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Modeling and utilization of laurel leaves as a biomass source for the removal of zinc and copper

Çinko ve bakır gideriminde bir biyokütle kaynağı olarak defne yapraklarının kullanılması ve modellenmesi

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Abstract

Medicinal and aromatic plants which is one of the considerable non-timber forest products in Turkey, especially in the last century have become an important socio-economic values. In this study, *Laurus nobilis* L. leaves (LNL), an aromatic plant, were used as biosorbent in the treatment process. The effects of biosorbent dosage, biosorption time, solution pH, initial zinc and copper ions concentration, humic acid or ionic strength or competitive effects on the biosorption of Zn(II) and Cu(II) by LNL were investigated. The LNL biomass was characterized using SEM and FT-IR spectrum. The non-linearized and linearized isotherm equations were compared and discussed. Zn(II) and Cu(II) biosorption better matched with the Temkin equation and Pseudo second-order kinetic equation successfully defined the biomass behaviors of both heavy metal ions. Additionally, a single-stage batch bioreactor system for heavy metal biosorption based on the best fit non-linear isotherm equation also has been presented. It was found that heavy metal uptake was affected by competitive biosorption studies. Finally, these studies showed that the LNL can be used as an environmentally friendly and abundant biosorbent for removing zinc and copper ions from contaminated waters.

Özet

Türkiye'de kereste dışı orman ürünlerinden olan tıbbi ve aromatik bitkiler sosyo-ekonomik açıdan bu yüzyılda önem kazanmaya başlamıştır. Bu çalışmada aromatic bir bitki olan defne yaprakları arıtma prosesesinde biyosorban olarak kullanılmıştır. Biyosorban dozajı, çözelti pH'sı, temas süresi, başlangıçtaki ağır metal iyonları konsantrasyonu, iyonik kuvvet, hümik asit etkisi ve LNL ile Bakır (II) ve çinko (II) 'nun biyosorpsiyonu üzerindeki rekabetçi etkiler incelenmiştir. Biyosorban, FT-IR ve SEM görüntüleri kullanılarak karakterize edilmiştir. Doğrusallaştırılmış ve doğrusallaştırılmamış izoterm modelleri karşılaştırılmış ve tartışılmıştır. Zn (II) ve Cu (II) biyosorpsiyonu, Temkin denklemiyle daha iyi uyum sağlamış ve sahte ikinci derece reaksiyon kinetiği, her iki ağır metalin biyosorpsiyon davranışlarıyla da uyum göstermistir. Ayrıca, ağır metal biyosorpsiyonu için doğrusal olmayan en uygun izoterm denklemine dayanan tek kademeli bir biyoreaktör sistemi de sunulmuştur. Ağır metal giderimini ortamdaki diğer iyonların varlığı bir miktar etkilemiştir. Bu çalışmalar LNL'nin çinko ve bakır iyonlarını kirli sulardan uzaklaştırmak için, çevre dostu ve bol bulunan bir biyosorban olarak, değerlendirilebileceğini göstermiştir.

INTRODUCTION

Heavy metals such as copper and zinc used in several industries discharges into the water ecosystem through industrial or municipal wastewater. Because heavy metals in the water are not biodegradable, they accumulate in the food chain and cause serious environmental problems that threaten human health (Ngah and Hanafiah 2008). Zinc and copper are important essential elements for living beings. But excessive amounts of copper and zinc in humans causes detrimental effects. Various water treatment methods such as ion exchange, chemical precipitation, electrochemical treatment, filtration, dissolved air flotation, and reverse osmosis are suggested for removal of metal but these methods are complicated and expensive. The adsorption is better than other techniques for ease of applicability, ease of process, and simplicity of design. Biosorbents are still popular due to their ease of use, environmentally friendly and low cost. Many materials from nature like sudangrass (Saraeian et al. 2018), cocoa pod husk (Obike et al. 2018) and psidium guvajava leaf (Rao et al. 2010) are also utilized for heavy metal treatment from wastewater as a biosorbent.

