrophotometer (AAS), from which serial dilution of the stock single and binary metal solutions were made.

Batch Adsorption Experiments

The influence of pH on the adsorption process was carried out by introducing 30 mL of 100 mg/L of each of the metal solutions as single and binary mixtures in different Erlenmeyer flasks containing 0.5 g of the prepared *Luffa cylindrical* biosorbent. The pH of the medium was varied from 2.0 to 7.0 using either 0.1 M HNO_3 or 0.1 M NaOH. The flasks were agitated on a rotary shaker at 150 rpm for 2 h and after which were filtered, centrifuged and 5 mL of the filtrate was taken and analyzed for the residual metal content by Atomic Absorption Spectrophotometer (AAS). Each experiment was carried out in duplicate and mean residual concentration taken.

The effect of concentration on equilibrium adsorption of Cr(III) onto the adsorbent was carried out by introducing 30 m/L of different concentrations ranging from 25 mg /L to 150 mg/L of the metal ions as single and binary solutions of Cr, Cr-Pb, Cr-Ni and Cr-Cd respectively into 250 mL Erlenmeyer flasks. This was followed by the addition of 0.5 g of the adsorbent at a temperature of 27 ^{0}C and pH 4.0. The flasks were shaken for 120 min on a rotary shaker and at the end of the contact time (2 h), the mixtures were filtered rapidly into separate sample bottles. The residual metal ion concentration in the filtrate was determined using UNICAM (solar AAS 969) atomic absorption spectrophotometer.

Data analysis

The percentage removal R(%) of the metal ions was calculated as:

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

While the specific metal uptake q_e (mg/g) was calculated as follows:

$$q_e = \frac{(C_i - C_f)V}{m} \quad (2)$$

Where C_i and C_f are the initial and final (equilibrium) concentrations in mg/L respectively, V is the volume of the metal solution in mL, *m* is weight of the biomass in g.

RESULTS AND DISCUSSION

Effect of pH on biosorption

One of the most important factors affecting the biosorption of metal ions is the pH of solution. The acidity of the medium affects the competitive ability of hydrogen ions with metal ions for active sites on the biosorbent surface [18]. The effect of pH on the biosorption of Cr(III), Cr(III)-Pb(II), Cr(III)-Cd(II) and Cr(III)-Ni(II) as single and as binary metal systems onto *Luffa cylindrica* fibre biomass was studied by adjusting the pH values of the solutions in the range of 2-7 and the results are shown in Figures 1-4. Low removal of Cr(III) by *Luffa cylindrical* fibre biomass was observed at pH values lower than 3.0 in the single metal ion system. A 75.67 % was adsorbed at pH 3.0. As the pH values increased above 4, the amount of Cr(III) adsorbed decreased. The maximum removal was found to be 79.37% for single Cr(III) at the optimum pH of 4.0. This observation led the measurement of all the equilibrium biosorption experiments of Cr(III) as a single metal system at a pH 4.0.

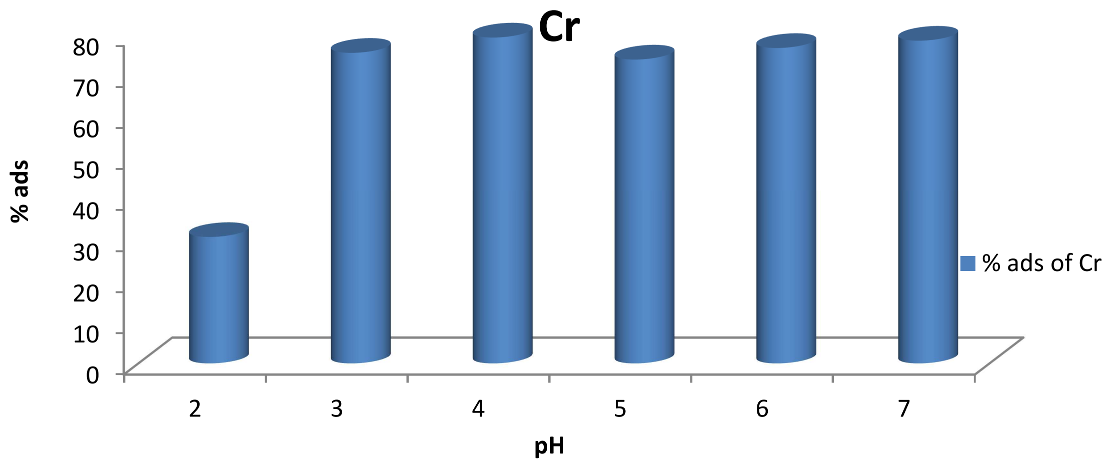

Figure 1 Effect of pH on the biosorption of single chromium(III) by Luffa cylindrical fibre (initial concentration 100 mg/L; contact time 120 min; Temperature 27 ^{o}C)

