

Removal of Cadmium(II) Ions from Water by Adsorption using Water Hyacinth (*Eichhornia crassipes*) Biomass

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The kinetics and equilibrium binding of Cd(II) ions onto raw water hyacinth (*Eichhornia crassipes*) biomass (RBH) were investigated with the view to utilize it as a low-cost biosorbent for removal of toxic metal ions from water. The biosorption was analyzed through batch experiments with respect to the effect of contact time, agitation speed, biosorbent dosage, solution pH, Cd(II) concentration, and the presence of other metal ions. Cadmium adsorption onto *Eichhornia crassipes* biomass was pH- and temperature-dependent, and complete Cd(II) removal from solution was achieved at all Cd(II) concentrations up to 10 mg/L. The biosorption equilibrium was described by Langmuir and Freundlich isotherms, and the RBH Cd(II) uptake capacity was 104 mg/g. The biosorption process followed the pseudo-second-order model ($R^2 > 0.99$). The root biomass of water hyacinth had one of the highest Cd(II) sequestration efficiencies when compared to other biosorbents that have been used to remove Cd(II) from water.

Keywords: Biosorption; Cadmium(II); Isotherms; Kinetics; Water hyacinth (*Eichhornia crassipes*)

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INTRODUCTION

The harmful environmental effects of heavy metals are well known (Manahan 2003). Metal ions are non-biodegradable and accumulate in the food chain, causing health problems in many different kinds of organisms. Cadmium, in particular, is a non-essential element that is highly toxic to humans. Intake of Cd(II) leads to high blood pressure and kidney and liver damage (Akerstrom *et al.* 2013; Yazıhan *et al.* 2011). Conventional techniques for the removal of toxic metal ions from water are ineffective, especially at metal ion concentrations lower than 100 mg/L (Volesky 1990). The development of clean-up technologies for environmental remediation of toxic metals is therefore of major interest at present (Argun and Dursun 2008). New technologies being investigated for easy metal clean-up of wastewaters include adsorption using sorbent biomasses. Use of low-cost adsorbents for wastewater treatment is recommended at the moment because the adsorbents are usually available in large amounts and are therefore cost-effective. The biomasses that have attracted the highest interest for metal ion sequestration from water include primarily agriculture waste products such as legume pods (Panda *et al.* 2008), rice husks (Goodhead and Dagde 2011), sugar beet pulp (Pehlivan *et al.* 2008), and corncobs (García-Rosales *et al.* 2012).

At the moment, the water hyacinth (*Eichhornia crassipes*) is a major environmental challenge on Lake Victoria and on several other water bodies in eastern Africa. After its introduction in the last few decades, the plant has multiplied and invaded

water systems (Win *et al.* 2003), causing serious ecological disruption and interference in economic activities on the water bodies. Management of the weed using herbicides is undesirable, and mechanical clearance is untenable. After an initial success with biological control using *Neochetina* spp., resurgence of the weed has occurred in several parts of the lake (Julien 2001), and in view of the increasing economic menace of the weed, it is therefore desirable to explore alternative approaches to its management.

Water hyacinth (*Eichhornia crassipes*) plant has also received attention because of its potential for removal of pollutants when utilized as a biological filtration system. A number of phytoremediation studies have been carried out (Muramoto and Oki 2009; Liao and Chang 2004; Ibrahim *et al.* 2009; Ibrahim and Al-Fifi 2010; Hasan and Talat 2007). However, use of this method takes a lot of time, as it is inefficient when dealing with large volume of industrial waste water. Furthermore, live plants when used are cumbersome.

Dried roots from water hyacinth have been used to study its removal behavior from mono-component aqueous metal solutions. Schneider *et al.* (1995) studied the feasibility of dried water hyacinth roots for the removal of Pb(II), Cu(II), Cd(II), and Zn(II) ions from aqueous solution. Biosorption capacity of water hyacinth was found to be greater than that of yeast, bacterial, and fungal strains. Hasan *et al.* (2010) utilized dried water hyacinth powder of the aerial part of the weed (stem and leaves) for the removal of Cr(VI) and found that the sorption was negatively affected by pH, whereas temperature had a positive effect. In a more recent study Ibrahim *et al.* (2012) investigated possible usages of water hyacinth as a biosorbent for various metals ions; using density functional theory DFT and experimental FTIR, the model showed water hyacinth as a mixture of cellulose and lignin. The dried shoot and root were found to be good sorbent materials for Cd(II) and Pb(II) at optimum dosage of 5.0 g/L and pH 5.0 with equilibration attained within 30 to 60 min.

The current work was initiated to investigate the binding of Cd(II) ions to raw *Eichhornia crassipes* biomass (RBH) with the view to utilize the biomass as a low-cost biosorbent for heavy metal removal from water. The Cd(II) biosorption process using RBH was analyzed through batch experiments with respect to the effect of initial Cd(II) concentration, pH, the presence of other cations, mass of RBH, contact time, and shaking speed. The current article reports on the results of these tests.

EXPERIMENTAL

Materials

Samples of the root biomass of water hyacinth (*Eichhornia crassipes*) were obtained from Nairobi Dam, in the city of Nairobi, Kenya. They were washed with excess 0.1 M nitric acid and rinsed in de-ionized water until the pH of the water was 5.0 to 6.5, *i.e.*, the initial pH of the water from the dam. The biomass samples were then dried in an oven at 60 ± 0.5 °C for 24 h, crushed to pass through 1.0-mm mesh, and preserved in polythene bottles for biosorption experiments. A standard stock solution containing 1000 mg/L of Cd(II) as a nitrate salt (Merck) was prepared in distilled water. All working standards were obtained from this stock solution by dilution. Analytical grade reagents were used throughout this work.

Equipment

The pH measurements were conducted using a Jenway Model 3505 pH meter equipped with a standard calomel electrode (SCE). The batch adsorption mixtures were agitated at required shaking speeds on a constant shaker model CFC 3018, with the temperature being regulated using a thermostatic water bath model SB3D.A Centurion 6,000 series centrifuge machine was used for separation of the biomass from the Cd(II) solutions, and the analysis of residual Cd(II) ions in the solutions was carried out using an atomic absorption spectrophotometer(AAS) (Buck, model 210 VGP).

Batch Adsorption Tests

All the adsorption experiments, unless otherwise specified, were conducted in triplicates at 25 ± 0.5 °C. The amount, q_e (mg/g), and percentage (% q) of Cd(II) ions adsorbed were calculated as,

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%q = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_0 is the initial Cd(II) concentration (mg/L), C_e is the equilibrium Cd(II) concentration (mg/L), and m is the mass of adsorbent (g) per batch volume, V (mL). A known mass of RBH powder (0.1 g) was mixed with 100 mL of solution containing Cd(II) ions at initial concentrations of 10, 50, and 100 mg/L, respectively. The mixtures were agitated at a constant speed of 175 rpm for a period of 90 min. Aliquots (10 mL each) were drawn from the mixtures at predetermined intervals and centrifuged, and the remaining Cd(II) concentration in solution was determined. The results were used to determine equilibrium adsorption time for Cd(II) adsorption onto RBH and to evaluate the adsorption kinetics of the process.

