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Biosorption studies of lead and copper using rogers mushroom biomass ‘*Lepiota hystrix*’



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ABSTRACT

This study points out potential of rogers mushroom (*Lepiota hystrix*) biomass in biosorption of copper and lead from aqueous solutions. The efficiency of biosorption was tested in batch experiments and the metal ion concentration analyzed using flame atomic absorption spectrometry. The analysis of FTIR spectrum reveals that the metal ions uptake by roger mushroom involves interaction of metal ion and hydroxyl, carboxyl and carbonyl groups of the biomass at optimum pH of 4.5–6.0 and sorbent mass of 1.5–2.1 g for Cu and Pb, respectively. Adsorption capacities were found to be 3.9 and 8.9 mg/g at a contact time of 25–40 min and initial metal ion concentration of 300–500 µg/g for Pb and Cu, respectively. The biosorption process follows second order kinetics and fitted the Langmuir isotherm model. The result shows that rogers mushroom biomass has a good potential to be used in removal of metal ions and can be used up to three adsorption/desorption cycles without losing efficiency. Its use in real life situation can alleviate pollution and increase the quality of water for human consumption and sanitary purposes.

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1. Introduction

Uncontrolled discharge of industrial wastewater is a serious environmental problem encountered in many parts of the world today (Attahiru et al., 2012). This is because of increased human activities and increase of industrialization. These human activities are causing species to disappear at an alarming rate from the ecosystem and it has been estimated that between 1975 and 2015 species extinction occurred at a rate of 1–11% per decade (Ahalya and Ramachandra, 2002). The presence of industrial wastewater laden with pollutants in the water ecosystem has diverse effects such as affecting the quality of life, ending up in food chain and affecting various species of animals such as fish. The most common human activities that cause challenges to fresh water environment are agriculture, urbanization, and manufacturing industries (Jalali et al., 2002).

Of all pollutants in water, heavy metals have received a major concern due to the fact that they are toxic and they cannot be decomposed by *in situ* biological means and hence persist for a long time (Jackson et al., 2001; Mehmet and Sukru, 2006). Remediation of heavy metals from wastewaters has been studied and a number of various conventional technologies have been developed to remove heavy metals in water effluents before discharge. These techniques include: chemical precipitation, ion exchange, electro-deposition, biosorption, liquid–liquid extraction, adsorption, membrane separation, reverse osmosis and coagulation (Kratovichil and Volesky, 1998). These methods are suitable at high concentrations, are expensive to maintain and also result in production of large quantities of secondary pollutants such as sludge (Igwe and Abia, 2006; Abdel-Aty et al., 2013; Onyancha et al., 2008; Zouboulis et al., 2004). The search of more effective

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methods for heavy metal removal has led to the study of biosorption as an alternative (Nilanjana et al., 2007; Wang and Chen, 2009). Biosorption is non active metal uptake by biological materials such as algae, fungi, bacterial and agriculture biomass due to the presence of functional groups such as amino, hydroxyl and carboxyl which bind the metal via mechanisms such as adsorption, ion exchange and complexation (Wang and Chen, 2009; Nilanjana et al., 2007). The advantages of biosorption over the conventional technologies include cost effectiveness, high efficiency and the fact that no sludge is formed during (Volesky, 2001).

Among many biosorbents tested, fungal biomasses have proved to possess excellent metal uptake potential (Kapoor and Viraraghavan, 1995; Arvind et al., 2014). Other microbial biosorbents such as algae have also been extensively studied and others such as spirulina have been commercialized for heavy metal removal (Onyancha et al., 2008; Wang and Chen, 2009). Other biosorbents such as agricultural wastes have also been employed. A number of research work have been conducted and documented based on the absorption of heavy metals by both edible and non-edible varieties of mushrooms and the results show that heavy metals concentration is considerably higher in mushroom than in other agricultural crops. This is an indication that there is an effective mechanism in mushrooms that enables them readily accumulate heavy metal from the environment (Kalac et al., 1996; Fangkun et al., 2010). The aim of this work was to evaluate the potential of roger mushroom as an alternative biosorbent for removal of heavy metal ions from water.

2. Materials and methods

2.1. Instrumentation

Flame Atomic Absorption Spectrophotometer (AA 6200, Shimadzu, Japan) using air-acetylene flame system was used for metal determination. pH measurements were done using digital pH metre (pH 211, Hanna Instruments). The biomass spectrums were generated using Fourier Transform Infrared Spectrophotometer (8400 CE, Shimadzu, Japan) fitted with a pellet cell while filtration was done using Millipore filter funnel fitted with 0.45 μm membrane filter paper.

2.2. Chemicals and reagents

All the chemicals used in this work were of analytical grade (Sigma Aldrich). Metal ions stock solutions were first prepared by dissolving the appropriate amount of salt in distilled water and acidified using concentrated nitric acid. The working solutions were made by diluting the stock solutions using 0.1 M acetate buffer solutions.

2.3. Sample collection, sample identification and pretreatment

The fresh mushroom samples used in this study were collected from Kinari forest in Kiambu County and were identified by staff of National museum of Kenya based on microscopic and morphological characteristics of mushroom according to the method set out by Farid et al. (2013). Samples were then washed with deionized water followed by dilute hydrochloric acid before rinsing with deionized water. The samples were thereafter dried under the sun for about five days and then in the oven at 100 °C. The dry mushrooms were

then ground and sieved through 150 μm mesh and stored in desiccators prior to use.