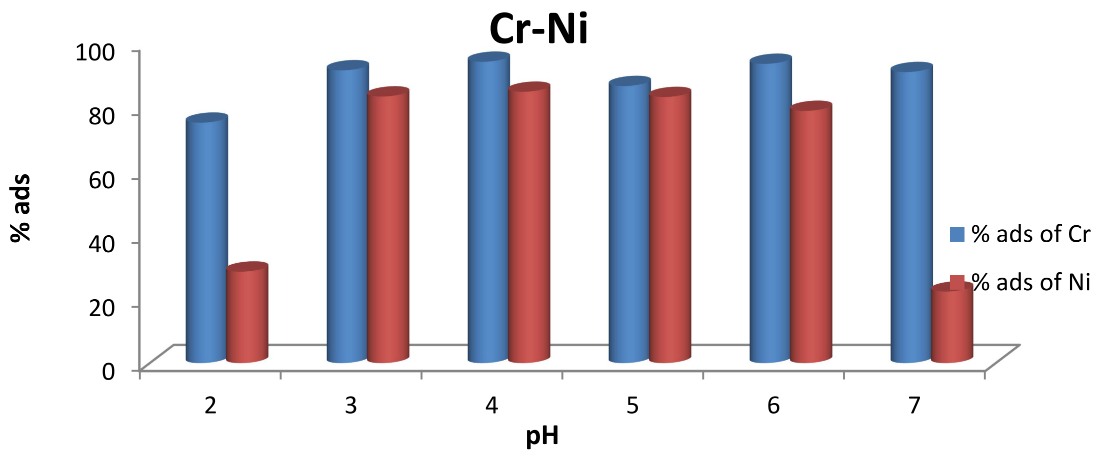

Figure 2 Effect of pH on the binary biosorption of chromium(III) and nickel (II) by Luffa cylindrical fibre (initial concentration 100 mg/L; contact time 120 min; Temperature 27 ^{o}C)

For adsorption of Cr-Ni binary metal system onto *Luffa cylidrica* fibre (LCF) biomass, the biosorption efficiency was observed to increase from 75.14 to 94.12% for Cr(III) biosorption and from 28.45 to 84.77% for Ni(II) at pH 4 as shown in Figure 2. In view of this, all biosorption experiments on Ni-Cr binary system were carried out at pH 4. At higher pH values (pH>4), the percentage removal for Ni(II) and Cr(III) ions were dramatically decreased.

In the case of Cr-Cd system, the biosorption efficiency was observed to increase from 46.88 to 91.78% for Cr(III) biosorption and from 47.82 to 98.05% for Cd(II) ions at pH 4. This result led to investigation of all biosorption experiments on Cr-Cd binary system at pH 4. At higher pH values (pH>4), there was a drastic decrease in the percentage removal for Cd(II) and Cr(III) ions.

For the Cr-Pb binary system, 97.62 % and 52.82 % were observed for both Cr(III) and Pb(II) at pH 2 respectively while at pH 4, 98.74% and 90.16% were also observed for both chromium and lead ions respectively. Increase in pH value above pH 4 shows a decrease in the amount of both Chromium and lead adsorbed in the binary system by 5.8% and 8.43% respectively from pH 4 to pH 7. For all the four systems studied, a constant optimum pH of 4 was employed.

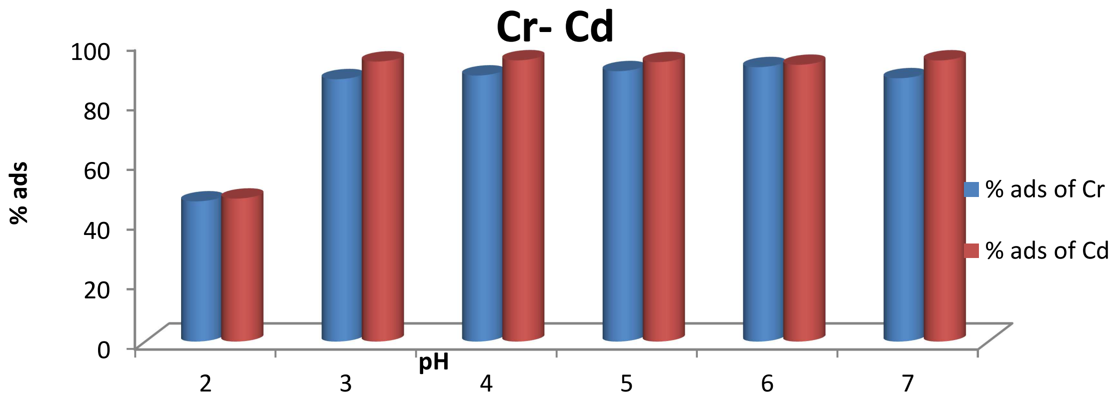

Figure 3 Effect of pH on the binary biosorption of chromium(III) and Cadmium(II) by Luffa cylindrical fibre (initial concentration 100 mg/L; contact time 120 min; Temperature 27°C)

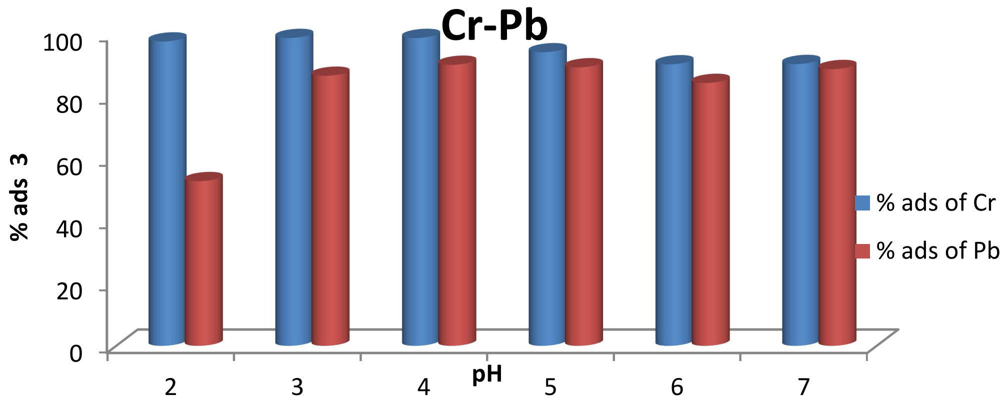

Figure 4 Effect of pH on the binary biosorption of lead(II) and Chromium(III) by Luffa cylindrical fibre (initial concentration 100 mg/L; contact time 120 min; Temperature 27°C)

