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Effect of Turbidity and Contact Time on the Rate of Biosorption of Ni^{2+}, Pb^{2+}, Cr^{3+} and Cu^{2+} from Wastewater Using *Moringa oleifera*

Chavaregi Geoffrey[1*], J. L. Kituyi[1] and S. Lutta[1]

[1]*Department of Chemistry and Biochemistry, University of Eldoret, Kenya.*

Authors' contributions

This work was carried out in collaboration between all authors. All the authors managed the analyses of the study and literature searches. Also, the authors read and approved the final manuscript.

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ABSTRACT

Heavy metals in water have been a major preoccupation for researchers for many years due to their toxicity towards aquatic life, human beings and the environment. As they do not degrade biologically like organic pollutants, their presence in industrial effluents and drinking water is a public health problem. Consequently, there is need to come up with novel methods of heavy metals remediation which are more effective and reliable. The biosorption processes using biosorbents like *Moringa oleifera* have been found to be affected by various physical and chemical factors. Therefore, the present study sought to determine the effect of turbidity and contact time on the rate of biosorption of Ni^{2+}, Pb^{2+}, Cr^{2+} and Cu^{2+} from wastewater using *Moringa oleifera.* Atomic absorption spectrometer (AAS) was used to analyse samples for levels of massive metal species; Pb^{2+}, Cr^{3+}, Cu^{2+} and Ni^{2+} before and after treatment with *oleifera* biosorbent. The effect of turbidity and contact time on the biosorption of the heavy metals by the Moringa *oleifera* biosorbent was

**Corresponding author: E-mail: jfcom@rocketmail.com;*

studied by varying these parameters. Results obtained in the study showed that percentage adsorption decreased from 99, 96, 95 and 87% in 20 ml of turbid solution to 70, 92, 93 and 60% in 50 ml cloudy solution for Pb^{2+}, Cr^{3+}, Cu^{2+} and Ni^{2+} respectively. Sixty minutes of equilibration time was found to be adequate for adsorption of the considered metal ions. Several kinetic models were applied to the adsorption data, and it was found that pseudo-second order fitted well with the adsorption data. It was therefore concluded that *M. oleifera* could be used as a low-cost adsorbent for the removal of heavy metals from aqueous solutions.

Keywords: Turbidity; contact time; Moringa; heavy metals; biosorption.

1. INTRODUCTION

According to Allitt [1], environmental pollution is one of the pressing global concerns in the 21st century. Anthropogenic activities mainly agricultural, industrial and domestic wastes discharge their wastewaters containing pollutants including toxic heavy metals into the environment. Heavy metals are amongst the most dangerous pollutants of both surface and groundwater [2]. Because metal ions are not degradable, they have a tendency to accumulate in water streams, endangering human health. Therefore, removal of such metals from the environment is necessary. Various techniques have been employed in the removal of heavy metal ions from the environment. These include chemical precipitation, ion-exchange, adsorption, membrane filtration and electrochemical treatment technologies. Most of these methods have been used with some limitations such as high costs of maintenance which have affected their efficiency in removal of heavy metals. Therefore, a cost-effective and reliable treatment method that is capable of removing heavy metals from aqueous solutions [3] is needed. Biosorption of heavy metals from aqueous solutions is a relatively new process that is proven very promising in the removal of contaminants from aqueous effluents. The biological materials that have been investigated for heavy metal uptake include bacteria, fungi, yeast and algae [4]. The major advantages of this method over the other conventional ones include not only its low cost, but also its high efficiency, the minimization of chemical or biological sludges, the ability to regenerate biosorbents, and the possibility of metal recovery following adsorption.

Moringa oleifera is also known horseradish tree or drumstick tree is a fast-growing, drought tolerant, deciduous tree plant of the genus *Moringa* [5]. Traditional cultures in various parts of the world have long used Moringa in their herbal medicine repertoire for ailments ranging from gout to various inflammations and fevers [6]. The powdered seed of the plant *Moringa oleifera* has coagulating properties that have been used for various aspects of water treatment such as turbidity, alkalinity, total dissolved solids and hardness. However, its biosorption behaviour for the removal of toxic metals from water bodies has not been given adequate attention [7]. The biosorption processes using biosorbents like *Moringa oleifera* have been found to be affected by various physical and chemical factors [8]. These factors determine the overall biosorption performance of a given biosorbent, that is its uptake rate, its specificity for the target, and the quantity of target removed. Various studies have been carried out on the effect of solution temperature, pH, ionic strength, initial pollutant concentration biosorbent dosage, biosorbent size, contact time and agitation speed [7,9,10,11]. However, there is scanty information on the effect of turbidity on the rate of biosorption of Ni^{2+}, Pb^{2+}, Cr^{2+} and Cu^{2+} from wastewater using Moringa oleifera. Therefore, this study sought to fill this lacuna.