L. nobilis which is native to the southern Mediterranean region an aromatic plant commercially grown in Turkey, France, Italy, Spain, Portugal, Morocco, Mexico and Algeria. One of the most important non-timber forest products in Turkey, medicinal and aromatic plants, especially in the last century have become important socio-economic values (Bayram et al. 2010). Bay leaf production is regulated in accordance with the communiqué principles of the General Directorate of Forestry and annual production programs. 90% of the world's laurels demands are met by Turkey and bay leaves have a 24% of the exportation total of aromatic plants in Turkey (Semerci and Çelik 2017). Although we are one of the leading bay leaves producers in the world, in our country there are limited studies where laurel leaves are used as biosorbent for heavy metal uptake. Laurus nobilis leaves have been widely used in the pharmaceutical industry, fragrance and flavor industry (Kumar et al. 2004 Peixoto et al. 2017 Gümüş 2019).The pharmaceutical, food and cozmetic industries are utilized LNL. At the same time, it can be evaluated as biosorbent material for heavy metal removal due to its renewability and abundant availability. In the literature, there are limited number of studies about the heavy metal ions biosorption onto LNL (Laskar et al. 2016, Yasin and Qasim 2018), but more comprehensive research is required on heavy metal biosorption by LNL. The aim of the study was to show that LNL can be used as an alternative biomass source to eliminate Cu^{2+} or Zn^{2+} ions from wastewaters.

MATERIALS and METHODS

Preparation of Biosorbent And Chemicals

Laurus nobilis L. leaves (LNL) were collected from Sinop, Turkey. LNL were washed with distilled water (DW) and then were dried at 60 °C for 24 h, The dried leaves were then powdered using domestic mixer and sieved to obtain particle size in the range of 125-250 µm. The biosorbent was stored in a glass bottle for further use. Stock heavy metal solutions were prepared by dissolving $Zn(SO_4)·7H_2O$ (zinc sulfate), $CuSO_4·5H_2O$ (copper sulfate), $Cd(NO_3)_2·4H_2O$ (cadmium nitrate) and $Pb(NO_3)$ (lead nitrate) in distilled water (DW). The reagents were purchased from Sigma-Aldrich (Germany). According to the method of Bayo et al. (2012) 1 g L^{-1} stock Ca^{2+} ($CaCl_2$) and Na^+ (NaCl) solutions were prepared and diluted to the required concentrations of 100 mg L^{-1} for the studies of common ion effect. Commercially sourced humic acid sodium salt (HA) solution of stock 500 mg/L was prepared according to the method of Gümüş and Akbal (2017).

Batch Biosorption Experiments

The studies were performed at room temperature of 25 ^{0}C. In the experiments, 0.2 g of LNL was mixed to a series of Erlenmeyer flasks containing 100 mL solutions of 10 mg/L metal concentration and shaken during the biosorption time (150 rpm). The LNL were centrifuged at 4000 rpm for 15 minutes and separated from the solution. The heavy metal concentrations were determined using inductively coupled plasma mass spectrometry (Agilent Technologies / 7700X ICP-MS). qt and qe, (mg g^{-1}) were the quantity of LNL biosorbed at t time and equilibrium time, respectively.

$$q_e = \frac{(Co-Ce).V}{m} \quad (1)$$

$$q_t = \frac{(Co-Ct).V}{m} \quad (2)$$

where qe and qt are the quantities of Zn^{2+} or Cu^{2+} ions (mg/L) biosorbed at equilibrium and t time, respectively, Ce, C_0 and Ct (mg L^{-1}) are the equilibrium, initial and t time concentrations of Zn^{2+} or Cu^{2+} ions in the aqueous solution, respectively, V(L) is the aqueous solution volume and m is the dry LNL amount (g).

All experimental studies were performed in in triplicates and the average data were taken into account. The statistical data were determined using Microsoft® Excel Solver.

Characterization of Biosorbent

The surface characterizations of untreated and metal ions loaded biomass were examined with a Scanning Electron Microscope (SEM)(x2500) (Quanta 400F Field Emission). The FT-IR spectrum of untreated and metal loaded LNL were recorded by Hyperion 1000, Fourier Transform Infrared Spectroscopy, in the wavelength range of 400-4000 cm^{-1}.

RESULTS and DISCUSSION

Characterization of LNL

Fig. 1(a) demonstrates the morphological structure of the biosorbent which determined biosorption process of metal ions. Figs. 1 (b and c) show SEM micrographs obtained after the uptake of Cu^{2+} and Zn^{2+} ions. The structure of LNL surface was heterogeneous and porous, after the metal biosorption, these surfaces were covered with metal ions. The surface of biosorbent distinctly changed after the metal biosorption.