2.4. FT-IR characterization

FT-IR analysis of metal loaded and metal free mushroom biomass was done as follows: approximately 1.0 mg each of dried sample of metal loaded and free biomass was mixed with approximately 5.0 mg potassium bromide. The mixtures were then ground to fine powder and pressed under vacuum into pellets, which were then analyzed using FTIR.

2.5. Biosorption studies

Biosorption experiments were performed by equilibrating appropriate weight of adsorbent biomass with 50 mL of Pb^{2+} and Cu^{2+} solutions of the desired concentration in 250 mL stoppered conical flasks. The flask contents were shaken using a mechanical shaker machine at 150 rpm at room temperature. The mixtures were then filtered through 0.45 μm membrane filter and the filtrate was analyzed for the metal ions. All the experiments were done in triplicate. Parallel experiments (controls) were conducted in the absence of mushroom biomass to determine metal ion loss due to precipitation. Determination of metal ions concentration was done using flame atomic absorption spectrometry. The percent metal uptake by the biomass and equilibrium adsorption amount q_e were expressed as

$$\% \text{Removal} = \frac{100(C_0 - C_e)}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

respectively, where q_e (mg/g) is equilibrium adsorption amount, C_0 is the initial metal ion concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of the solution and W is the mass of biomass (g).

2.5.1. Optimization of pH

To determine the effect of pH on the adsorption of the metal ions, 0.2 g of the biomass was equilibrated with 50 mL of 50 mg/L of metal ions solution in 250 mL conical flasks for 120 min at room temperature. A pH range of 3–7 was investigated. The solutions were then filtered and metal ion concentrations in the filtrate were determined. The pH of the solutions was adjusted using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solutions.

2.5.2. Optimization of biosorbent dosage

The effect of biomass dosage was determined by equilibrating different adsorbent doses (0.2–3.0 g) with 50 mg/L metal ion solution at the optimum pH for 120 min.

2.5.3. Optimization of contact time

Stock solutions of copper and lead were diluted to obtain 1000 mL solutions of 100 mg/L. The pH of the solutions was adjusted to the optimum pH values for each metal ion. Exactly 1.9 g of dried and ground adsorbent biomass was added to each 800 mL solutions of metal ions and equilibrated for 120 min at a constant room temperature and shaken continuously. A 10 mL portion of reaction mixture was withdrawn at regular time intervals and immediately filtered and the metal ion concentration in the filtrate was determined.

2.5.4. Optimization of initial metal concentration

The effect of initial metal concentration was studied by equilibrating the biomass with metal ions solutions of concentration ranging from 25 mg/L to 1000 mg/L with the solutions pH set to their optimum pH.

2.5.5. Desorption studies

In order to study the desorption and recovery of metal ions adsorbed, 20 mL solution of 50 mg/L of each metal ion was equilibrated with 1.9 g of biomass and shaken in a rotary shaker for 2 h at a speed of 150 rpm. After adsorption, the solutions were filtered through 0.45 μm filter membrane and the filtrate was analyzed for metal concentration. The loaded biomass was shaken with 50 mL of 0.1 M EDTA and 0.1 M HCl for 2 h at a speed of 150 rpm in order to provide the same conditions of adsorption as desorption. After desorption step, solutions were filtered with 0.45 μm filter membrane and the filtrate was analyzed for metal concentration and the residual was reused for a second batch adsorption. The adsorption–desorption process was repeated three times. The amount of metal ion desorbed from the loaded biomass was calculated using equation:

$$\% \text{Desorption} = \frac{\text{Desorbed}}{\text{Loaded}} \times 100$$

2.5.6. Determination of effect of competing ions

Adsorption has been shown to favour some elements better than others. In order to study the effect of concomitant cations on the adsorption of Pb^{2+} and Cu^{2+} by the *Lepiota hystrix* biomass, 50 mL of solution containing a mixture of metals of concentration 10 mg/L was equilibrated with 1.9 g of biomass and shaken in a rotary shaker for 2 h at a speed of 150 rpm. After equilibrium was achieved, solutions were filtered and the filtrate was analyzed for metal concentration.

2.5.7. Application to real water sample

Nairobi river water sample was used to evaluate the efficiency of *L. hystrix* for the removal of the target heavy metal ions. The water sample was filtered through 0.45 μm membrane filter paper and used without further treatment.

3. Results and discussion

3.1. Characterization of mushroom biomass

The FTIR spectrum profiles for roger mushroom free and loaded with copper and lead are shown in Fig. 1a, b and c, respectively. The spectra show the presence of characteristics absorption bands assigned to hydroxyl, carboxyl, amine, and amide on the surface of the biomass. Broad band at region 3431–3396 cm^{-1} attributed to $-\text{OH}$ stretching of a polymeric compound (Kamasonlian et al., 2011; Sannasi et al., 2009). Bands at 2927–2925 cm^{-1} are as a result of asymmetric vibration of C–H which represents the aliphatic nature of the adsorbent (Kamasonlian et al., 2011). The peak at 1651 cm^{-1} is typical of a C–N and N–H deformations. The bands observed at 1382 cm^{-1} were assigned to COO^- group and the one observed at 1041 to C–O stretching of alcohol and carboxylic acids. The comparison of the FTIR spectrum of raw biomass and after metal ions biosorption shows that the stretching vibration of O–H group shifted from 3396 cm^{-1} to 3425 and 3431 for biomass loaded with lead, copper respectively. The

result reveals that chemical interaction between the metal ions and the hydroxyl group occurs on the surface of the biomass (Jalali et al., 2002; Kamasonlian et al., 2011; Sannasi et al., 2009).