2. MATERIALS AND METHODS

2.1 *Moringa oleifera* Seed Biomass

Moringa oleifera seeds were collected from the environs of Usage town, Kenya. The leaves were transported to the University of Eldoret Chemistry lab where they were washed thoroughly with distilled water and then dried under shade for a week. The dry seeds were then crushed into a fine powder using mortar and pestle. A half-kilogram of the powder was added to 2 litres of 0.1M HNO_3 for acid treatment and 0.1M NaOH for alkali treatment. The mixture was boiled for about 20 minutes. The powder was then washed using distilled water until maximum colour removal is achieved and water was obtained. Finally, the fresh powder was dried again in an oven at 50°C for 6 hrs.

2.2 Preparation of Cr^{3+}, Ni^{2+}, Pb^{2+} and Cu^{2+} Ion Solutions

Stock solutions of Cr^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} were prepared by dissolving 3.05g of $Cr(NO_3)_2$, 2.10g of $Ni(NO_3)_2$, 1.59g of $Pb(NO_3)_2$ and 2.67 g of $Cu(NO_3)_2$ in 10 mL of 1:1 nitric acid and then diluted to 1 L to give 1000 ppm of the metals. A working solution of 100 ppm was prepared by pipetting 10 mL from 1000 ppm stock solution into 100 mL volumetric flask then made to the mark using distilled water for each metal.

2.3 Biosorption Studies

A batch method was employed for studying the biosorption of Cr^{2+}, Ni^{2+}, Pb^{2+} and Cu^{2+} by *Moringa oleifera* seed biomass. A set of 250 mL Erlenmeyer flask containing 50 mL of metal solution (5 ppm) was used, and 0.4 g of biosorbent (*Moringa oleifera* seeds powder) was added followed with shaking after which the contents of the flask were filtered and filtrates analysed. To study the effect of variation of contact time on the rate of biosorption, experiments were carried out with an optimum initial concentration of the heavy metals (5 ppm), pH (6.8) and optimum dose of the biosorbent (0.4 g). Then the optimum dose of biosorbent was added and immediately subjected to biosorption. A stopwatch to note the time was started simultaneously. Samples for determination of the extent of biosorption were drawn from the biosorption vessel at different time intervals 1, 2, 3 and 4hrs. On the other hand, the turbidity of the model wastewaters was varied from 5 NTU to 50 NTU by 5 NTU intervals. This was done using soil particles which were washed thoroughly to avoid contamination of the sample wastewaters. The wastewater samples with different turbidity levels than were exposed to the *Moringa Oleifera* biosorbent for a fixed time and the extent of biosorption studied for each sample to determine the effect of variation of turbidity of the wastewater on the size of biosorption.

2.4 Analytical Procedures

Atomic Absorption Spectrophotometer (AAS) was used to determine the concentrations of the biosorbed metals. To achieve this, a reagent blank sample was first taken through the method, analysed and subtracted from the samples to correct for reagent impurities and other sources of errors from the environment. The concentrations of the metals were then determined in triplicates to ensure accuracy and precision of the analytical procedure.

After biosorption, the concentrations of these metal ions were analysed. The extent of biosorption regarding percentage removal was calculated using the following relationship.

$$\%\ \text{Removal} = \frac{C_1 - C_2}{C_1}\ x\ 100$$

Where C_1 = Initial concentration
C_2 = Final concentration

3. RESULTS AND DISCUSSION

3.1 Effect of Turbidity of Wastewater on the Rate of Biosorption of Pb, Cu, Cr and Ni by *Moringa oleifera*

Results in Fig. 1 indicate that turbidity affected the adsorption of the considered metals. Generally, % adsorption of the metal ions decreased with increase in turbidity.