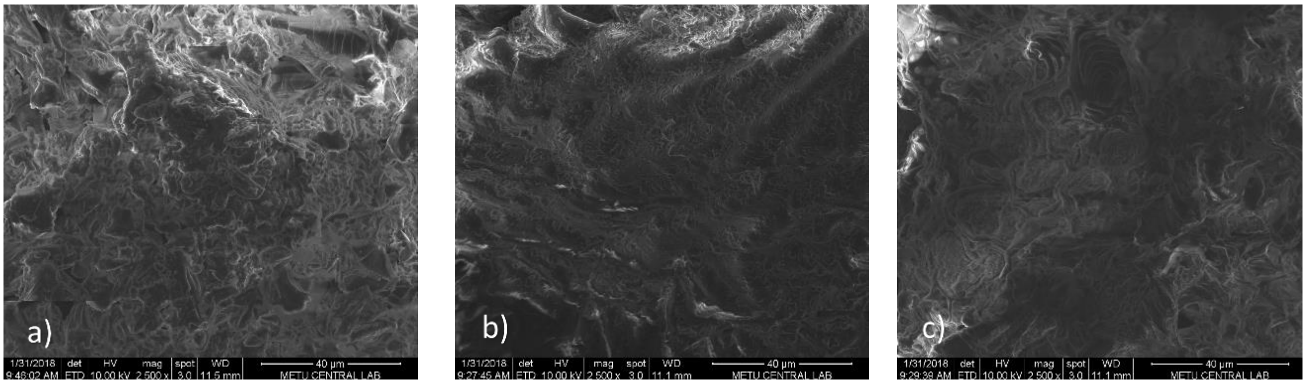

Figure 1. Scanning electronic microscope images of LNL before (a) and after Copper(II) (b) and Zinc(II) (c) biosorption

Fig. 2 presents the FTIR spectrum of LNL biosorbent before and after copper(II) and zinc(II) biosorption. The FTIR spectrum indicated the major bands corresponding to the chemical components of the biosorbent. Various chemical groups observed at the peaks of 3302, 2918, 2850, 1729, 1608, 1513, 1445, 1371, 1317, 1236, 1151, 1022, 831, 782, 719 and 518 cm^{-1} cm^{-1} may contribute to the uptake of Cu(II) or Zn(II) ions. After uptake of heavy metal ions, the shifting bands are groups corresponding to the OH, NH, C-H, carboxylic acid, COOH and C-O functional groups, which are probably the most important participating groups in biosorption on the biomass surface (Gümüş 2019). After biosorption, the shift in the bands is shown in Figure 2.

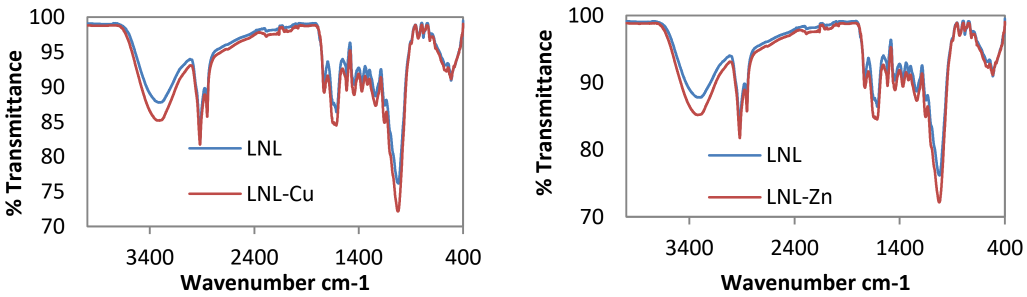

Figure 2. FTIR spectrum of LNL

Effect of Initial Solution pH

The uptake of heavy metal ions from water and wastewater by sorption is strongly dependent on the solution pH as it affects the degree of biosorbate ionization and the surface charge of biosorbent (Xiong and Yao 2009). The effect of solution pH was studied on the sorption of copper and zinc ions in the pH range of 3–7 and the findings are illustrated in Figure 3. The increase in aqueous solution pH enhanced the removal of copper or zinc ions. The optimum value of pH determined to be 6.5 for both metals.

