Bull. Chem. Soc. Ethiop. **2013**, 27(1), 35-47. ISSN 1011-3924
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v27i1.4

REMOVAL OF Ni(II) FROM AQUEOUS SOLUTION USING LEAF, BARK AND SEED OF *MORINGA STENOPETALA* ADSORBENTS

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(Received December 14, 2011; revised November 13, 2012)

ABSTRACT. The present study investigates the possibility of using leaf, bark and seed of *Moringa stenopetala* as alternative adsorbents for removal of Ni(II) from aqueous solutions. The optimum adsorption conditions for removal of Ni(II) were found to be 30, 20 and 50 mg/L initial concentration, 1.5, 2 and 2.5 g adsorbent dose, 250, 250 and 300 rpm agitation speed, 90, 120 and 90 min contact time, 40, 30 and 23 ^{o}C temperature and pH of 5, 6 and 6 using leaf, bark and seed as adsorbent, respectively. At optimum experimental conditions the percent adsorption of synthetic wastewater sample was found to be 93.90, 96.25 and 97.50 for leaf, bark and seed, respectively. The tested experimental data best fits to pseudo-second order ($R^2 > 0.98$) than pseudo-first order, Elovich and intraparticle diffusion kinetic models indicating rate limiting step to be chemisorption. It also fits to Langmuir ($R^2 > 0.895$ using adsorbate variation and also $R^2 > 0.998$ using both time and temperature variation data) than Freundlich, Temkin and D-R isotherm models. D-R isotherm and thermodynamic study reveals formation of physical adsorption. Hence the adsorption mechanism could be regarded as physico-chemical adsorption process. The adsorption results of industrial wastewater also reveal that for removal of nickel 83% and 85% was obtained using bark and seed adsorbents, respectively. The new method of adsorption developed in this study is cheap, fast and environmental friendly.

KEY WORDS: *Moringa stenopetala*, Ni(II) adsorption, Isotherms, Kinetics, Thermodynamics, Industrial wastewater

INTRODUCTION

Pollution load of the environment is increasing due to global rise in population and our quest to lead comfortable life resulting in explosive growth of industrial and agricultural activities. Environmental contamination with metal ions represents a potential threat to human, animals and plants. Metal ions which many of them are soluble in aqueous solutions become more available for living systems and accumulate in the environment are of vital concern [1, 2].

Nickel is released into the environment in a large number of processes such as electroplating and steel manufacturing. High nickel concentrations on sandy soils can clearly damage plants and high nickel concentrations in surface waters can diminish the growth rates of algae and microorganisms. Nickel is present in wastewaters from metal processing, steel foundry, motor vehicle and aircraft, leather and chemical industries [3].

Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage and skin irritation. Nickel may cause dermatitis upon exposure to the skin, and gastrointestinal distress upon ingestion. In India, the acceptable limit of Ni(II) in drinking water is 0.01 mg/L and 2.0 mg/L is the industrial discharge limit in waste water [4, 5].

Some of the techniques which have been used in the removal of metals from effluents include ion-exchange, chemical precipitation, electro dialysis, electrolytic extraction, reverse

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*Corresponding author. E-mail: alemayehuabebaw@yahoo.com osmosis and cementation. These methods are expensive and have the inability to remove metals at low concentration. Compared to the aforementioned techniques, adsorption has shown to be a more economically favorable alternative for the removal of metals from aqueous solutions. Activated carbon is the most widely used adsorbent, but due to its relatively high cost, cost effective adsorbents for treatment of metal contaminated wastewaters are necessary particularly in developing countries [6-8].

This research focuses on the adsorption behavior of different parts of *M. stenopetala* for the removal of Ni(II) present in industrial effluent. Literature review shows that no work has been reported for removal of Ni(II) using *M. stenopetala* as an adsorbent from industrial effluents in Ethiopia. Therefore a work on adsorption mechanism and optimum condition determination is initiated.

EXPERIMENTAL

Preparation of adsorbents

The samples of *M. stenopetala* (leaves, barks and seeds) were collected from kola share village, near Arbaminch which is about 500 km from Addis Ababa, Ethiopia after authenticated by an expert. These samples were sealed in cleaned polyethylene plastic containers preserved inside of an ice bag and transported to the laboratory. The fresh leaves and barks were cleaned with distilled water separately to remove any contaminants. The cleaned leaves were dried for a period of three days at room temperature (23 ± 2 ^{o}C). The cleaned barks were chopped with table knife into small pieces and then dried at 105 ^{o}C over night in a thermostatically controlled oven to attain constant weight. Seeds were deshelled by hand and cleaned with distilled water. The cleaned seeds were chopped into small pieces and then dried for 24 h at 110 ^{o}C in oven. All these dried adsorbents were ground by mortar and pestle into fine powder, sieved by 0.25 to 0.5 mm sieve in order to get particle size of less than 0.5 mm [9, 10].