Highest % adsorption for Pb, Cu, Cr and Ni was recorded to be 99, 96, 95 and 87% respectively at 20 ml of turbidity. At 50 ml of turbidity, lowest % adsorption of 70, 92, 93 and 60% was observed for Pb^{2+}, Cu^{2+}, Cr^{2+}, and Ni^{2+}, respectively. This could be attributed to coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, a higher concentration of other pollutants will, therefore, reduce the sorptive removal of the target pollutant. Organic compounds present in water are, and they adsorb to the mineral surface (Covelo et al., 2008). Previously, Schnitzer and Khan [12] reported that physical adsorption could cause OM-clay mineral interaction through Van der Waal forces, electrostatic attractions and the ligand exchange process. Various researchers have published similar findings. Sen et al. [13] said that increase in solid pollutants in water led to significant reduction in % removal of heavy metals. A study by Park et al. [14] reported that growth in turbidity in wastewater led to a reduced biosorption of heavy metals. The researchers argued that the coexisting pollutant in the wastewater competes with a target pollutant for binding sites or forms any complex with it, the higher concentration of another contaminant will reduce the sorptive removal of the target pollutant. Previously, Huang et al. [15] reported that the uptake of heavy metals by sludge particulate was significantly affected by dissolved organic matter which is a measure of turbidity.

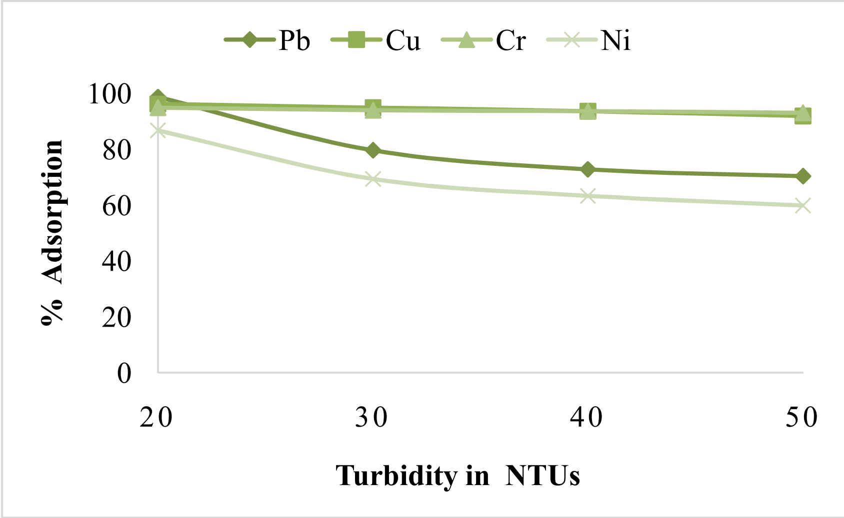


Fig. 1. Effect of turbidity on percentage sorption of Pb^{2+}, Cu^{2+}, Cr^{2+} and Ni^{2+} ions onto *M. oleifera*

3.2 Effect of Contact Time

The minimum time required for quantitative uptake of metal ions from solution was determined and the results recorded in Fig. 2. Useful contact times were obtained by plotting the % adsorption of metal ions against time. The adsorption process was found to be rapid with higher percentage of adsorption noted immediately the metal ions came in contact with the adsorbent. However, the percentage adsorption reduced and later remained almost constant after 2 hrs of contact time.

Among the four metals, Pb recorded higher percentage of adsorption in all the four test periods than Ni, Cu and Cr. All the four metal ions attained equilibrium within the first 60-120 minutes. Hence the useful contact times for the selected metals were found to be 120 minutes. This can be attributed to the fact that all the binding sites have been occupied by the metal ions hence the plateau nature of all the three graphs in the Fig. 2. The binding sites become saturated and cannot take any more of the metal ions or all the metal ions have been removed and there are no more ions to be adsorbed.