Biosorption equilibrium models

Adsorption isotherms represent the equilibrium distribution between the amount of metal ions adsorbed onto the biosorbent to that remaining in the bulk solution at a given temperature as a function of concentration of the metal ions. A biosoption isotherm is characterized by certain constant values, which express the surface properties and affinities of the biosorbent and can also be used to compare the biosorption capacities of the bisorbent for different adsorbates. In this study, three important sorption isotherm models were selected to fit experimental data and these include: Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models.

Langmuir Isotherms

Langmuir model assumes uniform energies of sorption onto the surface and suggests monolayer sorption on a homogenous surface without interaction between adsorbed molecules. The linearized Langmuir isotherm equation is expressed as:

$$ {}^{1}/_{q_e} = \frac{1}{C_e}\left(\frac{1}{q_{max}b}\right) + \left(\frac{1}{q_{max}}\right) \quad (3) $$

Where q_{max} (mg/g) and b are Langmuir constants relating to adsorption capacity and energy of adsorption respectively and can be determined from the intercept and slope of linear plots of ${}^{1}/_{q_e}$ versus ${}^{1}/_{C_e}$ as shown in Figures 5-8. Table 1, shows that the single chromium metal ion system and the binary metal ions system of Cr-Ni had high correlation coefficient of 0.929 for single chromium(III), 0.995 and 0.966 for the Cr and Ni respectively, while Cr-Pb and Cr-Cd binary systems are observed to have a moderate fitting. Lead in Cr-Pb binary metal system, had R^2 value of 0.802. Only Cadmium in Cr-Cd binary metal system is observed to have low R^2 value of 0.739. Table 1 Shows the values of b and q_{max} for *Lufa cylindrica* fibre sorption of the different metal ions in the three binary and single metal ions system. The Langmuir parameters obtained show that *Luffa cylindrica* fibre biomass has potential for the removal of Cr, Ni, Pb and Cd metal ions from their single and binary metal systems.

The equilibrium data for biosorption of the different binary metal ion systems were also analyzed in the form of biosorption capacity of one metal ion in its binary metal system, Q^{mix}, to the biosorption capacity for the same metal ion when it is present alone in the solution, Q^0 and the following deductions are used to assess the effect of co-ions on the adsorption of the metal of interest by the *luffa cylidrica*:

For $\frac{Q^{mix}}{Q^0} > 1$, the biosorption is promoted by the presence of other metal ions.

For $\frac{Q^{mix}}{Q^0} = 1$, there is no observable net interaction

And for $\frac{Q^{mix}}{Q^0} < 1$, the biosoprtion is suppressed by the presence of the other metal ions.

The values of Q^{mix}/Q^0 for chromium in Cr-Ni and Cr-Pb were found to be 2.097 and 1.228 respectively, suggesting that the simultaneous presence of chromium metal ions in both binary mixtures was affected by the presence of other metal ions through competition for biosorption sites on the *Luffa cylindrica* fibre. The Q^{mix}/Q^0 ratio for chromium(III) ion in the presence of cadmium ions which is 0.0875, suggests that the simultaneous presence of competing cadmium ions strongly reduces the biosorption of chromium(III) ions through competition.

Freundlich Model

This isotherm also considers monolayer sorption with a heterogeneous distribution of active sites of the sorbent. The linearized Freundlich equation is given as:

$$Log_e\, q_e = \log_e K_f + \frac{1}{n}\log_e C_e \qquad (4)$$

Where K_f and 1/n are constants relating to the biosorption-capacity and the biosorption intensity respectively and both constants are determined from the intercept and slope of linear plots of log (q_e) vs. log (C_e) as shown in Figures 9-12. Table 2 Shows the Freundlich isotherm parameters, K_f and n obtained for the biosorption of Cr, Cr-Ni, Cr-Pb and Cr-Cd single and binary systems onto *Luffa cylindrica* fibre biomass. The R^2 value for single metal system of chromium was 0.880 while 0.974 was obtained for chromium(III) biosorption in the binary metal system of Cr-Ni and 0.938 for nickel biosorption in the binary metal system of Cr-Ni, indicating a good fit for the two systems. Cr-Pb and Cr-Cd binary systems were found to have a relatively moderate R^2 values, indicating that, the Freundlich model could not adequately describe the relationship between the amount of metal ions (Cr-Pb and Cr-Cd) adsorbed by the biomass and its equilibrium concentration in the solution.