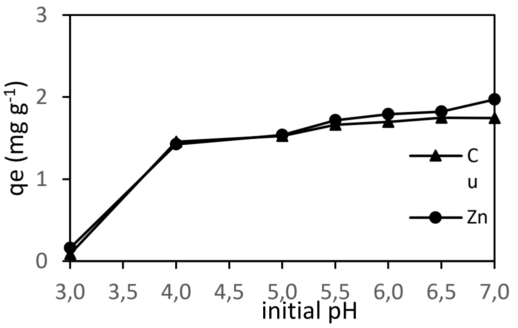

Figure 3. Effect of initial solution pH

Effect of Biosorbent Dosage

The effects of LNL amount on the uptake of copper(II) and Zinc(II) ions are presented in Figure 4. It was reported that increasing dosages of LNL resulted in decreases in the sorption efficiency and increases in the removal efficiencies. Sorption capacities, decreased from 2.55 to 0.77 mg g^{-1} for Cu and 2.86–0.86 mg g^{-1} for Zn as biosorbent concentrations increased from 0.2 to 1 g $100mL^{-1}$. The increase in removal efficiency can be attributed to increased surface area of LNL and the availability of more sorption sites, in contrast, the decrease in biosorption capacity can be explained by the decrease in the amount of heavy metal ions absorbed per unit weight of the biosorbent. For further experiments, the biosorbent amount of 0.2 g $100mL^{-1}$ was determined to be an optimum amount.

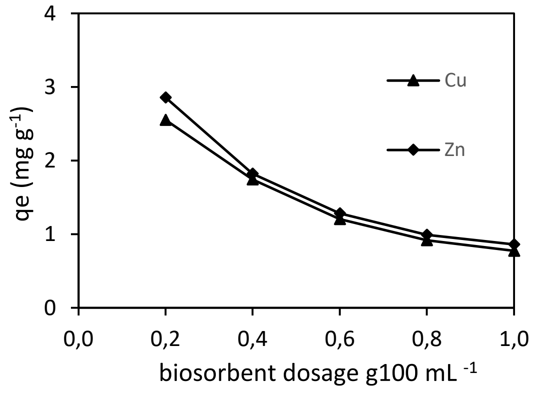

Figure 4. Effect of biosorbent dosage

Effect of Initial Heavy Metal Concentration

Figure 5 presents the effect of initial metal ions concentration on the uptake of copper or zinc ions. The uptake capacities of copper and zinc ions increased from 1.39 to 4.94 mg g^{-1} and 1.51-5.98 mg g^{-1}, respectively with the increases of the initial metal ions concentration. The increase in biosorption capacities may be due to the higher rate of biosorption and the use of all available active sites for biosorption at increased heavy metal concentration(Gümüş 2019, Morosanu et al. 2017).

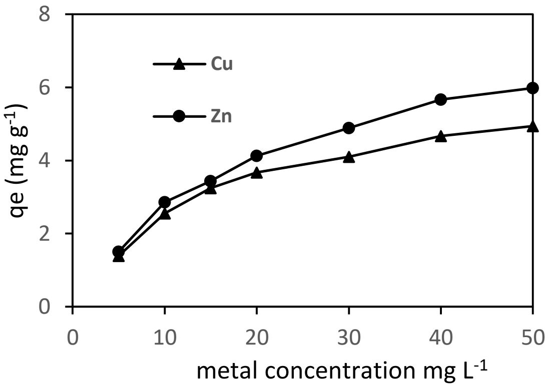

Figure 5. Effect of initial heavy metal concentration

Biosorption İsotherm Studies

Biosorption equilibrium studies indicate the biosorbate–biosorbent interaction and biosorption capacities of a sorbent. The equilibrium biosorption behavior of these processes were analyzed using linear and non-linear forms of Freundlich, Langmuir and Temkin, isotherm models. Freundlich, Langmuir and Temkin models were used in the experimental data. The non-linear and linear equations of these models can be indicated as:

Freundlich $qe = K_F \, Ce^{1/nF}$ (3)

$$log(\mathrm{q_e}) = log(K_F) + \frac{1}{n} log(Ce)$$

Langmuir $qe = \frac{qmK_L \; Ce}{1+K_L \, C_e}$ (4)

$$\frac{\mathrm{C}_e}{q_e} = \frac{1}{kL \, q_m} + \frac{C_e}{q_m}$$

Temkin $qe = B_T \ln(K_T \, C_e)$ (5)

$$qe = \left(\frac{RT}{b_T}\right) \ln A_T + \left(\frac{RT}{b_T}\right) ln \, C_e$$

where Ce (mg/L), qe and qm (mg g^{-1}) are the heavy metal ion concentration, biosorption capacity of the biosorbent at equilibrium and maximum heavy metal biosorption capacity of biosorbent, respectively. n_F (i) and K_F (mg/g (L/ mg) 1/nF) are Freundlich model constants related to the biosorption intensity and capacity, K_L (L mg^{-1}) is Langmuir equilibrium constant related to the biosorption energy, and T and R are temperature (K) and universal gas constants (8.314 J/ mol K). b_T (kJ/mol) and A_T (L/g) are the heat of biosorption and Temkin constants that are related to the maximum binding energy, respectively (Freundlich 1906, Langmuir 1918, Temkin and Pyzhev 1940).