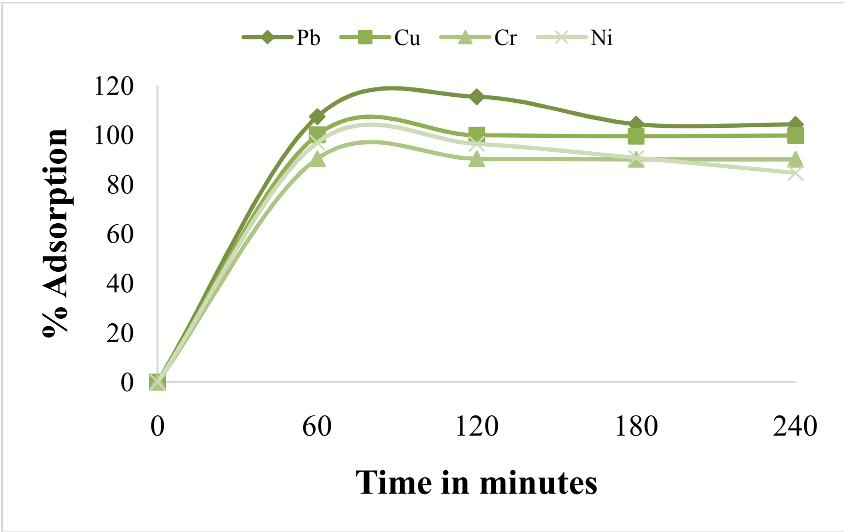
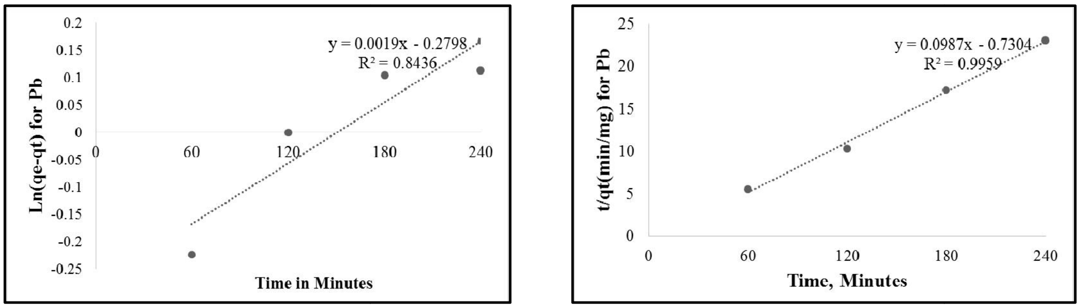
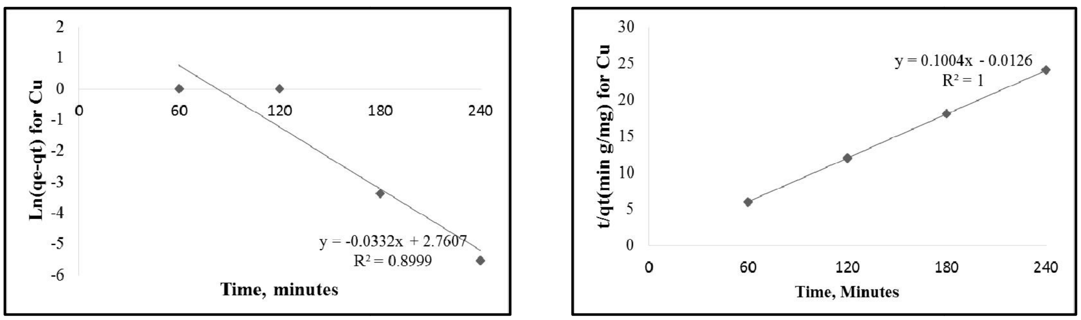


Fig. 2. Effect of contact time on sorption of Pb^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} ions by 5 g of *M. oleifera*

Similar results have been reported by other workers. Masamba et al. [16] reported a decrease in % of adsorption of metals ions using algae due to the saturation of adsorption sites.



a



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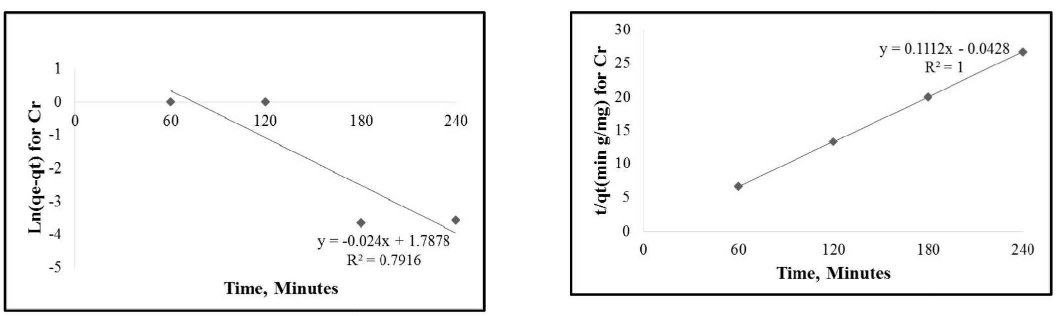