3.2. Effect of pH

pH is an important factor in adsorption of metal ions not only because of its influence on the solution chemistry but also because it affects the surface characteristic of the adsorbent. The effect of pH on percentage removal of metal ions is shown in Fig. 2. An increase in the solution pH from 3.0 to 6.5 has a significant effect on biosorption of Pb^{2+} and Cu^{2+} . Percentage removal of the metal ions has increased from pH 3 to pH 6.5 but decreased thereafter. An optimum pH of 4.5 and 6 for copper and lead, respectively was established and was used for subsequent experiments. At low pH values the surface of adsorbent is closely associated with protonation of functional groups which consequently decreases the percentage removal of metal ions. At $\text{pH} > 7$ precipitation of low solubility metal hydroxides starts. Precipitation interferes with the biosorption process because it immobilizes the metal ions thus making them unavailable for biosorption. These results also agree with many adsorption studies which report pH range of 4–6 as the optimum pH for Cu and Pb adsorption by various biosorbents (Jalali et al., 2002; Mehmet and Sukru, 2006; Kalac et al., 1996; Putra et al., 2014).

Metal speciation which is also pH dependent is also another aspect that must be considered (Ningchuan et al., 2011). Studies of Cu^{2+} and Pb^{2+} metal ion predominant species as a function of the solution pH show that at pH below 6, Cu^{2+} and Pb^{2+} are the predominant species in the solution. At a pH value > 6 , other metal ions species such as $\text{Cu}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$ which are low soluble species are formed.

3.3. Effect of adsorbent dosage

The effect of biosorbent dosage was investigated by varying the sorbent mass from 0.2 to 3.0 g and equilibrating with 50 mL model solutions of 50 $\mu\text{g}/\text{mL}$. Fig. 3 shows the metal removal efficiency against dosage. The biosorption efficiency by biomass increases rapidly with increase in biomass dosage from 24.2 and 42.8 and level off at 67.4 and 78.9% when the biomass dosage increases from 0.1 g to 1.9 g for Pb and Cu respectively. The results can be attributed to the fact that increasing the biomass dosage progressively increases the adsorption sites for the metal ions. Further increase of adsorbent dose has no significant increase in adsorption, a situation which could be attributed to overlapping of adsorption sites as a result of overcrowding of biomass (Kosa et al., 2012). From the results, a minimum adsorbent dosage of 1.9 g per 50 mL of adsorbate solution was employed for Pb and Cu, respectively in all subsequent experiments.

3.4. Effect of contact time

The rate of adsorption is important for designing batch adsorption studies. The effect of contact time was determined by monitoring the uptake of the metal ions in model solutions over a period of 120 min at room temperature. For both metal, percentage metal uptake reached a maximum within 30 min (Fig. 4). Thereafter there was no considerable change. The short contacts times demonstrate the potential of *L. hystrix*