The separation factor (R_L) or equilibrium parameters confirmed the favorability of biosorption in a given concentration range, as shown in Eq. (6).

$$R_L=1/\left(1+K_L C_o\right) \tag{6}$$

A low RMSE and high R^2 indicated that the models fitted the biosorption process (Tsai and Juang 2000).

$$RMSE=\sqrt{\frac{1}{n}\sum(q_p-q_o)^2} \tag{7}$$

where q_p is the biosorption capacity predicted from the isotherm equation (mg g^{-1}), q_o is the equilibrium capacity obtained from experimental result (mg g^{-1}), and n is the number of samples(7).

The calculated biosorption parameters for the linear and non-linear equations are listed in Table 1 and Table 2, respectively. The small values of RMSE point out that the isotherm equation successfully describes the experimental data.

The plots of linear isotherm models for two metals are presented in Fig. 6. The parameters of linear isotherm model are presented in Table 1. As seen in the Table 1, Temkin model best described the sorption of copper and zinc by LNL. The isotherm model data shown that Langmuir model was the second best isotherm that may also describe the equilibrium study of Zn and Cu biosorption by linear analysis, while the Freundlich model fitted worst. The maximum biosorption capacities determined using linear Langmuir model are 7.11 and 5.68 mg g^{-1} for Zn^{2+} and Cu $^{2+}$, respectively.

Table 1. Langmuir, Freundlich and Temkin isotherm parameters obtained by linear fitting for Cu^{2+} and Zn^{2+}

Linear-isotherm parameters	Cu(II)	Zn(II)
Freundlich		
K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.1973	1.30
1/n	0.4077	0.442
RMSE	0.683	0.287
R^2	0.9362	0.9579
Langmuir		
qm (mg g^{-1})	5.68	7.11
K_L (L mg^{-1})	0.149	0.128
R_L	(0.07-0.44)	(0.13-0.61)
RMSE	0.53	0.19
R^2	0.9968	0.9945
Temkin		
A_T (L mg^{-1})	1.262	1.218
B_T (KJ mol^{-1})	2.085	1.653
RMSE	0.10	0.120
R^2	0.9931	0.9929

The plots of non-linear isotherm models for two metals are presented in Fig. 7. The non-linear isotherm parameters are given in Table 2. RMSE values for each parameter obtained in Temkin isotherm model are correspondingly lower than that of the other two isotherm models. The K_T values obtained from the Temkin isotherm are < 8 kJ mol^{-1} and thus the mechanism involved is physical biosorption (Araújo et al. 2018, Choudhary and Paul 2018). At the same time, these values also indicate that both Temkin model and the Langmuir model can achieve a satisfactory fit to the experimental data. The values of maximum biosorption capacities calculated using non-linear Langmuir model are 5.57 and 7.01 mg g^{-1} for Cu^{2+} and Zn^{2+} ions, respectively. All RMSE values are lower than those determined in linear analysis, which indicates that the non-liner modeling of Temkin for the biosorption system is acceptable. The linear fitting of experimental data into these models may cause fluctuation of R^2, and the predicted parameters may induce deviation. As a result, by comparison, the order of the non-linear isotherm model best fits in the study is Temkin>Langmuir > Freundlich.

Table 2. Langmuir, Freundlich and Temkin isotherm parameters obtained by non-linear fitting for copper and zinc ions.

Non-linear isotherm parameters	Cu(II)	Zn(II)
Freundlich		
K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	1.419	1.504
1/n	0.3470	0.390
RMSE	0.237	0.225
R^2	0.9489	0.9722
Langmuir		
qm (mg g^{-1})	5.57	7.01
K_L (L mg^{-1})	0.159	0.132
R_L	(0.11-0.56)	(0.13-0.60)
RMSE	0.1097	0.1848
R^2	0.9890	0.9813
Temkin		
B_T (L mg^{-1})	1.189	1.501
K_T (KJ mol^{-1})	1.626	1.385
RMSE	0.095	0.124
R^2	0.9917	0.9915

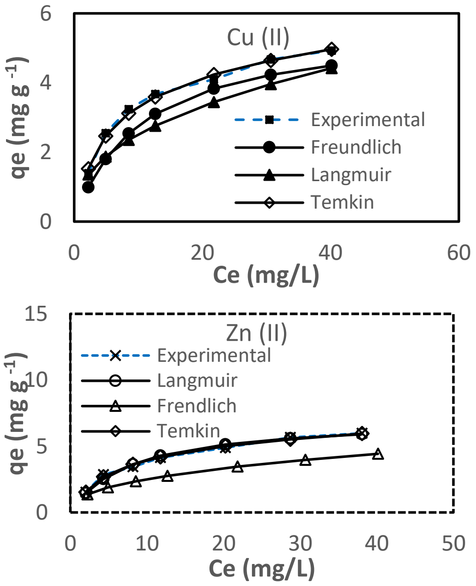

Figure 6. Linear fitting of Langmuir, Freundlich, and Temkin isotherm models for copper and zinc.