Similar tests were then conducted at different constant rates of agitation (0 to 200 rpm) to determine the most effective shaking speed for Cd(II) uptake by RBH. To evaluate the effect of the change in mass of the adsorbent on Cd(II) adsorption onto RBH, such tests were conducted using different adsorbent masses (0.1 to 0.5 g) per 100 mL of Cd(II) solution at a constant temperature, agitation rate, and contact time. The effect of change in temperature on Cd(II) biosorption onto RBH, on the other hand, was thereafter investigated in a similar way using optimized contact time, agitation rate, and sorbent dosage at temperatures of 15 to 55 °C. The effect of change in solution pH, on the other hand, was studied using Cd(II) solutions at different initial pH values (0 to 7.0), the pH pre-adjustment being achieved by the addition of small amounts of 0.1 M HNO₃ or 0.1 M NaOH as appropriate. To study the effect of Cd(II) concentration on its adsorption onto RBH. Varying initial Cd(II) concentrations (10 to 600 mg/L) were employed, keeping all other parameters constant. The data were fitted to the Langmuir and Freundlich adsorption isotherms to characterize the reaction mechanism. The effect of solution cations on Cd(II) adsorption onto RBH was then investigated using a 10 mg/L Cd(II) solution containing known concentrations (10 mg/L) of either Na⁺, K⁺, Ca²⁺, or Mg²⁺ ions at optimized adsorption conditions.

RESULTS AND DISCUSSION

Effect of Contact Time

Figure 1 shows the variation of Cd(II) adsorbed by RBH with contact time. The amount of Cd(II) adsorbed onto RBH rapidly increased with increasing contact time to near saturation of the RBH surface in about 30 min. It then increased more gradually toward the equilibrium, reaching it in about 150 min. Similar results have been reported for heavy metal adsorption on *Sargassum fluitans* biomass (Oliveira *et al.* 2008). The initial rapid adsorption suggested that physisorption or ion-exchange reactions at exposed surface sites of RBH were the main mechanism of Cd(II) immobilization. The equilibrium time of 150 min, which was then adopted in all subsequent tests, was comparable to that reported in the literature for Cd(II) uptake by various biosorbents (Benguella and Benaissa 2002; Sheng *et al.* 2005; Zamil *et al.* 2008).

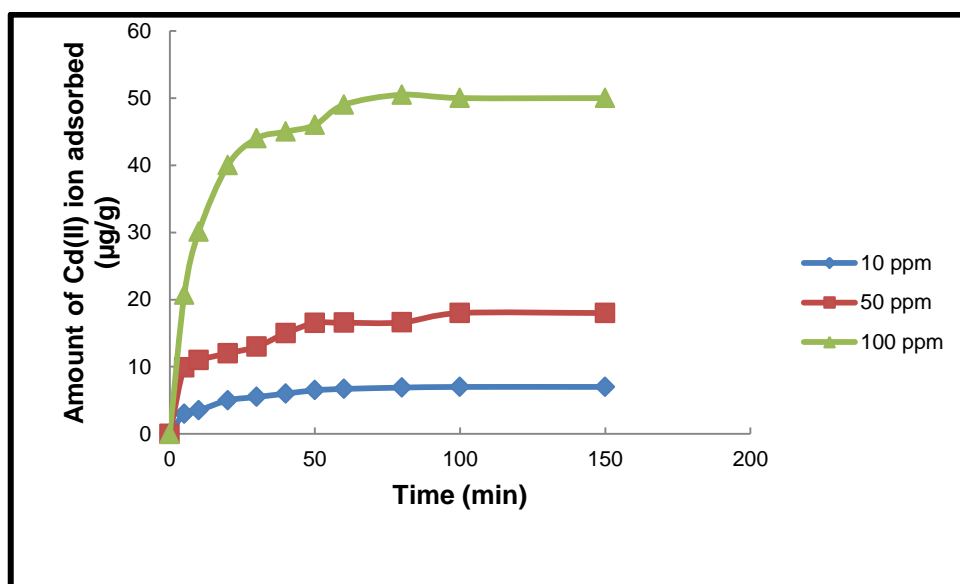


Fig. 1. Effect of contact time on the adsorption of Cd(II) ions by *E. crassipes* at pH 6.0; agitation speed 175 rpm, and temperature 25 ± 0.5 °C

Effect of Shaking Speed

The effect of batch agitation speed on Cd(II) adsorption onto RBH is depicted in Fig. 2. The amount of Cd(II) adsorbed increased with increasing agitation speed, and maximum adsorption occurred at 175 rpm. This is because increasing agitation speed increases the convective mass transfer of solute from the bulk solution, and it also decreases the thickness of the boundary film close to adsorbent surfaces. Optimum agitation therefore increases external film mass transfer and the rate of adsorption (Lee and Low 1997). Under conditions of optimized agitation, surface reactions or intraparticle diffusion would be rate-limiting (Mckay 1982). A constant agitation speed of 175 rpm was adopted in all subsequent experiments.

Effect of Sorbent Dose

Figure 3 shows the effect of variation in RBH mass on its Cd(II) uptake. The percentage of Cd(II) adsorption onto RBH increased from 63% to 86% when the RBH dosage increased from 0.1 to 0.2 g /100 mL and remained constant from there on. This

shows that at higher RBH doses, RBH particles tend to coagulate and decrease the surface area available to incoming Cd(II) ions from solution. This reduces the capacity of the adsorbent to sorb Cd(II). As a result, the highest concentrations (mg/g) of Cd(II) in RBH were achieved at the lowest RHB dose. Therefore, an RBH dose of 0.1 g/100 mL was maintained in all subsequent tests.

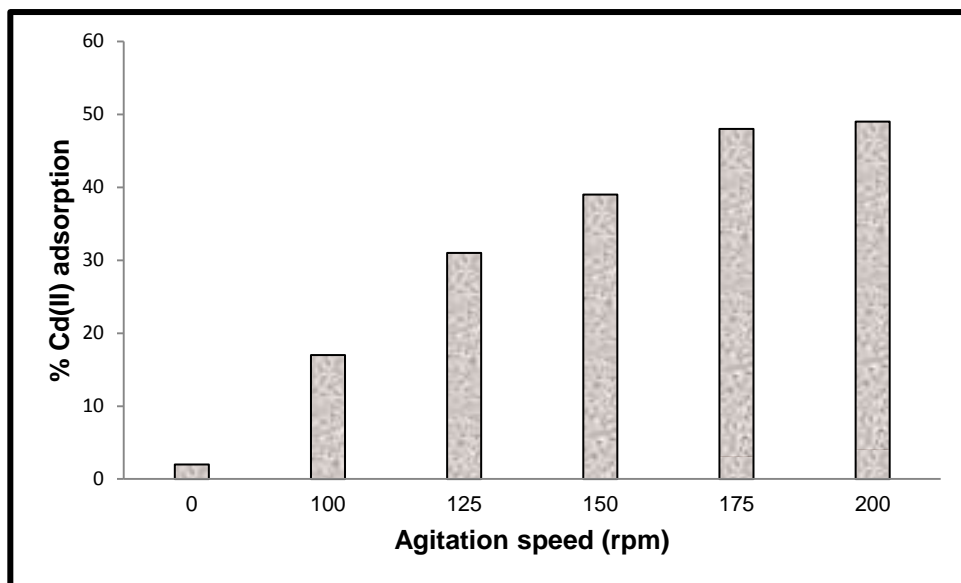


Fig. 2. Effect of shaking speed on adsorption of Cd(II) ions onto *E. crassipes*; initial ion concentration 10 mg/L, pH 6.0, temperature 25 ± 1 °C, and time 150 min