Preparation of metal ion solutions

The stock solutions of Ni(II) having concentration 1,000 mg/L was prepared by dissolving the analytical grade of $Ni(NO_3)_2.6H_2O$ (99%) with distilled water. The other working solutions were prepared by diluting the stock standard solution with distilled water.

Batch mode adsorption studies

Adsorption experiments were conducted for nickel ion by varying metal ion concentration (5-50 mg/L), adsorbent dose (0.5-3.0 g), contact time (30-240 min), agitation speed (100-350 rpm), temperature (23-60 ^{o}C) and pH (2-8) until optimum conditions of adsorption was obtained for Ni(II) in each adsorbents. In these optimization procedures one parameter was varied while the others were kept constant. The pH of each solution was adjusted to the desired value by adding 0.1 M NaOH (BDH, England or 0.1 M HCl (NICE Chemicals, India). Agitation of the samples were carried out in Gemmy orbit (model: VRN-480) and water bath shakers using 250 mL Erlenmeyer flasks and the total volume of the reaction mixture was kept at 50 mL [10, 11].

The mixtures were filtered through Whatman No. 42 filter paper. The filtrates were analyzed by the flame atomic absorption spectrometry (ELICO SL 194, India). The concentration of nickel was measured at 232.0 nm wavelength, 2.5 nm slit width and 12 mA current. The FAAS was adjusted to measure each sample five times and the results taken as an average.

Determination of adsorption models

After identifying the optimum conditions of adsorption parameters, kinetic, isotherm and thermodynamic studies were carried out to distinguish the adsorption mechanism occurred through the adsorption process. The adsorption kinetic studies were carried out by varying contact time around the optimum condition obtained from the optimization procedure and keeping the other parameters at optimum. The experimental contact time variation data were carried out for nickel at 20 mg/L concentration, 2 g of bark, 250 rpm agitation speed, 30 ^{o}C and pH of 6 for bark adsorbent and at 50 mg/L concentration, 2.5 g of seed, 300 rpm agitation speed, 23 ^{o}C and pH of 6 for seed adsorbent. Each of the five prepared solutions was repeated three times in the batch adsorption procedure. The adsorption isotherm studies were carried out using the temperature variation, using contact time variation and also by varying the adsorbate concentrations around the optimum condition obtained in the optimization procedure as follow. The experimental adsorbate concentration variations were carried out for Ni(II) at 2 g of bark, 250 rpm agitation speed, 120 min. contact time, 30 ^{o}C and pH of 6 upon studying using bark adsorbent and at 2.5 g of seed, 300 rpm agitation speed, 90 min contact time, 23 ^{o}C and pH of 6 for seed adsorbent. Each of the five prepared solutions was repeated three times in the batch adsorption procedure. Adsorption thermodynamic studies were also carried out using the temperature variation.

Studies on industrial wastewater

Industrial wastewater was collected at the point of discharge from Modjo Tannery Share Company which is about 80 km from Addis Ababa. Wastewater sample was collected in polyethylene plastic containers previously cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 h and finally rinsed with distilled water prior to usage. Composite sampling method (at different distance of discharge channels and at different time intervals) was used in collecting the wastewater samples. These samples were transported to the laboratory, stored in the refrigerator at about 4 ^{o}C to lower vapor pressure. For preventing chemical reactions (for example, metal ions may oxidize to form insoluble oxides or hydroxides), the samples were acidified with HNO_3 to a pH below two, as most nitrates are soluble, and excess nitrate prevents precipitation [12, 13]. Keeping the optimum conditions of adsorption in synthetic wastewater, adsorption studies were carried out in real wastewater sample.

RESULTS AND DISCUSSION

Effect of initial metal ion concentration on adsorption

The effect of initial concentrations of nickel on adsorption was studied by varying the adsorbates concentration from 5-50 mg/L with respect to leaf, bark and seed adsorbents by holding the other parameters constant. The results are presented in Figure 1.