Dubinin-Radushkevich model

The Dubinin-Radushkevich (D-R) model is used to estimate the characteristic porosity of the biomass and the apparent energy of adsorption. The linearized D-R model is represented by:

$$Inq_e = Inq_m - \beta\varepsilon^2 \qquad (5)$$

$$\varepsilon = RTIn\left(1 + \frac{1}{C_e}\right) \qquad (6)$$

Where ε is the Polanyi potential, β is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution, and q_m is the Dubinin-Radushkevich isotherm constant relating to the degree of sorbate sorption by the sorbent surface. A plot of In q_e against

$\left[RT\ln\left(1+1/C_e\right)\right]^2$ yielding a straight line confirms the model as shown in Figures 13-16. The apparent energy of adsorption from Dubinin-Radushkevch isotherm model can be computed using the relationship.

$$E = \frac{1}{(2B_D)^{1/2}} \qquad (7)$$

The equilibrium adsorption data were applied to the D-R isotherm model to determine the nature of biosorption processes whether it is physical or chemical. This isotherm gave interpretation of equilibrium adsorption data for single chromium metal ion and Cr-Ni binary metal ion biosorption with R^2 values of 0.900 for Cr(III) and 0.973 for Cr(III) in the presence of nickel ions and 0.820 for nickel in Cr-Ni binary system . For Cr-Pb and Cr-Cd binary metal ions system, a poor fitting were observed. Table 3 shows the D-R parameters (q_D, β and E) obtained for the four metal systems studied. The biosorption free energy gives information about biosorption mechanism. For E values between 8 and 16 kJ/mol, the biosorption process follows chemical ion-exchange mechanism and if E< 8 kJ /mol, the biosorption process is of physical nature [19]. The mean biosorption energy was calculated as 8.5 kJ/mol for biosorption of chromium(III) ions in the presence of lead and 10 kJ/mol for cadmium in the presence of chromium ions, which suggest that the biosorption mechanism of both metal ions onto *luffa cylindrical* fibre biomass may be by chemical ion-exchange since the sorption energies are within 8-16 J/mol. The rest of the metal ions in the binary and single systems were known to follow a physisorption process because the calculated sorption energies were found to be less than 8 kJ/mol.

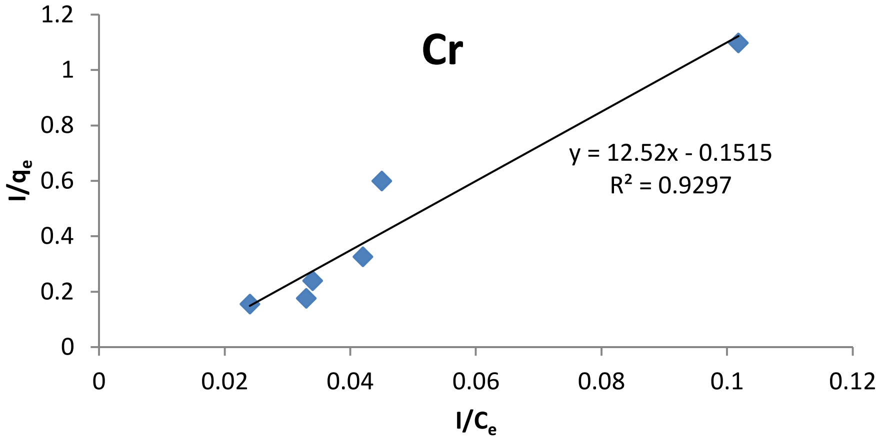

Figure 5 Langmuir isotherm for the biosorption of chromium(III) by *Luffa cylindrica* fibre

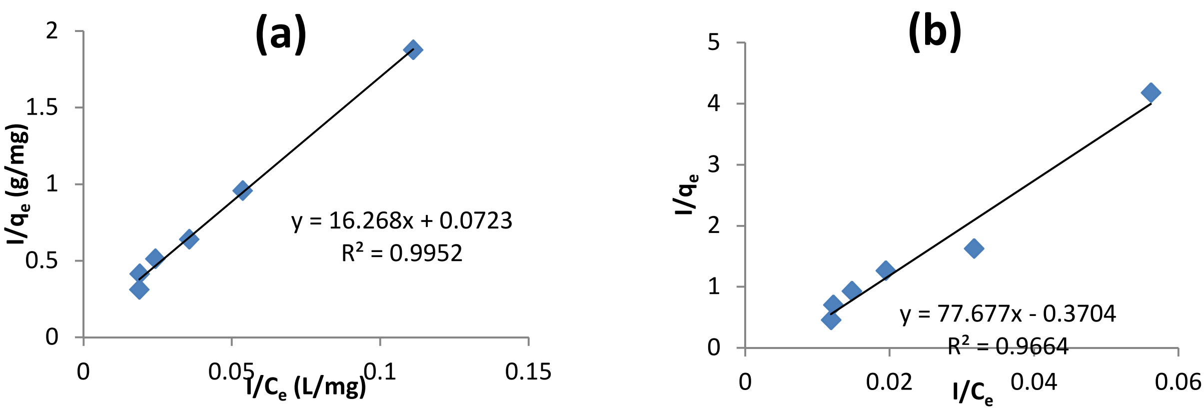

Figure 6 Langmuir isotherm for the binary biosorption of (a) chromium(III), and (b) nickel(II) metal ions by *Luffa cylindrica* fibre