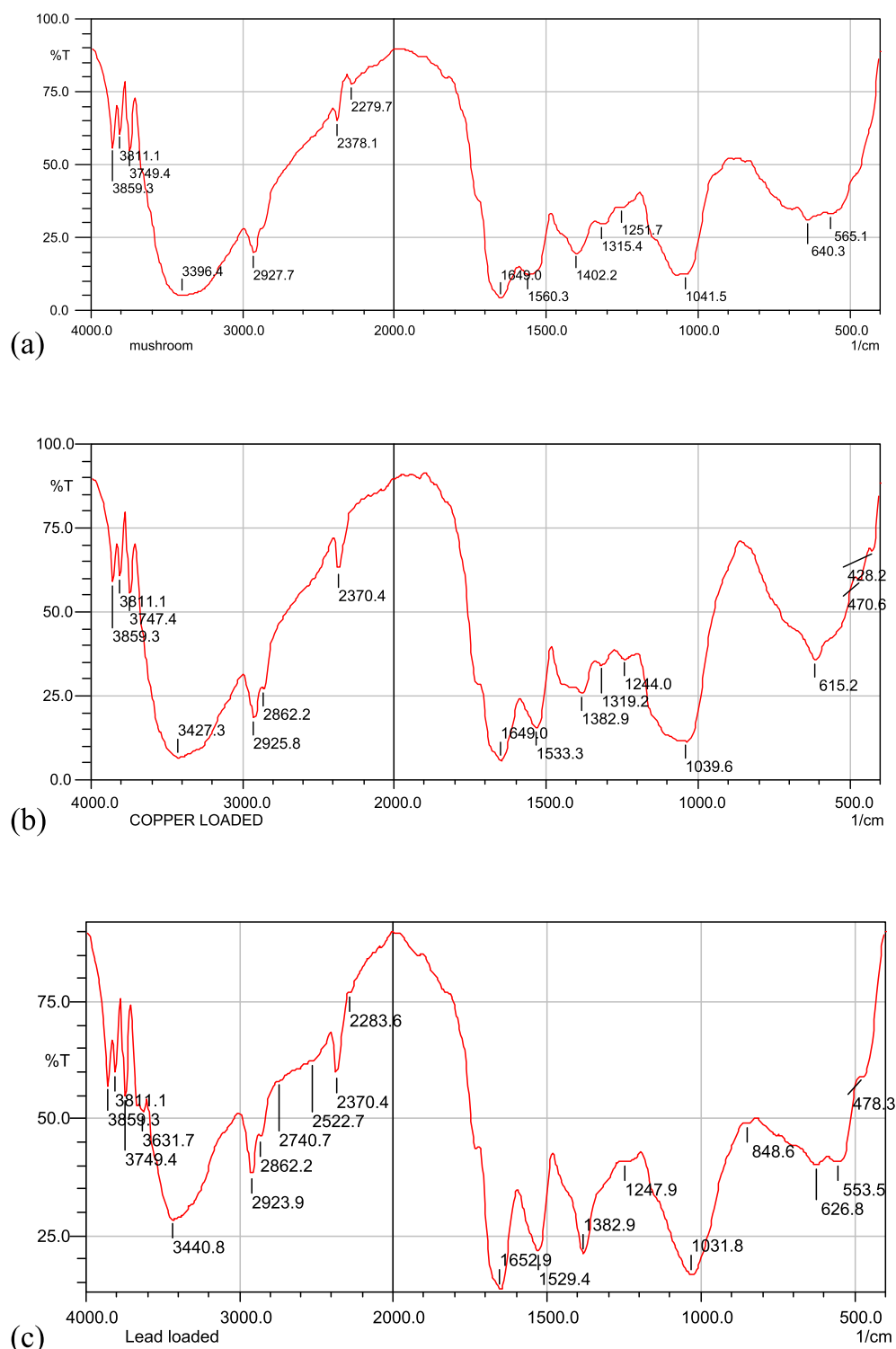


Fig. 1 – Infra-red (FTIR) spectra of *Lepiota hystrix* biomass: (a) unloaded, (b) Cu loaded and (c) Pb loaded.

biomass as a suitable biosorbent for fast removal of heavy metals from contaminated waters.

3.5. Effects of initial metal concentrations

Kinetic and equilibrium properties of adsorption are significantly determined by initial metal ion concentration (Ahalya and Ramachandra, 2002). The effect of initial metal concentration was examined by varying the initial concentration from 25 to 1000 mg/L and keeping all the

other factors constant. As shown in Fig. 5, when the metal concentration was increased from 25 to 1000 $\mu\text{g/mL}$, the percentage of Pb^{2+} and Cu^{2+} adsorbed by *L. hystrix* decreased sharply from 90.7 to 11.3 and 73.5 to 23.3%, respectively. A near constant partition of metal ions between the solid and the aqueous phase was observed at concentration above 500 and 300 $\mu\text{g/mL}$ for Pb and Cu. This can be attributed to oversaturation of the adsorption site since a constant mass of biosorbent has a constant number of binding sites.

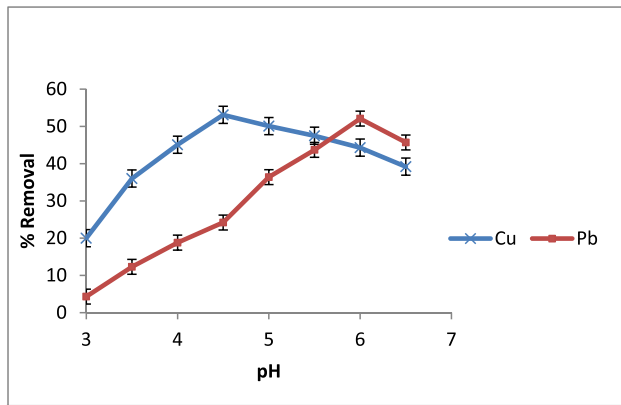


Fig. 2 – Effect of pH on the biosorption of Pb^{2+} and Cu^{2+} onto *Lepiota hystrix* biomass.

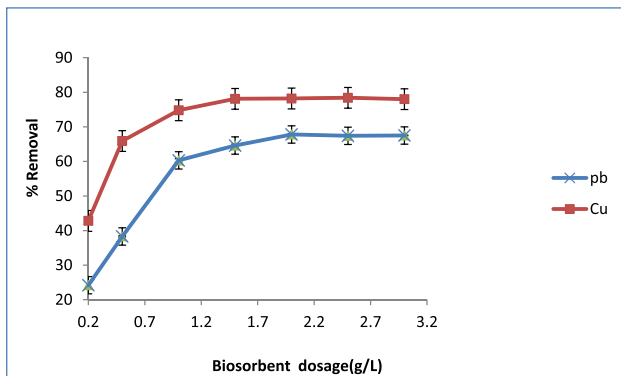


Fig. 3 – Effect of biomass dosage on biosorption of Pb^{2+} and Cu^{2+} onto *Lepiota hystrix* biomass.