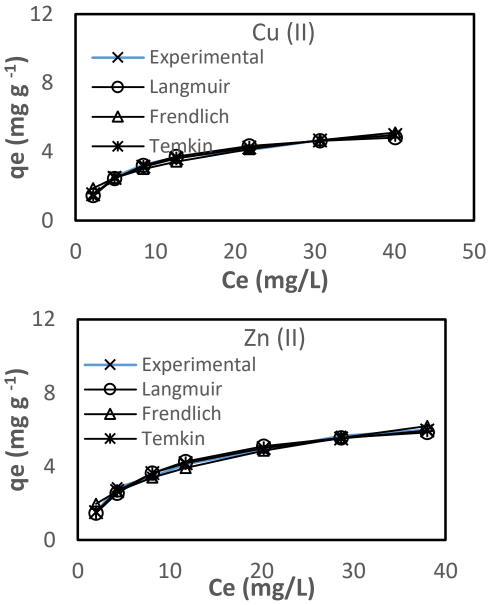

Figure 7. Nonlinear fitting of Langmuir, Freundlich, and Temkin isotherms for Cu(II) and Zn(II).

Effect of Biosorption Time And Kinetics Modelling

The effects of biosorption time on the uptake of heavy metal ions have been submitted in Figure 8 with calculated kinetic data comparatively.

The biosorption kinetics of copper and zinc ions removal were evaluated using pseudo-first order (Lagergren 1898), pseudo-second-order (Ho 2006) and intra-particle diffusion (Hussin et al. 2015) models and the linearized equations can be indicated as:

Pseudo first-order $\log(qe-qt)=\log(qe)-(\frac{k1}{2,303})\,t$ (8)

Pseudo second- order $\frac{t}{qt}=\left(\frac{1}{k_2\,q_e^2}\right)+\left(\frac{1}{q_e}\right)t$ (9)

Intra-particle diffusion $qt= k_{id}*t^{1/2} + C$ (10)

where qt (mg/g) and q_e are (mg/g) the biosorption capacity at equilibrium and t time, respectively, k_1 (min^{-1}) and k_2 (g/mg min) are the pseudo- first- order and pseudo- second- order rate constants, respectively. t is the biosorption time (min), k_{id}, the intra-particle diffusion rate constant (mg/g $min^{-0.5}$) can be obtained from the slope of the t $^{1/2}$ and qt plot (Hussin et al. 2015 Ho 2006 Lagergren 1898).

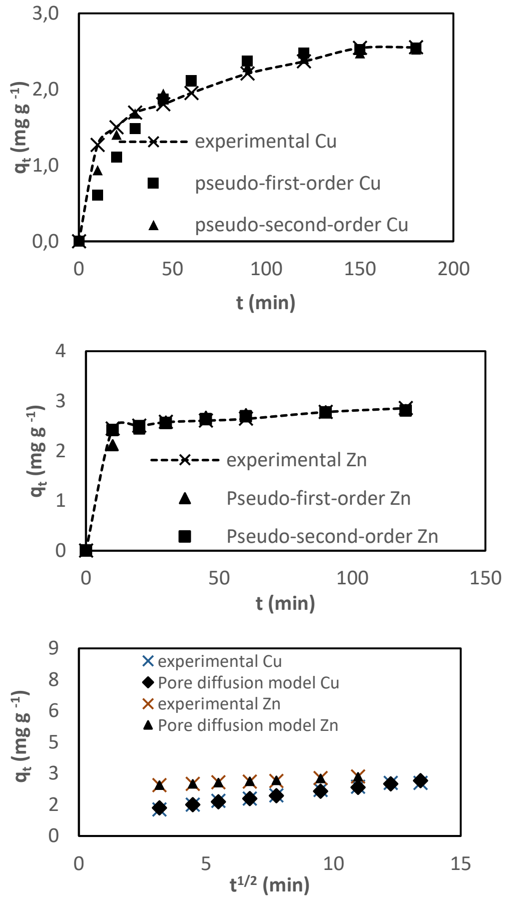

Figure 8. Kinetics of Cu(II) and Zn(II) biosorption

The kinetics parameters of each model are presented in Table 3. A high R^2 and smaller RMSE values point out that the kinetic equation successfully describes the experimental data.