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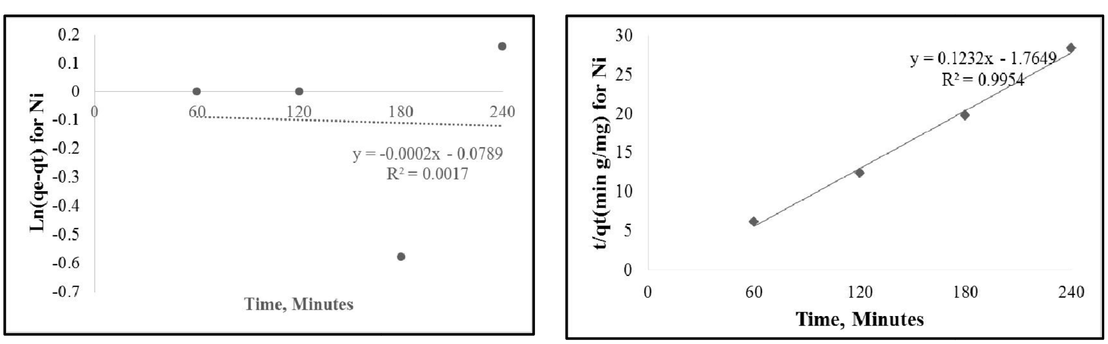

d

Fig. 3. First and second order linearity test for Pb^{2+} (a), Cu^{2+} (b), Cr^{2+} (c) and Ni^{2+}(d) adsorption on *M. oleifera*

Table 1. Kinetic parameters for Pb, Cu, Cr and Ni metal adsorption on *M. oleifera*

Metal	Initial concentration (mg/L)	Calculated metal uptake at equilibrium between me, (mg/g)	R^2 value for first-order linearity test	R^2 value for second order linearity test
Pb	10	1.12	0.8636	0.9959
Cu	10	0.4	0.8999	1.0000
Cr	10	0.28	0.7916	1.0000
Ni	10	1.17	0.0017	0.9954

The researchers further elaborated that the high charge density and small size of the metal ions results in them being strongly hydrolysed by water. Thus the solution will compete with the binding sites for the metal ions resulting in the slow release with time. A study by Salehzadeh [17] reported that most of the maximum percent Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+} removal using *Xanthium Pensylvanicum* was attained after about 90 min of shaking time. In addition, in biosorption of selected heavy metal ions using Spirogyra species, biosorption increases with increase of contact time from 0-120 minutes [18]. Results reported by Nuhoglu and Oguz [19] showed that the biosorption efficiency of selected ions increased by increasing contact time. The study further revealed that using cone biomass, adsorption occurred in two steps and equilibrium was reached after 60 minutes.

3.3 Order of Reactions

The mass q_t of metal adsorbed after time *t* is related to the equilibrium metal uptake $_{me}$ by the integrated first and second order equations. A plot of ln($_{age\ -}$ q_t) against time (minutes) was used for the first order linearity test, while a parcel of qt (ming/mg) against time (minutes) was used for the second order linearity test and the calculation of age, which is the metal uptake in milligrams per gram of biosorbent at equilibrium. The order of reaction for each metal was deduced from the linearity of the respective plots. Fig. 3 and gives the slopes and the R^2 values from which he and the linear correlation coefficients may be obtained.

The second order plots for all metals have higher R^2 values than the corresponding first-order plots as shown in Table 1. The process is, therefore, the second order for all metals.

The prediction of adsorption rate gives essential information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for the full-scale batch process. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first-order and pseudo-second-order dynamic model. Results obtained in the present study showed that the pseudo-second-order plot for displayed higher correlation coefficient (R^2 ≥0.99) on adsorption of Pb, Cr, Cu and Ni ions onto *M. oleifera* biomass than the pseudo-first-order kinetic model. The process is, therefore, second order for all the metals. This agrees with literature [20,21,22].

4. CONCLUSION

Results obtained from the present study recorded high % removal of the studied metals from wastewater at optimum conditions using *M. oleifera*. Results further showed that the removal of metal ions was affected by turbidity. Increased turbidity reduced the % removal of the considered metals. Also, contact time was reported to affect metal ions' removal with maximum removal of metals attained within the first 60 minutes. The adsorption data fitted well for pseudo-second-order mode for all the alloys under study. The study concluded that *M. oleifera* biomass could be used as a natural sorbent for the removal of heavy metals from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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