3.6. Sorption kinetics

Kinetic studies are important in determining the efficacy of biosorption. This is because it gives useful information for designing full scale batch or continuous metal removal systems. In addition, kinetic models have been used to test the experimental data and to find the mechanism of adsorption and its potential rate controlling step that include mass transport and chemical reaction (Mehmet and Sukru, 2006; Onyancha et al., 2008; Kapoor and Viraraghavan, 1995). Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Several kinetic models are used to explain the mechanism of adsorption processes in liquid–solid phase sorption systems (Ahment and Mustafa, 2009; Kosa et al., 2012).

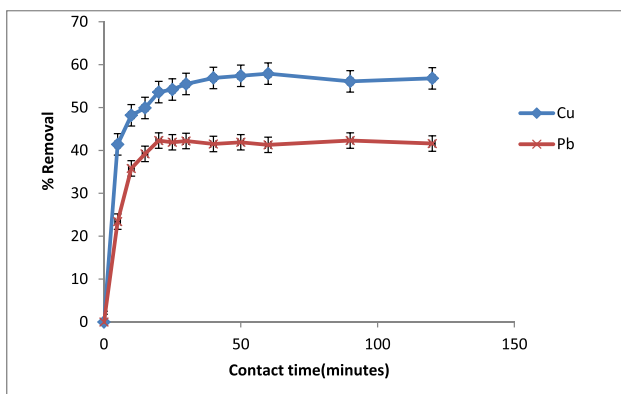


Fig. 4 – Effect of contact time on biosorption of Pb^{2+} and Cu^{2+} onto *Lepiota hystrix* biomass.

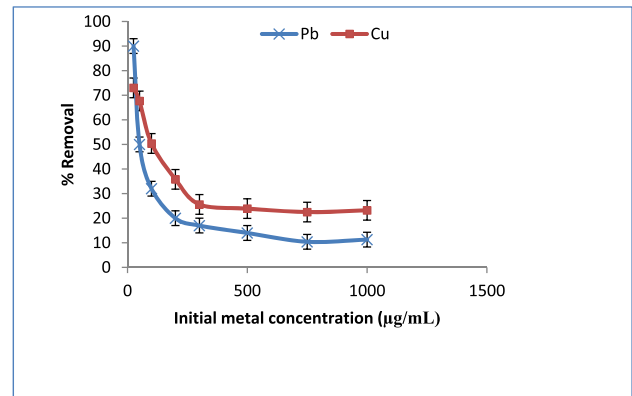


Fig. 5 – Effect of initial Pb^{2+} and Cu^{2+} concentration on adsorption by *Lepiota hystrix* biomass.

The kinetics of Pb and Cu adsorption were evaluated by applying pseudo-first order and pseudo-second order kinetic models. The variation of metal ion concentration with time during the adsorption process was used to follow the kinetics of the adsorption until equilibrium was achieved. The integrated linear pseudo-first and pseudo-second order equations are

$$k_1 t = \ln q_e - \ln(q_e - q_t) \quad \text{Pseudo - first order}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad \text{Pseudo - second order}$$

where k_1 and k_2 are the pseudo-first and pseudo-second order rate constants respectively. q_e and q_t are the metal uptakes (mg/g) at equilibrium and time t , respectively. The pseudo-first order kinetic model assumes that the uptake rate of Pb^{2+} and Cu^{2+} with time is directly proportional to the amount of available active sites on the adsorbent surface whereas pseudo second order model assumes that chemical adsorption is the limiting stage involving bond formation through sharing or exchange of electrons between adsorbent and adsorbate. A plot of $\ln(q_e - q_t)$ against time (min) was used for the pseudo first order linearity test and q_e and k_1 were determined from the slope and intercept respectively, while a plot of t/q_t against time was used for the pseudo second order linearity test where the slope and intercept represent q_e and k_1 respectively (Figs. 6 and 7).

Table 1 gives the results of pseudo-first order and pseudo-second order constants for the biosorption of Pb^{2+} and Cu^{2+} by *L. hystrix* biomass. q_e (calculated), determined from the plot of pseudo-first order model for each metal differs significantly from that obtained experimentally, q_e (experimental). In addition, the correlation coefficients (R^2) for pseudo-first order kinetic model for both metal ions are low, an indication that the adsorption did not fit the equation well. On the other hand the pseudo-second order model fitted the kinetics equation well for both metal ions as the difference between q_e (cal) and q_e (expt) is less with good correlation coefficients (R^2) values.

3.7. Adsorption isotherms

Equilibrium sorption isotherms are used to describe the capacity of a biomass which is characterized by certain constants whose values express the surface properties and affinity of the biomass. They describe the equilibrium correlation between the adsorbate concentration, mass loading, adsorbent dose and equilibrium concentration of the