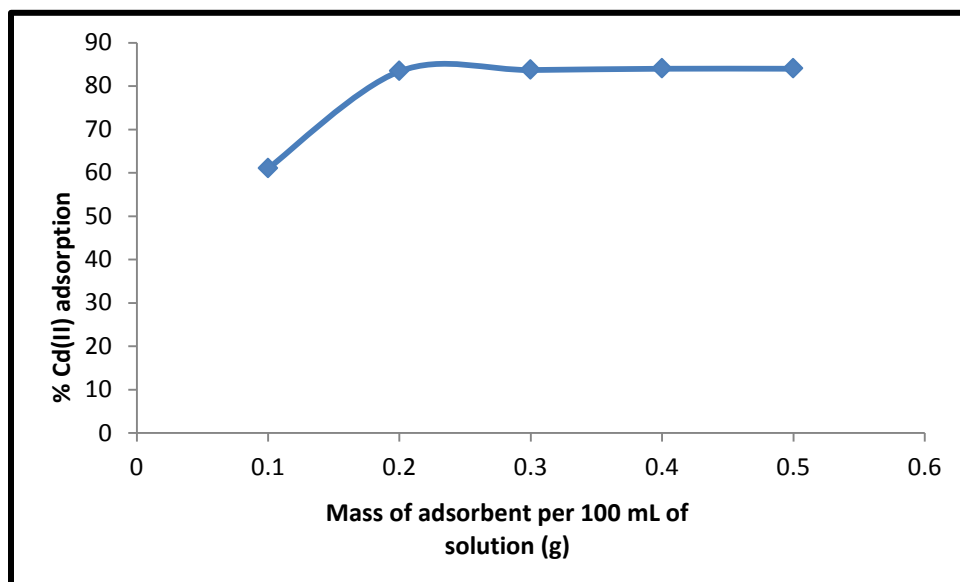


Fig. 3. Effect of adsorbent dose on the biosorption of Cd(II) ions; initial ion concentration 10 (mg/L, pH 6.0, temperature 25 ± 1 °C, time 150 min, and agitation speed 175 rpm

Effect of Temperature

Figure 4 shows that Cd(II) adsorption onto RBH increased from 42% to 58% when the temperature was increased from 20 to 45 °C and that it decreased thereafter. Similar observations have also been reported for Cd(II) biosorption (Benhima *et al.* 2008). This shows that Cd(II) adsorption onto RBH could be endothermic. Higher temperatures increase the kinetic energies of ions and open up additional sorption sites in the adsorbent, increasing the adsorbent's capacity. Above 45 °C, excess heat decomposes RBH-Cd(II) surface adsorption complexes and alters the biosorbent surface sites (Herrero *et al.* 2008), resulting in decreased Cd(II) removal by RBH.

Adsorption Kinetics

An adsorption protocol normally is composed of up to four separate, but not necessarily independent, steps. These include: transfer of the adsorbate from the solution to the adsorbent surface, interactions of the adsorbate particles with the available active sites on the surface of the adsorbent, the adsorbate transfer from the adsorbent surface into the intra-particle active sites in the adsorbent structure, and the interactions of the solute particles with the available sites on the internal surface of the adsorbent or relaxation of the materials into the adsorbent Surface (McKay 1984). Depending on the properties of the adsorbent and of the adsorbate, the overall rate of the adsorption process is determined by any or more of the four stages in the adsorption process, which may occur parallel to, or in succession of, each other.

To determine which of the four stages could be the overall rate-determining step(s), the data from the adsorption of Cd(II) ions onto RBH were modeled by Lagergren's pseudo-first order (Lagergren 1898) and pseudo-second order (Ho 1995) kinetics equations, as well as the Weber-Morris intra-particle adsorption kinetics equation (Weber and Morris 1963) in linearized forms, as shown in Table 1. The best fits of the three kinetic models are shown in Figs. 5 through 7, and parameters for the model fitting are compared with those of similar low-cost biosorbents in Table 2. Cd(II) adsorption onto RBH fitted both pseudo-first order and pseudo-second order kinetics models, with R^2 values of 0.959 and 0.998, respectively, showing that the external transfer rate for Cd(II) ions is comparable to the surface reaction rate in controlling the overall rate of Cd(II) adsorption onto RBH.

Table 1. Kinetic Models and their Linearized Expressions

| Equation | Pseudo-first order kinetics | Pseudo-second order kinetics | Weber-Morris intra-particle diffusion kinetics |
|--------------------|---|--|--|
| Linear form | $\ln(q_e - q_t) = \ln(q_e) - k_1 t$ | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ | $q_t = k_i t^{0.5} + C$ |
| Constants | k_1 =first order rate constant (per min) q_e = equilibrium adsorption capacity(mg/g) | k_2 =second order rate constant (g/mg min) q_e = equilibrium adsorption(mg/g) | k_i =intraparticle diffusion rate constant(mg/g/min ^{1/2}) C = degree of deviation from intraparticle diffusion kinetics (mg/g) |
| Plots | $\ln(q_e - q_t)$ versus t | t/q_t versus t | q_t versus $t^{0.5}$ |

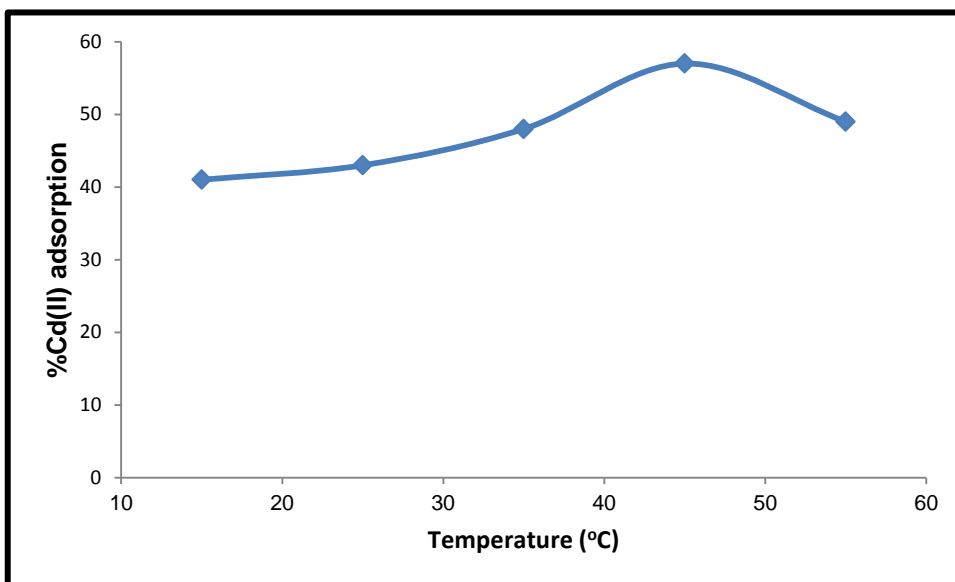


Fig. 4. Effect of temperature on the biosorption of Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

The data fit to the pseudo-second order model was, however, somewhat better. The pseudo-second order model considers metal-biosorbent reactions as the rate-limiting step. This implies that some adsorption sites become progressively more difficult for adsorbate molecules to reach – maybe because they are deeper within tiny pores, as also observed by Hubbe *et al.* (2012). In this case, the metal diffusion both in the bulk solution and in the biosorbent is considered to occur faster than the diffusion process or reactions that take place in the active binding sites on the adsorbent surface (Davis *et al.* 2003).