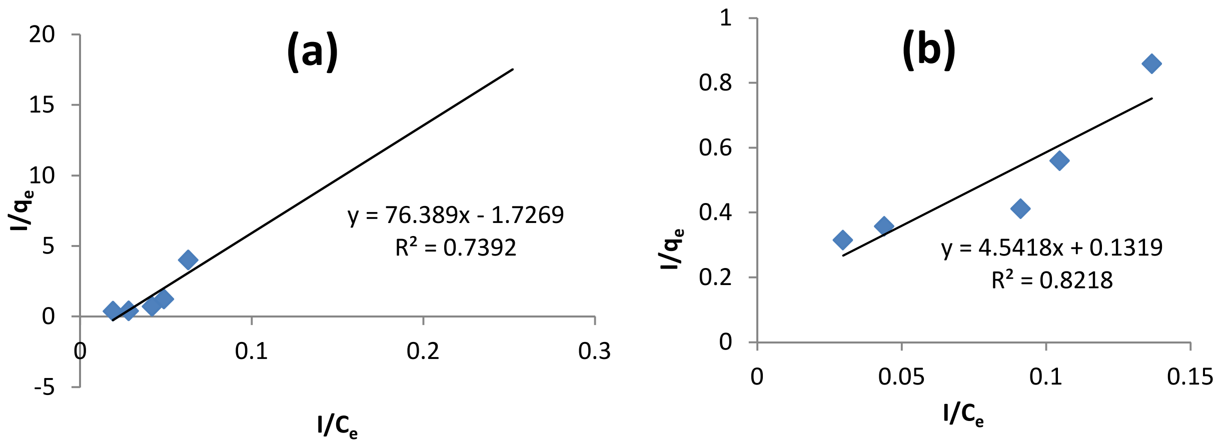

Figure 7 Langmuir isotherm for the binary biosorption of (a) chromium(III), and (b) cadmium(II) metal ions by *Luffa cylindrica* fibre

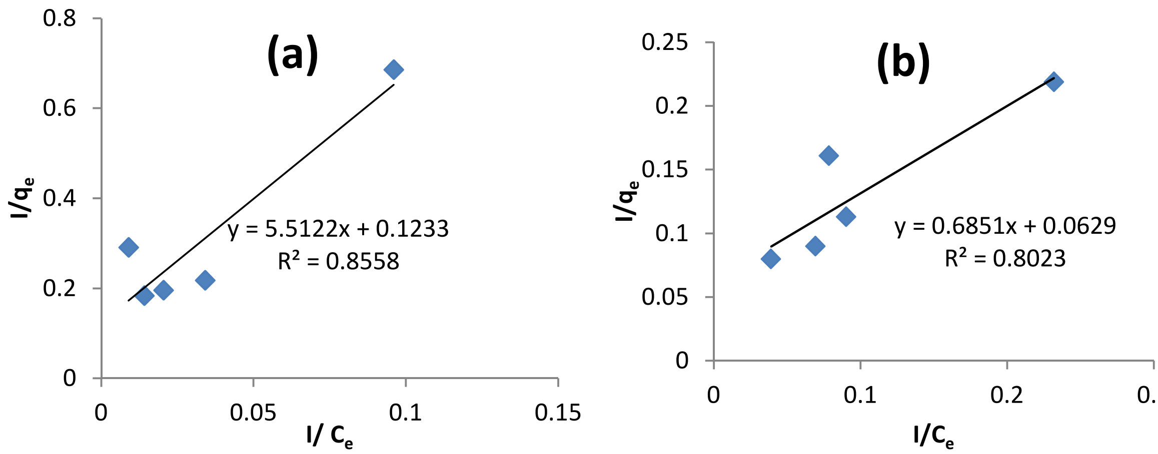

Figure 8 Langmuir isotherm for the binary biosorption of (a) chromium(III), and (b) lead(II) metal ions by *Luffa cylindrica* fibre

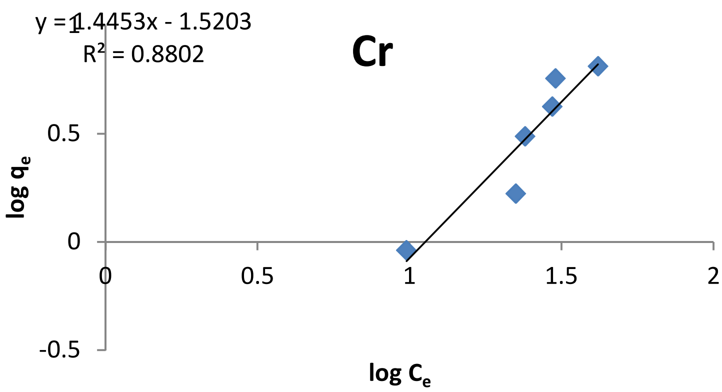

Figure 9 Freundlich isotherm for the biosorption of chromium(III) by *Luffa cylindrica* fibre