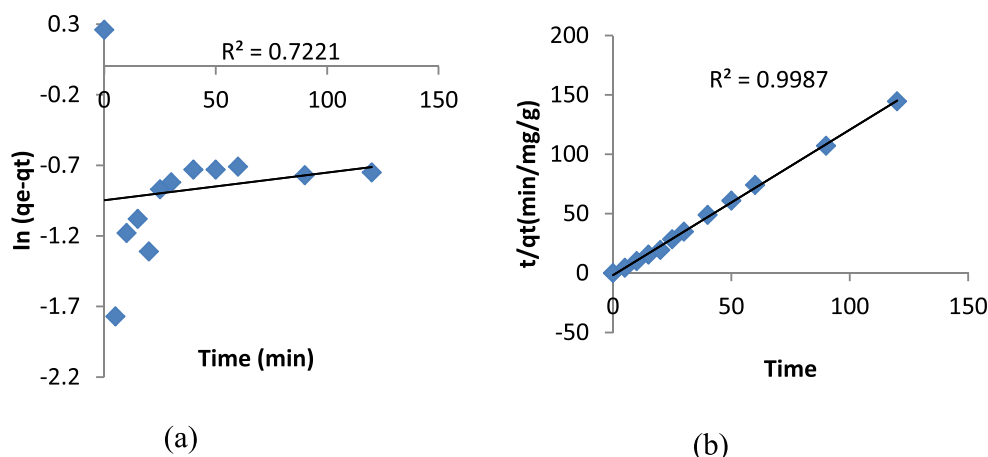


Fig. 6 – Pseudo-first order kinetic plot (a) and pseudo-second order kinetic plot (b) for copper biosorption onto *Lepiota hystrix* biomass.

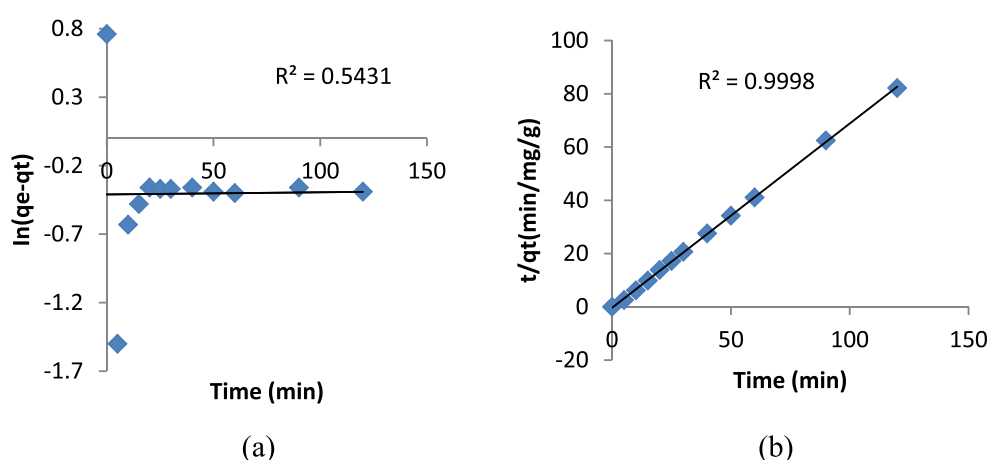


Fig. 7 – Pseudo-first order kinetic plot (a) and pseudo-second order kinetic plot (b) for lead biosorption onto *Lepiota hystrix* biomass.

adsorbate at a selected temperature. Adsorption isotherm experiments were carried out at pH 6.0 and 4.5 for Pb and Cu respectively by varying the initial metal ion concentration in the range of 25–1000 mg/L and the adsorption isotherms were constructed by plotting initial metal concentrations against percentage metal ions removal and the results are presented in Figs. 8 and 9. To further assess adsorption process and determine the maximum adsorption capacity of the adsorbent, the adsorption data were fitted to the Langmuir and Freundlich equations. Langmuir equation is based on the assumption that a maximum sorption corresponds to saturated monolayer of sorbate molecule on the sorbent surface.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}b} + \frac{C_e}{q_{\max}} \quad \text{Langmuir}$$

where q_{\max} (mg/g) represents limiting adsorption capacity when the surface is fully covered by metal ions, b ($\text{d m}^3 \text{g}^{-1}$) is a

constant relating to the adsorption/desorption energy, C_e is the equilibrium concentration ($\mu\text{g/mL}$) and q_e is the amount of metal ions adsorbed (Onyancha et al., 2008; Badalona et al., 2009). A plot of C_e/q_e against C_e gives a straight line plot with a slope of $1/q_{\max}$ and an intercept of b .

The empirical Freundlich isotherm equation (v) is used to estimate adsorption intensity of the sorbent toward the adsorbent.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Freundlich}$$

K_F and n are Freundlich constants. The plot of $\ln q_e$ against $\ln C_e$ of linearized Freundlich equation gives a straight line graph with $(1/n)$ as the slope and $\ln K_F$ as the intercept. Figs. 8 and 9 show the graph of linearized Langmuir and Freundlich adsorption isotherm for adsorption of Cu^{2+} and Pb^{2+} respectively. The corresponding constants and correlation coefficient associated with each model are shown in Table 2.

The experimental data results indicate that biosorption of the metal ions onto *L. hystrix* biomass better fits Langmuir isotherm model than Freundlich isotherm model an indication that a monolayer adsorption is prevalent. On the other hand the Freundlich isotherm model was not able to adequately describe the relationship between the amount of sorbent metal ions and their equilibrium concentration in the solution as shown by the lower R^2 values.

Table 1 – Kinetic parameters obtained from pseudo-first order and pseudo-second order for Pb^{2+} and Cu^{2+} biosorption onto *Lepiota hystrix* biomass.