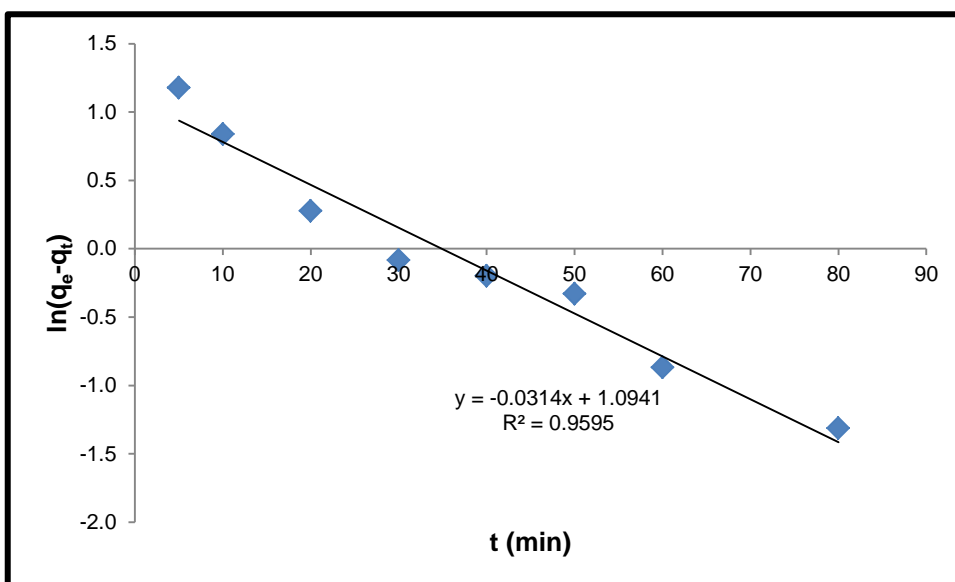


Fig. 5. Fit of pseudo-first order equation for the biosorption of Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

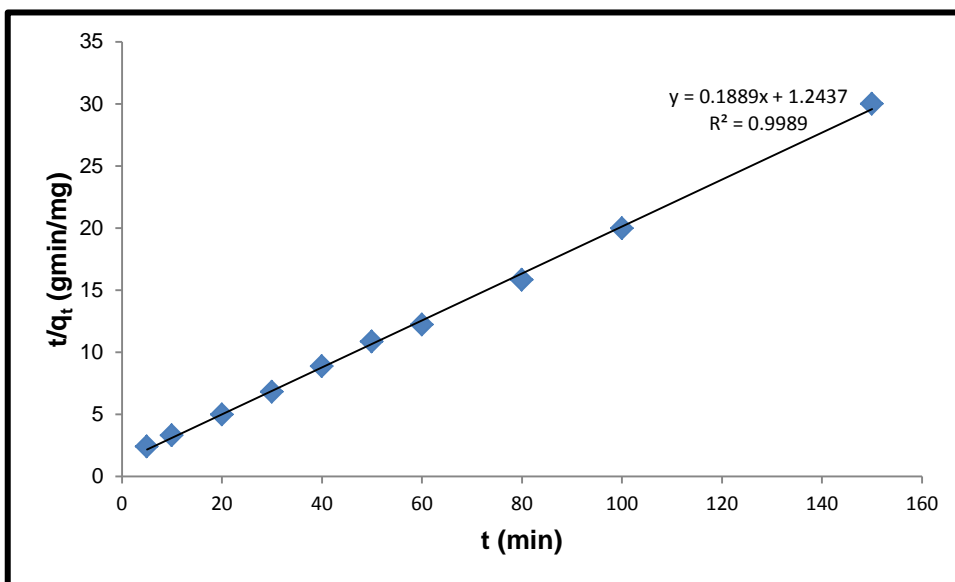


Fig. 6. Fit of pseudo-second order equation for the biosorption of Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

The rate of the pseudo-second order reactions is therefore dependent on the fractional filling up of the adsorbent surface by the amount of solute adsorbed at any time, t , compared to the amount adsorbed at equilibrium. This was consistent with postulates under *The effect of initial Cd(II) concentration* that indicated that Cd(II) ion adsorption onto RBH increased with increasing Cd(II) concentration in the aqueous phase.

As can be seen from Table 2, the kinetic fit of data for Cd(II) adsorption to the three kinetic models was consistent with the values found in the literature.

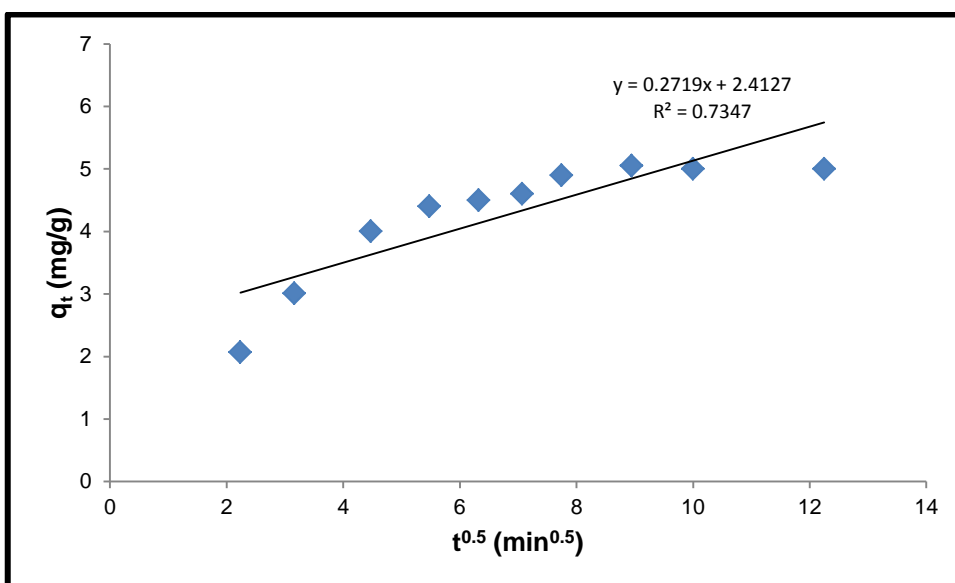


Fig. 7. Fit of Weber-Morris intra-particle equation for the biosorption of Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

Correlation of Cd(II) adsorption to second order kinetics is the usual case in the literature, and in most cases, high R^2 values are obtained for the pseudo-second order kinetics, usually greater than those of the first order kinetics. The correlation of first order kinetics was also consistent with those found in the literature for biomasses of higher plants, which, as in the current work, have R^2 values close to 0.90. The adsorption kinetics did not, however, fit the intraparticle diffusion. This is important for easy clean-up of the spent RBH adsorbent for reuse and disposal.