Table 3. Kinetic parameters

Kinetic parameters	Cu(II)	Zn(II)
Pseudo-first order		
qe (mg g^{-1})	2.615	1.851
k_F (min^{-1})	0.0297	0.0193
R^2	0.9142	0.9347
RMSE	0.28	0.13
Pseudo-second order		
qe (mg g^{-1})	2.8027	2.9078
k_s (g mg^{-1} min^{-1})	0.0178	0.0916
R^2	0.9937	0.9986
RMSE	0.141	0.03
Interparticle diffusion		
k_{id}	0.128	0.0524
α (mg g^{-1}min^{-1})	0.9392	0.0524
R^2	0.9857	0.9836
RMSE	0.145	0.17

The smallest RMSE values of 0.14 and 0.03 suggest their superiority to the second-order reaction model for copper and zinc ions respectively. The biosorption kinetic data for two metal ions onto the LNL were best modeled by pseudo second order model which chemical reactions in the biosorption surface play an important role. The intraparticle diffusion was not the rate limiting step for Cu^{2+} and Zn^{2+} biosorption on LNL (Choudhary and Paul 2018).

Single-Stage System Design from The Best Fit Equilibrium Data

Experimental studies are not very comprehensive. Therefore, empirical design methods based on the best fitted isotherm finding are widely used to predict the amount of biosorbent (Dawood and Sen 2012 Reddy et al. 2017). Fig. 9 exhibits the amount of LNL biomass required for the desired % uptake of zinc(II) and copper(II) for different solution volumes.The mass balance for zinc(II) and Copper(II) ions in the single-stage biosorber system is represented as:

$$V(C_0-C_t)= W (q_t-q_0) = Wq_t \qquad (11)$$

At equilibrium

$$Ct \longrightarrow C_e \text{ and } q_t \longrightarrow q_e,$$

then Eq. 11 becomes Eq. 12:

$$V (C_0-Ce)=Wq_e \qquad (12)$$

The aim of system design was to reduce initial heavy metal concentration of C_0 to C_t (mg/L) for that heavy metal containing aqueous solution is V (L). The used biosorbent dosage was W and the solute loading varies from q_0 (mg g^{-1}) to qt (mg g^{-1}).

Temkin isotherm equation was used for Zn^{2+} and Cu^{2+} ions, respectively in the single-stage studies. The Eq. (12) was readjusted based on the best fit equilibrium model for Zn(II) and Cu(II), respectively (Eq. (13).

$$W/V= (C_0-Ce)/[B_T.\ln(K_T.Ce)] \qquad (13)$$

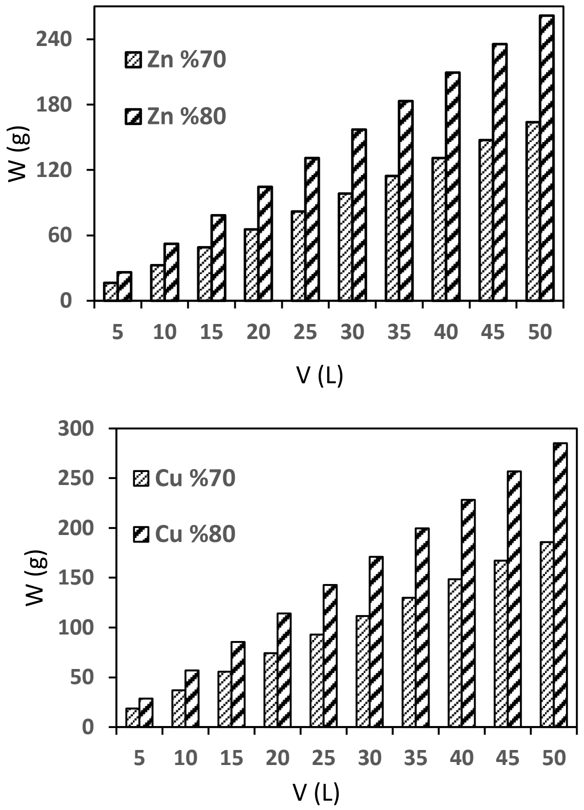

Figure 9. The amount of LNL biomass required for the desired % removal of copper and zinc ions for different solution volumes