	Metal	q_e (cal)	q_e (expt)	R^2
Pseudo-first order kinetics	Pb	0.325	2.140	0.543
	Cu	0.324	1.303	0.722
Pseudo-second order kinetics	Pb	2.204	2.140	0.999
	Cu	1.382	1.303	0.998

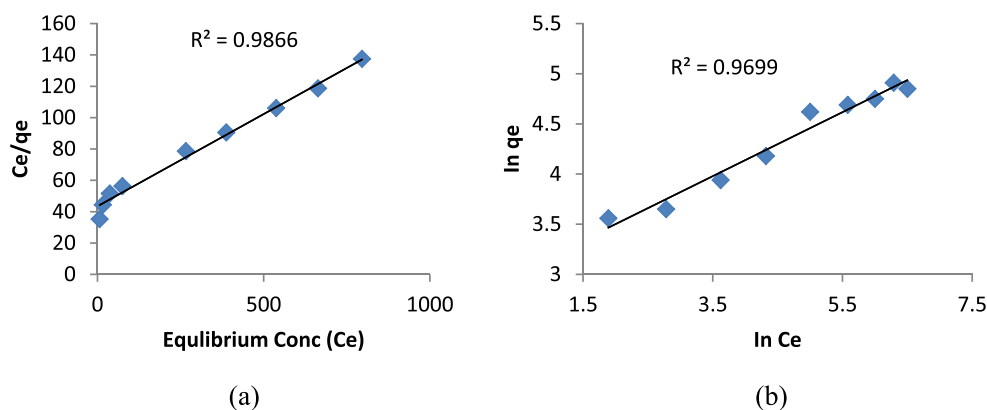


Fig. 8 – Linearised Langmuir isotherm (a) and Freundlich isotherm (b) plots for the biosorption of Cu^{2+} onto *Lepiota hystrix* biomass.

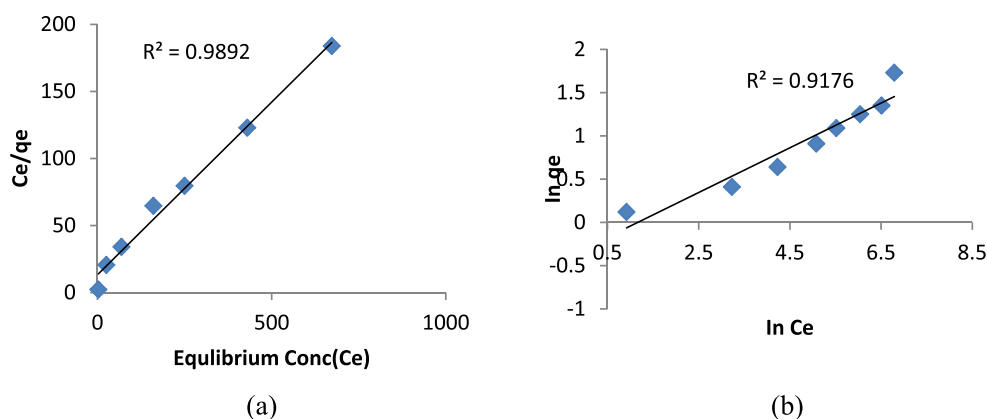


Fig. 9 – Linearised Langmuir isotherm (a) and Freundlich isotherm (b) plots for the biosorption of Pb^{2+} onto *Lepiota hystrix* biomass.

3.8. Desorption and metal recovery

Desorption is the process of removing adsorbed metal from the adsorbent. The regeneration and reusability of biosorbent is important for keeping the process costs low, reducing the dependency of the process on the continuous supply of biomass and also helps in recovering and pre-concentrating the metal ions extracted from the liquid phase (Vijayaraghavan and Balasubramanian, 2015). The common practical method for desorption of the heavy metals from the biomass is leaching with dilute acid. This is due to the fact that most biosorption exhibit an ion-exchange mechanism for metal ions and thus increasing the acidity of the metal-loaded biosorbent leads to leaching of metal cations from biosorbent (Nazmi et al., 2010; Badalona et al., 2009; Vijayaraghavan and Balasubramanian, 2015). First sorption experiments were performed using 50 mL of 50 $\mu\text{g/L}$ of each metal ion at optimum pH and 1.9 g of biomass. Then the desorption of metal ions Pb^{2+} and Cu^{2+} was carried out by equilibrating the residue with 20 mL of 0.1 M EDTA and 0.1 M HCl in a batch system separately for 60 min. The results are given in Fig. 10. From the

results, desorption of the metal ions from the mushroom biomass with HCl is high compared with the one performed with EDTA. Complete recovery was not achieved probably because mechanism other than ion exchange may be involved in adsorption of metal ions.

3.9. Effect of competing metal cations

Effluents from industrial wastewater contain many metal ions, with each of them interacting with the biomass in different ways and different capacity thus they compete for binding sites of the biomass. Calcium and magnesium are bivalent ions that occur in significant amounts in natural waters. It is therefore important to study the competition between the heavy metals and magnesium/calcium for adsorption onto *L. hystrix* biomass. Fig. 11 shows the effect of competition on the adsorption of the selected heavy metals by the *L. hystrix* biomass. In general, the presence of other ions influences the biosorption of the target metal ion. From the result it can be observed that presence of Ca^{2+} and Mg^{2+} cations leads to a decrease in the amount of metal ions removed from the solution by the biomass. This can be due to the competition for the available binding sites of the biomass by the metal ions. The decrease in biosorption can also be attributed to increase in ionic strength of the solution since the cations are charged species. The observations also agree with results obtained regarding efficiency of biosorbent to bind heavy metals in presence of competing cations (Onyancha et al., 2008; Kapoor and Viraraghavan, 1995; Putra et al., 2014).