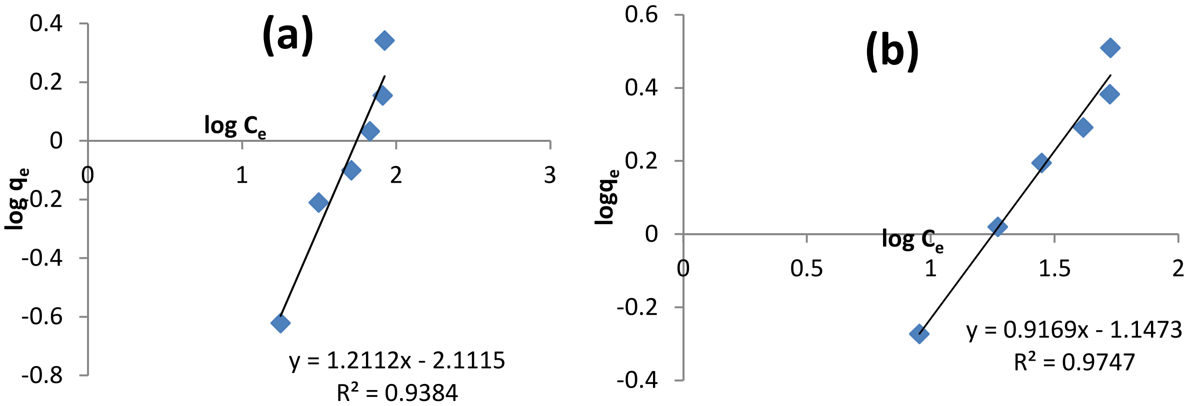

Figure 10 Freundlich isotherm for the binary biosorption of (a) chromium(III) and (b) nickel(II) ions by *Luffa cylindrica* fibre

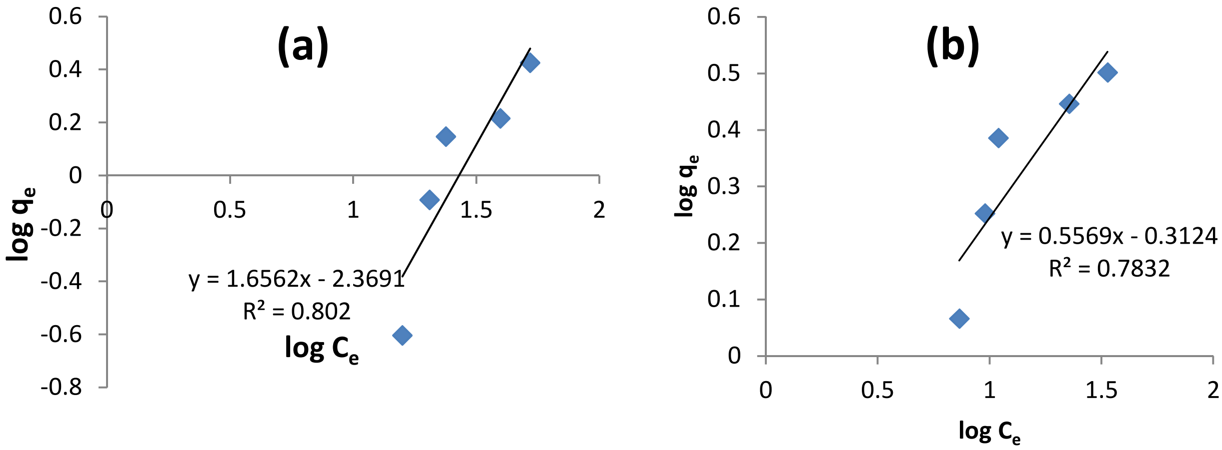

Figure 11 Freundlich isotherm for the binary biosorption of (a) Chromium(III) and (b) Cadmium(II) ions by *Luffa cylindrica* fibre

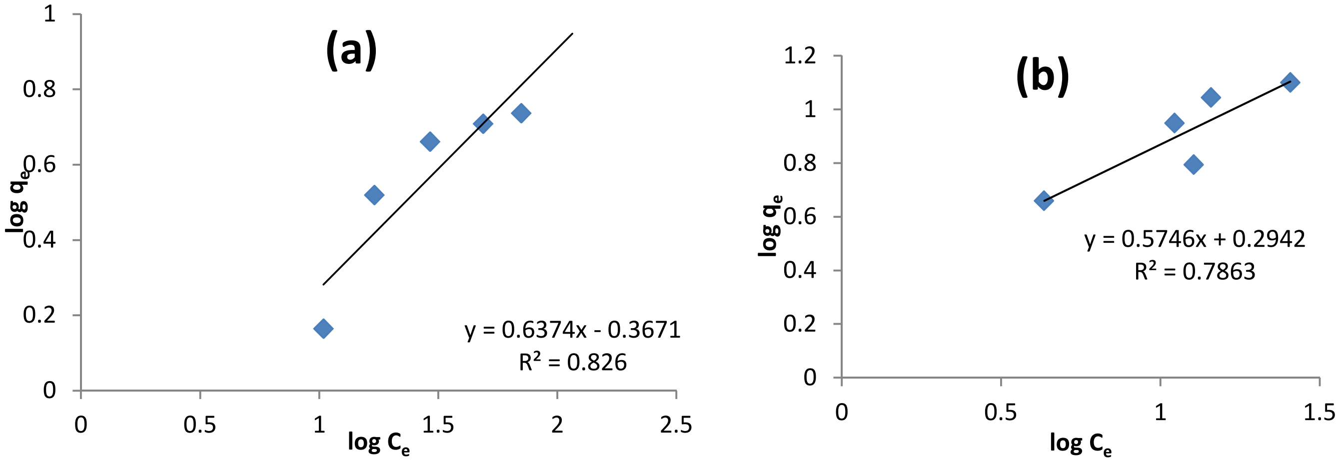

Figure 12 Freundlich isotherm for the binary biosorption of (a) chromium(III) and (b) lead(II) ions by *Luffa cylindrica* fibre