Effect of pH

The effect of pH on Cd(II) adsorption onto RBH is depicted in Fig. 8. For initial Cd(II) concentrations of 10, 50, and 100 mg/L, the maximum percentage amounts adsorbed were 44.4, 13.1, and 4.9%, respectively. The maximum Cd(II) ion adsorption occurred at a pH of 6.0, and the least Cd(II) ion adsorption occurred at pH values less than 3.0 for all the initial concentrations studied. The adsorption capacity of *Eichhornia crassipes* increased with increasing pH and reached optimum capacity at pH 6.0. Katircioglu *et al.* (2008) reported similar results in their research on the removal of Cd(II) ions from aqueous system using *Oscillatoris* sp. biomass. Similar results have also been reported for the adsorption of copper and Cd on *Laminaria japonica* and *Sargassum* sp. (Zhou *et al.* 1998). It can be assumed that as the solution pH increases, hydrolysis of the divalent metal ion, Cd^{2+} , takes place to form anionic hydroxide complexes that decrease the concentration of free metal ions and the affinity of the metal species for charged biosorbent sites. This decreases the metal sorption onto the biomass (Li *et al.* 2008).

Table 2. Comparison of the Adsorption Kinetic Parameters for Cd(II) Ion Recovery from Water using *Eichhornia crassipes* Biomass with Those of Other Low-cost Biosorbents

| Biosorbent | Biomass Type | Pseudo-first order | | Pseudo-Second order | | | Intra-particle diffusion | | | |
|-------------------------------|----------------|--------------------|--------------|---------------------|--------------|--------------|--------------------------|--------------|--------------|-------------------------------------|
| | | k_1 | R^2 | k_2 | q_e | R^2 | k_i | C_i | R^2 | Ref |
| <i>Sargassum</i> spp. | Brown algae | 0.0076 | 0.689 | 0.00579 | 44.3 | 0.998 | 0.4 | 36.8 | 0.911 | (Nessim <i>et al.</i> 2011) |
| <i>Gymnogongrus torulosus</i> | Brown algae | 0.04 | 0.618 | 93.8 | 0.26 | 0.999 | 0.32 | | 0.79 | (Areco & Afonso 2010) |
| <i>Cystoseira baccata</i> | Brown algae | 0.044 | | 1.07 | 0.51 | 0.9996 | | | | (Lodeiro <i>et al.</i> 2006) |
| <i>Pinus sylevestris</i> | Conifer | 0.007 | | 1.22 | 2.1 | | | | | (Taty-Costodes <i>et al.</i> 2003) |
| <i>Pinus nigra</i> | Conifer | 0.0026 | | 0.002 | 18.3 | | 1.56 | | | (Argun & Dursun 2008) |
| <i>Moringa oleifera</i> | Dicot | 0.016 | 0.808 | 0.096 | 0.894 | 0.991 | 0.017 | 0.621 | 0.955 | (Meneghel <i>et al.</i> 2013) |
| Coffee husks | Dicot | 0.0613 | 0.905 | 0.166 | 0.998 | | | | | (Oliveira <i>et al.</i> 2008) |
| <i>Ficus carcia</i> | Dicot | 0.018 | 0.977 | 0.11 | 41.67 | 0.9997 | | | | (Farhan <i>et al.</i> 2013) |
| <i>Eriobotrya japonica</i> | Dicot | 0.052 | 0.849 | 0.006 | 29.94 | 0.997 | | | | (Al-Dujaili <i>et al.</i> 2012) |
| <i>Ulva fasciata</i> | Green algae | 0.00144 | 0.625 | 0.00161 | 29.9 | 0.999 | 0.9 | 189.9 | 0.817 | (Nessim <i>et al.</i> 2011) |
| <i>Turbinaria conoides</i> | Green algae | 0.044 | 0.993 | 0.049 | 1.08 | 0.99 | | | | (Vijayaraghavan <i>et al.</i> 2012) |
| <i>Sargassum filipendula</i> | Green algae | 0.04 | 0.988 | 0.034 | 4.91 | 0.9997 | | | | (Costa <i>et al.</i> 2007) |
| <i>Zea mays</i> | Monocot | | | 0.0103 | 64.97 | 0.999 | | | | (Garcia-Rosales <i>et al.</i> 2012) |
| <i>Eichhornia crassipes</i> | Monocot | 0.031 | 0.959 | 0.0284 | 5.319 | 0.998 | 0.271 | 2.412 | 0.734 | Current work |
| Biosolids | Sludge | | | 0.0097 | 0.281 | 0.999 | | | | (Fard <i>et al.</i> 2011) |

In general, the optimum Cd(II) uptake by various biomasses occurs in acidic media of pH values 4.4 to 5.5 (Costa *et al.* 2007), but the optimum pH of Cd(II) biosorption on RBH occurred in near-neutral pH values, which is desired for easy treatment of contaminated natural water.

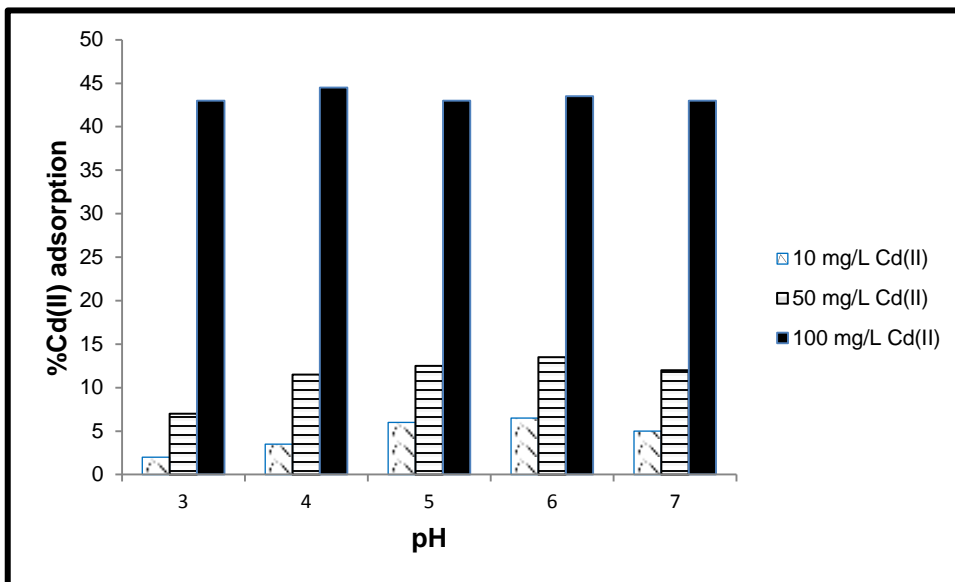


Fig. 8. Effect of pH on the adsorption of Cd(II) ions by *E. crassipes* at different Cd(II) initial concentrations (mg/L), and adsorbent dose 0.1g/100 L, time 150 min, and agitation speed 175 rpm

The Effect of Initial Cd(II) Concentration

Figure 9 shows the effect of initial Cd(II) concentration on its adsorption by *E. crassipes* biomass. About 70% of Cd(II) ions were adsorbed using an initial Cd(II) concentration of 10 mg/L.