Table 2 – Isotherms parameters associated with the biosorption of Pb^{2+} and Cu^{2+} onto *Lepiota hystrix* biomass.

Metal	Langmuir		Freundlich		
	q_{max}	R^2	$1/n$	K_F	R^2
Pb	3.89	0.986	0.2584	0.741	0.917
Cu	8.58	0.989	0.3189	17.51	0.969

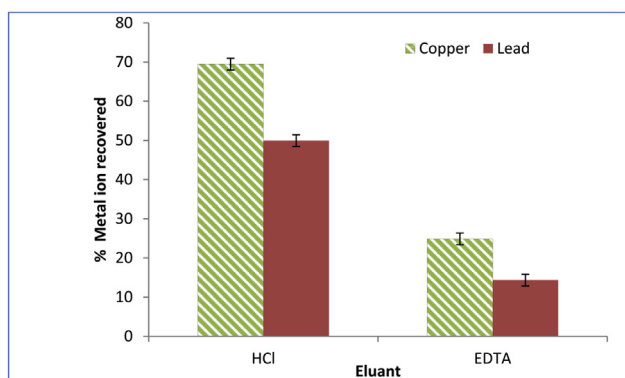


Fig. 10 – Percentage recovery efficiency of different desorbing agents on Pb^{2+} and Cu^{2+} adsorbed onto *Lepiota hystrix* biomass.

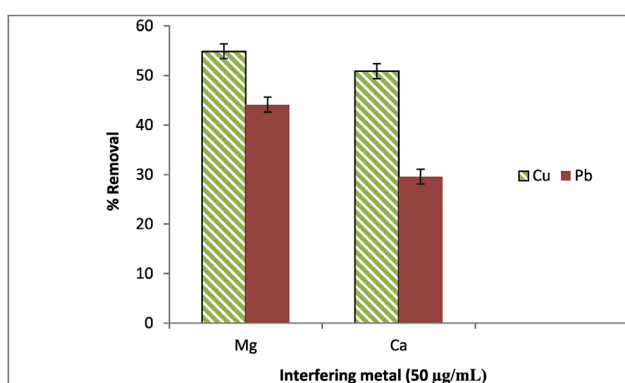


Fig. 11 – Effect of different metal ions on the biosorption of Pb^{2+} and Cu^{2+} by *Lepiota hystrix* biomass.

3.10. Regeneration studies

The effect of re-use of roger mushrooms as adsorbent was investigated. The biomass was regenerated thrice and used in equilibrium experiments while maintaining all the other conditions at their optimum values. The results of regeneration studies are shown in Table 3. The result shows that adsorption capacity did not decrease appreciably. Hence roger mushroom can be recycled for several times without losing its biosorption efficiency, an important factor to consider when choosing a biomass.

3.11. Application to real samples

Real polluted water from Nairobi River was used to test the application of the biomass in wastewater treatment. The river water was collected from Nairobi River and was used without further treatment except filtration through a membrane filter paper. Metal ion analysis using FAAS shows that the concentrations of the metal ions under investigation were

Table 3 – Effects of number of regeneration cycles on the Cu^{2+} and Pb^{2+} recoveries from *Lepiota hystrix* biomass.

Cycles	% Adsorption	
	Cu^{2+}	Pb^{2+}
1.	74.8 ± 1.23	62.52 ± 1.87
2.	73.8 ± 0.93	61.80 ± 1.63
3.	73.1 ± 1.42	60.89 ± 1.23

3.7 ± 0.32 and 5.8 ± 1.32 for copper and lead respectively. To test the applicability of the biomass in real water sample, 1.9 g of the biomass was equilibrated with 50 mL of the water sample and shaken in a mechanical shaker for 120 min. The adsorbed amount of metal ions in river water was 60.5% and 47.3% for copper and lead respectively. The result shows that *L. hystrix* biomass adsorbs considerable amount of Pb^{2+} and Cu^{2+} although the percentage adsorption was lower than those obtained with synthetic solutions. This may be attributed to high levels of competing cations and ligands present in natural waters.

4. Conclusions

This study provides significant information regarding the suitability of *L. hystrix* biomass as biosorbent of selected heavy metals. FTIR analysis reveals the presence of hydroxyl, carbonyl and carboxyl functional groups which are responsible for binding the metal ions. The batch biosorption study shows that the biosorption is pH dependent and the optimum pH for Pb and Cu removal using roger mushroom is 6.0 and 4.5 respectively. The optimum time for adsorption was found to be 30 min for both Pb and Cu. The kinetics of adsorption obeyed the pseudo-second order, while the adsorption isotherm obeyed was Langmuir. The adsorption capacity (q_{max}) was found to be 3.89 and 8.50 mg/g for Pb and Cu respectively. The recycling of the biomass demonstrates that it can be used in up to three times without losing efficiency. From this study, *L. hystrix* biomass was found to be suitable biosorbent for heavy metal removal from wastewater pollution.

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