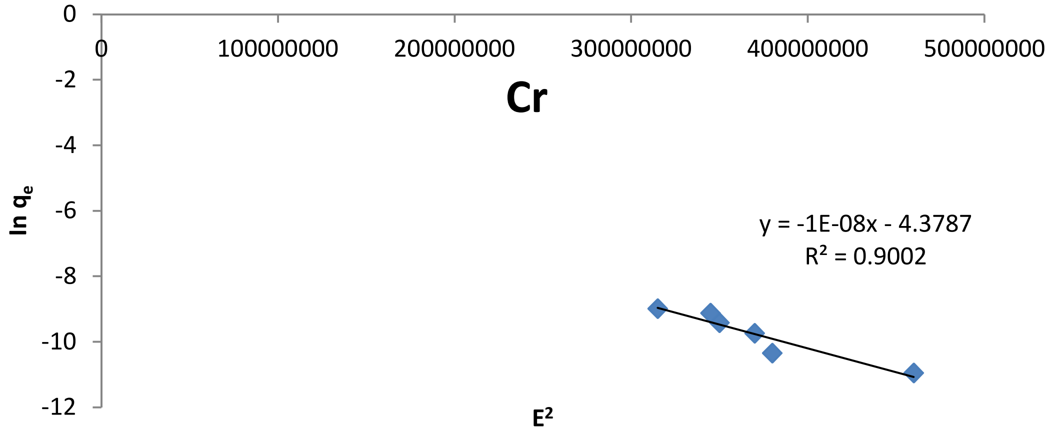

Figure 13 Dubinin-Radushkevich (D-R) isotherm for the biosorption of chromium(III) by *Luffa cylindrica* fibre

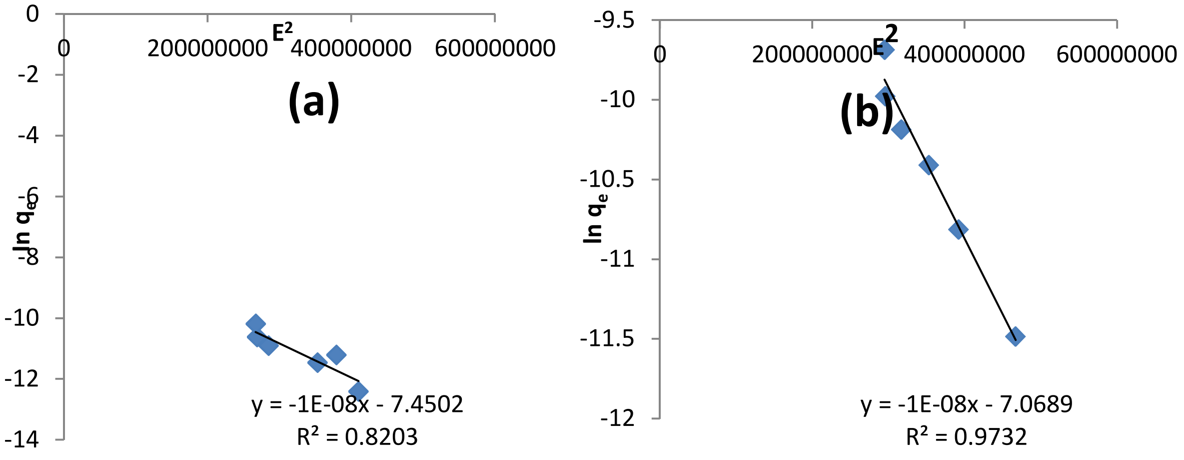

Figure 14 D-R isotherm for the binary biosorption of (a) nickel(II) and (b) chromium(III) ions by *Luffa cylindrica* fibre

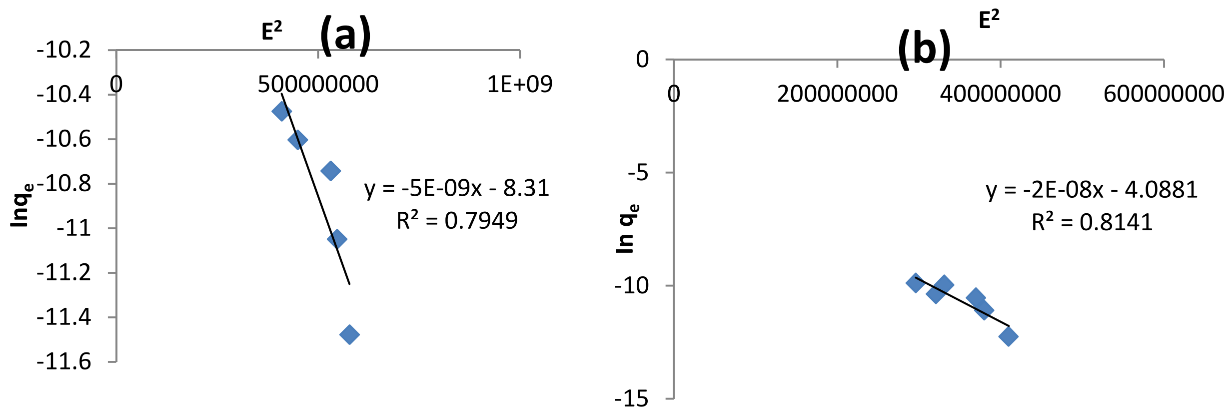

Figure 15 D-R isotherm for the binary biosorption of (a) cadmium(II) and (b) Chromiuml(III) metal ions by *Luffa cylindrica* fibre