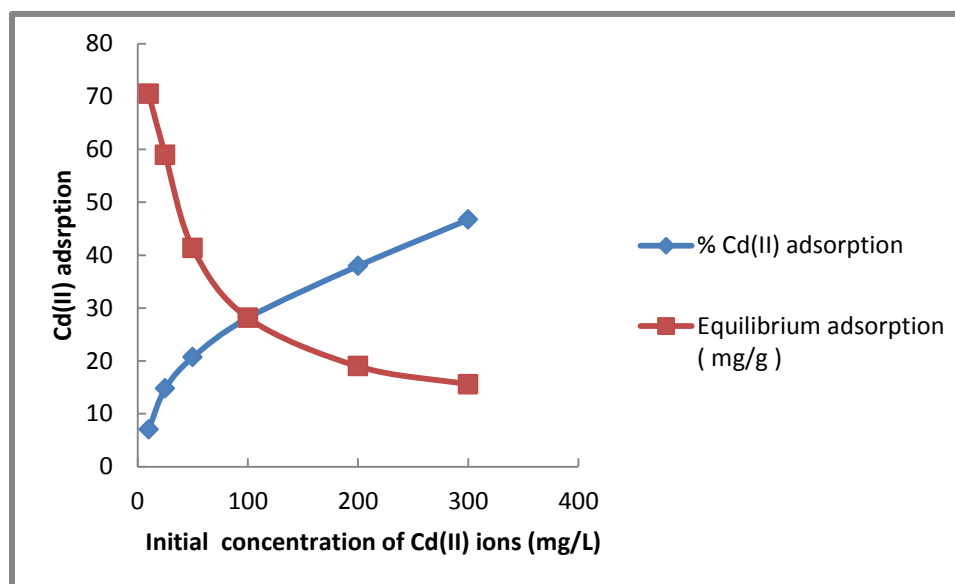


Fig. 9. Effect of Cd(II) ion concentration on its removal from solution; pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

An increase in the amount of Cd(II) adsorption was observed as the initial Cd(II) concentration increased from 10 to 300 mg/L; however, the percentage quantity adsorbed decreased. Thus, the metal ion uptake tends to reach saturation as the initial concentration increases. This shows that there is a progressive increase in mutual electrostatic interaction between sites of lower affinity for metal ions as the population of occupied sites in the biosorbent surface increases (Gupta *et al.* 2000)

Biosorption Isotherms

To clarify the nature of the adsorption that occurs between aqueous Cd(II) species and reactive sites in the biosorbent, the equilibrium biosorption data for Cd(II) ions were fitted into the Langmuir (1918) and Freundlich (1906) adsorption isotherms (Table 3).

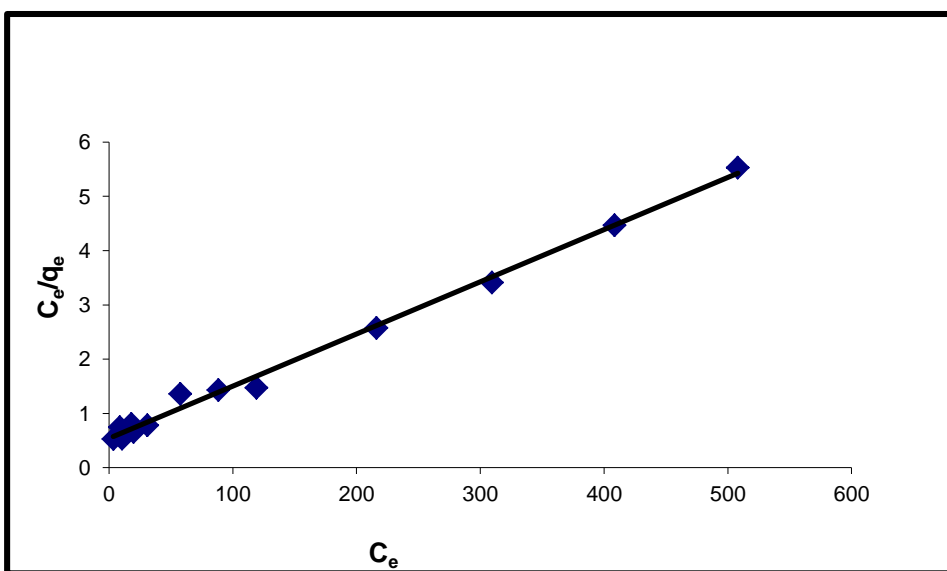


Fig. 10. Langmuir biosorption isotherm for Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

Table 3. Langmuir and Freundlich Adsorption Equilibrium Isotherms

| Isotherm | Form | Constants |
|---------------------|--|---|
| Langmuir isotherm | $q_e = \frac{bQ_{\max} C_{eq}}{1 + bC_{eq}}$ | Q_{\max} = adsorption capacity of the biosorbent surface (mg/g) b = affinity parameter (L/g) |
| Freundlich isotherm | $q_e = K_f C_e^{\frac{1}{n}}$ | K_f = Freundlich adsorption capacity (mg/g) n = Freundlich adsorption intensity |

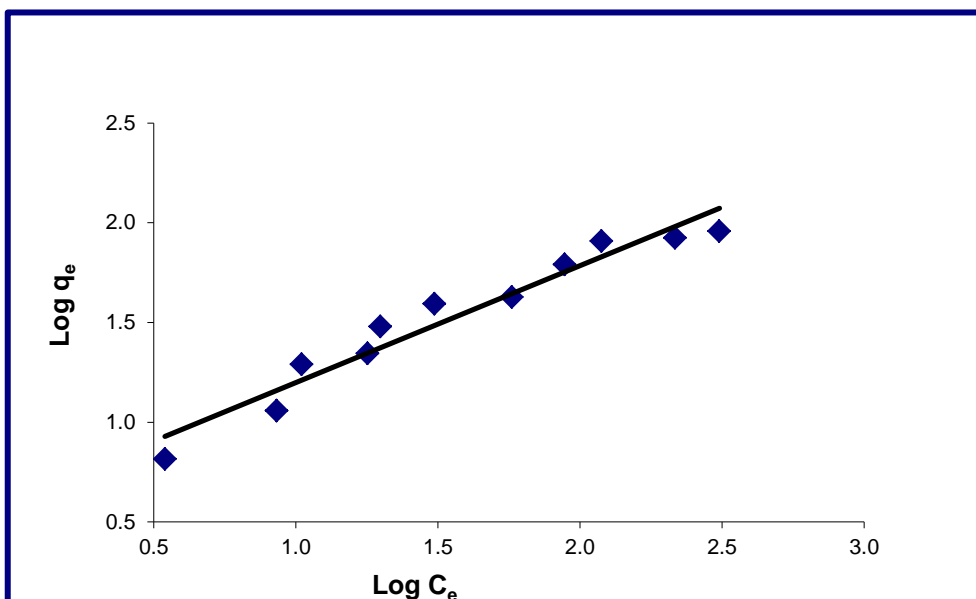


Fig. 11. Freundlich biosorption isotherm for Cd(II) ions; initial ion concentration 10 (mg/L), pH 6.0, adsorbent dose 0.1 g/100 L, time 150 min, and agitation speed 175 rpm

The respective Langmuir and Freundlich plots for Cd(II) adsorption onto RBH are depicted in Figs. 10 and 11. The R^2 values for Freundlich and Langmuir isotherms for Cd(II) biosorption onto RBH were 0.8939 and 0.9942, respectively. Thus, the Langmuir isotherm gave a better fit to the experimental data than the Freundlich. The maximum uptake, Q_{\max} , of Cd(II) ions was 104.16 mg/g. The affinity of Cd(II) for RBH surface sites typified by the Langmuir thermodynamic constant, b , was 0.0178 L/g. These values suggest that the biosorbent *E. crassipes* has a higher adsorption capacity for metal ions than conventional adsorbents (Benhima *et al.* 2008).