Competitive Studies

Fig. 10 shows the ability of LNL biomass to uptake of zinc (II) and copper (II) ions from an aqueous solution through batch experiments in competitive conditions. The percentage removal of zinc and copper ions, in a multi metal system including zinc, cadmium, lead and copper ions at the initial heavy metal concentrations of 5 mg/L. The removal efficiency of Zinc(II) and Copper(II) decreased from 60.4% (single-metal system) to 56.6% (multi-metal system) and from 55.8% to 46.02%, respectively. The amount of the fixed biosorbent has a limited number of active binding sites. These regions are expected to be saturated by competing metal ions (Yan et al. 2010). Although all the tested metal ions were bivalent, their removal capacities were different due to different interactions in the biosorption centers (Bayo et al. 2012). In the literature, similar studies were reported.

The effects of common ions such as Ca^{2+} and Na^{+} or HA were studied at optimum conditions, in this manner the selectivity of the sorption process was evaluated. The removal rates of zinc(II) and copper(II) decreased from 60.4% to 41.3% and from 55.8% to 49.4%, respectively with the effect of HA. The binding of humic acid with the biosorbent would reduce the metal removal rate due to competition effect (Tang et al. 2014). The removal efficiency values of Zinc(II) and Copper(II) decreased from 60.4% to 58.1% and from 55.8%-32.3%, respectively, with inclusion of the Ca^{2+} and Na^{+} ions. It is indicated that the presence of common ions reduced the uptake of heavy metals (Sahmoune 2018).

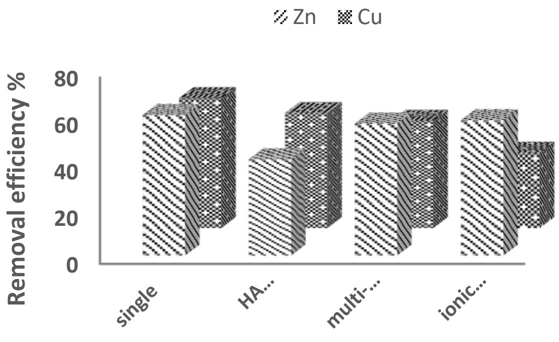

Figure 10. Competitive biosorption studies

Comparison Studies

The Zn^{2+} and Cu^{2+} ions uptake capacities of LNL biomass were compared with the other reported biosorbents. Table 4 listed the comparative study of the biosorption capacities Zn^{2+} and Cu^{2+} ions. LNL exhibited comparable biosorption potential for two heavy metal ions to the other biosorbents.

Table 4. Comparison of q_m (maximum biosorption capacities) of different biosorbents for Zn^{2+} and Cu^{2+} ions

Biosorption capacities (qm) (mg g^{-1})		Biosorbent	References
Zn(II)	**Cu(II)**		
4.79	-	Cedar leaf ash	Hafshejani et al. 2015
9.57	7.60	Groun nut shells	Shukla and Pai 2005
-	6.07	Moringa aptera Gaertn	Matouq et al. 2015
-	3.64	Jujube complex bead	Choi et al. 2012
-	2.76	Coconut dregs residue	Kamari et al. 2014
-	4.69	Cocoa pod husk	Obike et al. 2018
-	4.52	Modified rice husk	Jaman et al. 2009
7.01	5.57	*L.nobilis*	This study

CONCLUSIONS

This study shows that the LNL can be employed as a potentially environmental friendliness sorbent for the zinc and copper ions uptake from water. The biosorption experiments showed that the extent of biosorption was dependent on initial copper(II) and Zinc(II) concentration, aqueous solution pH, biosorption time, biomass amount, ionic strength and humic acid. The maximum removal rates of copper(II) and Zinc(II) are observed at the pH 6.5 for both metal ions. The linearized and non-linearized equilibrium models were compared and it can be concluded that the non-linear form of these equations are more suitable for model descriptions of the removal of Copper(II) and Zinc(II) using LNL biomass. The equilibrium isotherm data suggest that Copper(II) and Zinc(II) biosorption onto LNL are best explained by both Temkin and Langmuir equilibrium models. Pseudo second-order kinetic equation successfully defined the behaviors of both heavy metals onto LNL. The presence of studied foreign ions showed slightly effect in the competitive removal studies and therefore It was concluded that LNL could be effectively used for removal Zinc (II) and Copper(II) ions in the presence of other metal ions.

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