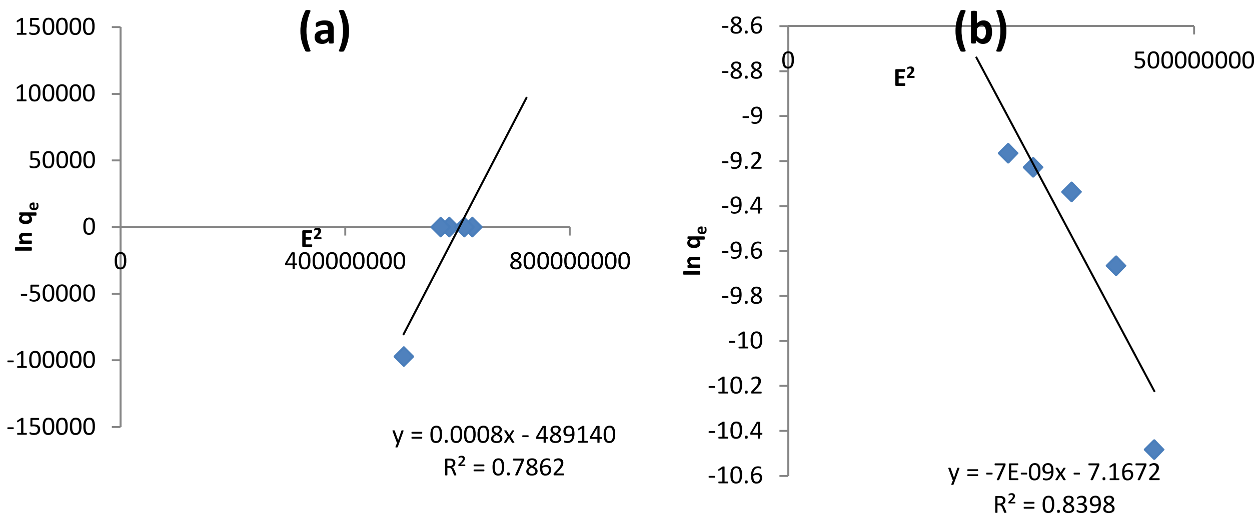

Figure 16 D-R isotherm for the binary biosorption of (a) lead(II) and (b) Chromium(III) ions by *Luffa cylindrica* fibre

Table 1 Langmuir isotherm parameter for the biosorption of single Cr system and Cr-Cd, Cr-Pb, Cr-Ni binary systems by *Luffa cylindrica* fibre

Metal system	Metal ions	R^2	q_{max}	K_L
Cr	Cr	0.929	-6.623	-82.91
Cr-Ni	Cr Ni	0.995 0.966	-13.89 -2.70	-225.85 -209.71
Cr-Pb	Cr Pb	0.855 0.802	8.13 16.13	44.81 11.05
Cr-Cd	Cr Cd	0.739 0.821	0.58 7.63	44.30 34.64

Table 2 Freundlich isotherm parameter for the biosorption of single Cr system and Cr-Cd, Cr-Pb, Cr-Ni binary systems by *Luffa cylindrica* fibre

Metal system	Metal ions	R^2	K_F	n
Cr	Cr	0.88	0.03	0.692
Cr-Ni	Cr Ni	0.974 0.938	0.071 0.0078	1.09 0.826
Cr-Pb	Cr Pb	0.826 0.786	0.43 1.968	1.57 1.742
Cr-Cd	Cr Cd	0.802 0.783	0.0048 0.488	0.6068 1.799

Table 3 D-R isotherm parameters for the biosorption of single Cr system and Cr-Cd, Cr-Pb, Cr-Ni binary systems by *Luffa cylindrica* fibre

Metal system	Metal ions	R^2	q_D	$B \times 10^{-8}$	E (kJ/mol)
Cr	Cr	0.900	0.013	1.0	7.1
Cr-Ni	Cr Ni	0.973 0.820	8.52×10^{-5} 5.8×10^{-4}	1.0 10	7.1 7.1
Cr-Pb	Cr Pb	0.839 0.786	6.81×10^{-8}	0.7 0	8.5 0
Cr-Cd	Cr Cd	0.814 0.794	1.68×10^{-2} 2.46×10^{-4}	2 0.5	5 10

CONCLUSION

The present work studied the biosorption of single Cr(III) and its binary mixtures with Ni(II), Cd(II) and Pb(II) ions by *Luffa cylindrica* fibre. Based on the findings of the present study and information obtained from Chemical literature, the following conclusion can be given:

The obtained results showed that pH of the solutions greatly affected the overall removal efficiency of the biomass. The affinity order of *Luffa cylindrica* fibre biomass for the four metals under study was established as:

Cr-Cd>Cr-Pb>Cr-Ni for binary metal systems and Pb>Cr>Ni>Cd for single metal system

The results suggest that there exist a competitive adsorption process as the adsorption capacity of chromium(III) decreased in the Cr-Cd binary metal solution.

The present results demonstrate that the Langmuir model gave better fitting than the Freundlich and Dubinin-Radushkevich (D-R) models for the adsorption equilibrium data of the metal systems in the examined concentration range.

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