Comparison with Other Low-cost Biosorbents

On the basis of the Langmuir and Freundlich isothermal constants for Cd(II) adsorption onto RBH, the efficacy of RBH for removal of Cd(II) ions from water was comparable with those of similar low-cost biosorbents reported in the literature; the results are presented in Table 4. The highest mean Cd(II) biosorption capacity was shown by the biomasses derived from bacteria (121 mg/g), brown algae (85 mg/g), monocotyledonous plants (78 mg/g), and green algae (64 mg/g). The adsorption capacity of RBH, which is a monocotyledonous biomass, was lower than that of *Aeromonas caviae* (Loukidouet *et al.* 2005), *Laminaria japonica* (Yin *et al.* 2001), *Sargassum filipendula* (Costa *et al.* 2007), *Cystoseira barbata* (Yalçın *et al.* 2012), *Turbinaria conoides* (Vijayaraghavan *et al.* 2012), modified orange peel (Li *et al.* 2008), *Ulva fasciata* (Nessim *et al.* 2011), and *Zea mays* (García-Rosales *et al.* 2012). The Cd(II) removal efficiency of RBH was, however, found to be superior to the mean Cd(II) biosorption capacities of all the classes of biosorbents, including brown algae, green algae, fungi, monocotyledonous, and dicotyledonous biomasses, and only lower compared to that of bacterial biosorbents.

Table 4. Comparison of the Freundlich and Langmuir Parameters of *Eichhornia crassipes* Biomass with Those of Other Low-cost Biosorbents for Cd(II) Ion Recovery

| Biosorbent | Temp (°C) | pH | Time (min) | Langmuir isotherm constants | | | Freundlich isotherm constants | | | Ref |
|--|-----------|-----|------------|-----------------------------|------------|--------|-------------------------------|-------|-------|------------------------------|
| | | | | Q_m (mg/g) | b (L/mg) | R^2 | K_f (mg/g) | n | R^2 | |
| <i>Eichhornia crassipes</i> | 25 | 6 | 150 | 104.16 | 0.0178 | 0.9942 | 2.7479 | 1.542 | 0.894 | Current work |
| BACTERIA (mean values, n = 3) | 25 | 7 | 90 | 121.5 | 0.048 | 0.941 | 14.755 | 2.58 | 0.902 | |
| <i>Aeromonas caviae</i> | 20 | 7 | 60 | 181.91 | 0.03 | 0.93 | 20.37 | 2.59 | 0.87 | (Loukidou et al. 2005) |
| <i>Pseudomonas fluorescens</i> BM07 | 30 | 7 | 120 | 61.1 | 0.066 | 0.952 | 9.14 | 2.57 | 0.935 | (Zamil et al. 2008) |
| <i>Sphaerotilus natans</i> | | 5 | 30 | 27.4 | 3.6 | 0.998 | 1.1 | 0.48 | 0.992 | (Agnanelli et al. 2002) |
| BROWM MACROALGAE (mean values, n = 9) | 25.5 | 5.2 | 155 | 85 | 7.7 | 0.969 | 33.67 | 3.3 | 0.93 | |
| <i>Sargassum</i> sp. | 22 | 5.5 | 120 | 87 | 5.65 | 1.000 | 71.92 | 3.2 | 0.96 | (Sheng et al.2005) |
| <i>Sargassum filipendula</i> | 40 | 4.5 | 120 | 136 | 0.04 | 0.984 | 13.10 | 2.4 | 0.956 | (Costa et al.2007) |
| <i>Turbinaria conoides</i> | 22 | 5 | 120 | 111.48 | 4.79 | 0.922 | 83.52 | 5.62 | 0.979 | (Vijayaraghavan et al. 2012) |
| <i>Sargassum kjellmanianum</i> | 19 | 5 | 600 | 101 | | | 31.03 | 4.54 | 0.98 | (Zhou et al. 1998) |
| <i>Sargassum</i> sp., brown | 25 | 5.5 | 240 | 94.3 | 0.321 | 0.987 | 18.10 | 2.72 | 0.974 | (Nessim et al. 2011) |
| <i>Cystoseira baccata</i> | 25 | 4.5 | 60 | 80.04 | 4.0 | 0.98 | 0.67 | 3.1 | 0.97 | (Lodeiro et al.2006) |
| <i>Mastocarpus stellatus</i> | 25 | 7 | 10 | 68.44 | 5.0 | 0.95 | 0.44 | 3.2 | 0.86 | (Herrero et al.2008) |
| <i>Sargassum filipendula</i> | 30 | 4 | 10 | 1.35 | 30.2 | 0.9894 | 4.00 | 1.97 | 0.752 | (Vieira et al. 2007) |
| <i>Padina</i> sp., | 22 | 5.5 | 120 | 88.16 | 11.34 | 0.94 | 80.04 | 3.1 | 0.96 | (Sheng et al.2005) |
| DICOTYLEDONS (mean values, n = 7) | 30 | 5.5 | 190 | 49.32 | 5.14 | 0.938 | 107.06 | 1.89 | 0.92 | |
| Raw orange peel | | 6 | 180 | 56.84 | 0.82 | 0.970 | 182.12 | 0.26 | 0.97 | (Li et al. 2008) |
| Sugar beet pulp | 25 | 5 | 120 | 139.2 | 13.90 | 0.740 | 7.16 | 1.02 | 0.99 | (Pehlivan et al. 2008) |
| Modified orange peel | | 6 | 180 | 131.08 | 0.61 | 0.980 | 651.92 | 0.37 | 0.95 | (Li et al.2008) |
| <i>Ficus carica</i> | 20 | 5 | 60 | 34.13 | 0.057 | 0.9994 | 7.15 | 3.31 | 0.958 | (Farhan et al. 2013) |
| Eucalyptus bark | 50 | 5 | 30 | 16.47 | 20.22 | 0.951 | 1.555 | 2.49 | 0.864 | (Ghodbane et al.2008) |
| <i>Moringa oleifera</i> Lam. Seeds | 25 | 7 | 160 | 7.864 | 0.036 | 0.987 | 0.47 | 1.552 | 0.999 | (Meneghel et al.2013) |
| Untreated coffee husks | 25 | 4 | >1440 | 6.854 | 0.3024 | 0.9972 | 3.188 | 5.05 | 0.973 | (Oliveira et al.2008) |
| Poplar Leaves and Branches | 35 | 6 | 600 | 2.1 | | 0.88 | 2.9 | 1.098 | 0.66 | (Al-Masriet et al. 2010) |
| FUNGI (mean values, n = 2) | 29 | 4 | 480 | 28.65 | 6.791 | 0.996 | 4.69 | 2.74 | 0.916 | |
| baker's yeast biomass | 30 | 4 | 60 | 43.268 | 13.153 | 0.993 | 4.3453 | 1.27 | 0.989 | (Sulaymon et al.2010) |
| <i>Rhodotorula</i> sp. Y11 | 28 | 4 | 900 | 14.03 | 0.429 | 0.998 | 5.04 | 4.20 | 0.843 | (Li and Yuan 2006) |
| GREEN ALGAE (mean values n = 5) | 23 | 5.8 | 198 | 64 | 3.24 | 0.975 | 10.64 | 2.59 | 0.935 | |
| <i>Ulva fasciata</i> | 25 | 4 | 240 | 119.1 | 0.06 | 0.954 | 13.10 | 2.79 | 0.867 | (Nessim et al.2011) |
| <i>Laminaria japonica</i> | 19 | 5 | 600 | 92 | | | 24.86 | 4.54 | 0.96 | (Zhou et al.1998) |
| <i>Chlorella vulgaris</i> | | 8 | 30 | 46.4 | 12.81 | 1.000 | | | 0.9 | (Fraile et al. 2005) |
| immobilized live <i>Oscillatoria</i> sp. H1 | 23 | 6 | 60 | 32.2 | 0.05 | 0.967 | 2.11 | 1.47 | 0.96 | (Katircioğlu et al.2008) |
| heat-inactivated <i>Oscillatoria</i> sp. H1 | 23 | 6 | 60 | 32.2 | 0.05 | 0.980 | 2.48 | 1.56 | 0.99 | (Katircioğlu et al. 2008) |
| MONOCOTYLEDONS (mean values, n = 5) | 31 | 4.8 | 366 | 78 | 7.7 | 0.9926 | 29.06 | 1.47 | 0.976 | |
| <i>Egeria densa</i> | 30 | 5 | 1440 | 145 | 0.43 | 0.9854 | 48.72 | 0.42 | 0.972 | (Pietrobelli et al. 2009) |
| <i>Zea mays</i> | 50 | 4 | 300 | 165.63 | 0.0044 | 0.9881 | 3.26 | 1.68 | 0.996 | (García-Rosales et al. 2012) |
| Rice Husk | 25 | 5 | 30 | 29.673 | 18.89 | 0.9986 | 39.695 | 1.81 | 0.928 | (Tan et al. 2011) |
| Wheat Stem | 25 | 5 | 30 | 26.0652 | 11.42 | 0.9993 | 31.3084 | 1.71 | 0.992 | (Tan et al.2011) |
| Corncob | 25 | 5 | 30 | 21.4832 | 7.6 | 0.9917 | 22.33 | 1.71 | 0.990 | (Tan et al. 2011) |

The values of both the thermodynamic Langmuir constant, b , and the Freundlich intensity parameter, n , were consistent with values reported in the literature and indicated efficient binding of Cd(II) ions onto reactive sites in RBH.

The differences in Cd(II) adsorption properties of various biosorbents are due in part to differences in the properties of the biosorbents, including their phytochemistry, structure, specific surface area, and functional groups. In addition to the adsorbent properties, the solution chemistry, including the pH, temperature, dissolved ligands, and the presence of competing cations, influences Cd(II) adsorption to different extents. In general, RBH could be utilized for Cd removal from water at room temperature over neutral pH values of water because its Cd(II) adsorption capacity is quite high. Moreover, the Langmuir thermodynamic constant, b , and the Freundlich affinity parameter, n , were indicative of efficient binding of the metal ions onto the RBH surface, and the adsorbent can be obtained cheaply in large quantities.

Effects of Other Metal Ions on the Biosorption of Cd(II) Ions

The effects of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} ions on the adsorption of Cd(II) ions by *E. crassipes* were studied, and the results are presented in Fig. 12. The results indicate that the adsorptive capacity of *E. crassipes* biomass decreased in the presence of these ions. The percentage reductions of the biosorption of Cd(II) ions in the presence of Na^+ and K^+ ion were 0.41% and 4.50%, respectively. This indicates that the effects of Na^+ and K^+ on the biosorption were almost negligible. However, the percentage reductions of the metal uptake by RBH in the presence of Mg^{2+} and Ca^{2+} ions were found to be 53.20% and 55.95%, respectively. Even though identical molar amounts were not used for this work, it was shown from calculation that a similar pattern may be expected. The singly charged ions have less impact on the biosorption of the metal ions than doubly charged ions. The reduced binding capacity may be a result of competition for binding sites (Lodeiro *et al.* 2006).

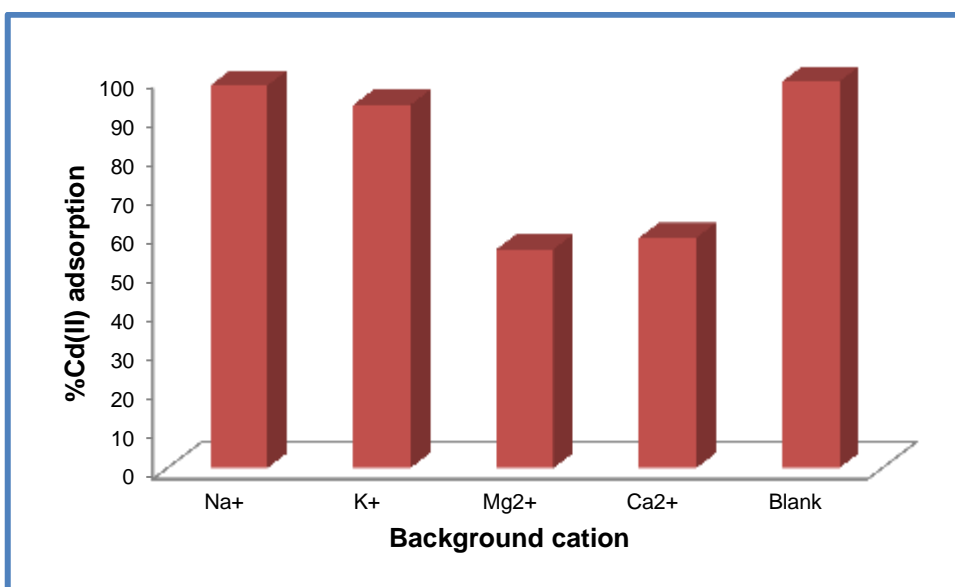


Fig. 12. Effect of selected metal ions on the biosorption of Cd(II) ions; pH 6.0, adsorbent dose 100 mg/100 L, time 150 min, and agitation speed 175 rpm

CONCLUSIONS

1. The results of this work indicate that low-value biomass materials obtained from the water hyacinth (*Eichhornia crassipes*) are promising materials for the development of a low-cost biosorption technology for the removal of Cd(II) ions from water. The root biomass has one of the highest Cd(II) sequestration efficiencies when compared to other biosorbents that have been used to remove Cd(II) from water
2. Metal sorption was controlled by the contact time, initial metal ion concentration, sorbent dose, solution pH, temperature, and agitation speed. The highest adsorption for Cd(II) ions was found at a pH of 6.0 using an initial Cd(II) ion concentration of 10 mg/L, adsorbent dose of 0.1g/100 L, 150 min of contact time, and agitation speed 175 rpm.
3. The adsorption data fit the Langmuir model for Cd(II) ions, and the maximum sorption capacity was found to be 104 mg/g at 25± 1 °C.
4. Kinetics analyses indicated that the adsorption process followed the pseudo-second order rate expression, but a significant amount of Cd(II) adsorption onto RBH was also found to be controlled by external diffusion processes described by pseudo-first order kinetics.

ACKNOWLEDGMENTS

The authors are grateful for the Nairobi Dam staff for helping us to retrieve the water hyacinths from the dam.

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Article submitted: November 11, 2013; Peer review completed: January 24, 2014;
Revised version received: March 21, 2014; Second revision: April 2, 2014; Accepted:
April 10, 2014; Published: May 1, 2014.