The percent removal of nickel ion by the adsorbents initially increase with increasing nickel ion concentration and a maximum value reached at concentrations of 30, 20 and 50 mg/L for leaf, bark and seed adsorbents respectively. Hence these concentrations were used to further study other parameters. The initial rapid increase in percent removal of metal ions can be attributed to the interactions between the metal ions and the active sites of the adsorbent. This may be due to the higher adsorption rate and the utilization of all the active sites available for adsorption at higher concentrations. However further increase in initial concentration of adsorbates cause to decrease the percent removal. This can be explained based on the fact that all the adsorbents had limited number of active sites, which would have become saturated above a certain metal ion concentration.

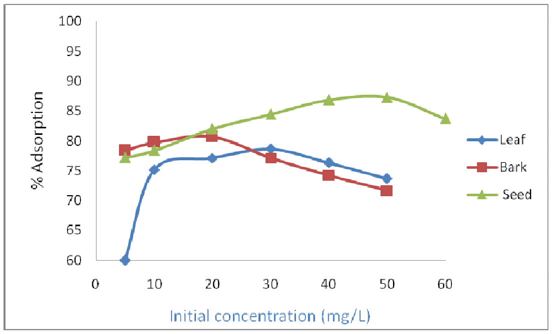

Figure 1.Effect of initial concentration on Ni(II) removal (1 g adsorbent, 250 rpm agitation speed, pH of 2.5, 60 min contact time and room temperature for each adsorbent).

Effect of adsorbent dose

The effect of adsorbent doses on adsorption of nickel was studied in the range of 0.5-3.0 g for leaf, bark and seed adsorbents. The results are given in Figure 2.

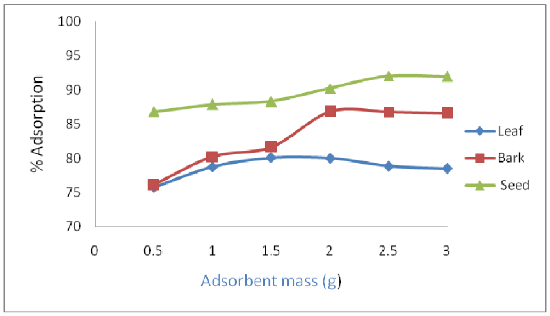

Figure 2. Effect of adsorbent dose on Ni(II) removal (room temperature, pH of 2.5, 250 rpm agitation speed and 60 min contact time for each adsorbent and also concentrations of 30, 20 and 50 mg/L for leaf, bark and seed respectively).

The optimum adsorbent masses for Ni(II) obtained were 1.5, 2.0 and 2.5 g of leaf, bark and seed, respectively. The increase in the adsorption percentage with rise in adsorbent dosage may be due to increase the available adsorption active sites on the adsorbents and thus making easier penetration of the metal ion to the sorption sites. However, any further addition of the adsorbent beyond the obtained optimum masses did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles and also due to decrease in the contact time required to reach apparent equilibrium as the adsorbent dose increase.

Effect of agitation speed

The effect of agitation speeds on adsorption for Ni(II) was studied in the range of 100-350 rpm for each adsorbent. The results are presented in Figure 3. From the results presented in Figure 3, the maximum adsorption of Ni(II) occurred at 250, 250 and 300 rpm for leaf, bark and seed adsorbents, respectively. At low agitation speed, the adsorbent do not spread in the sample but accumulated. This will bury the active sites of the lower layer adsorbent and only the upper layer adsorbent active sites adsorb the metal ion. This indicates that agitation rate should be sufficient to assure that all the surface binding sites are readily available for metal uptake. But for further increase in agitation speed, percentage removal decrease. This may be attributed to an increase desorption tendency of adsorbate molecules.

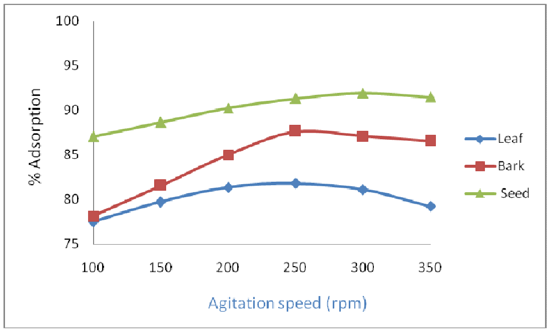

Figure 3. Effect of agitation speed for Ni(II) removal (room temperature, 30 mg/L, pH of 2.5, 1.5 g leaf and 60 min time for leaf, at room temperature, 20 mg/L, pH of 2.5, 2 g bark and 60 min time for bark and also at room temperature, 50 mg/L, pH of 2.5, 2.5 g seed and 60 min. time for seed).

Effect of contact time

The effect of contact times on adsorption for nickel was studied at 30, 60, 90, 120, 150 and 240 min with respect to leaf, bark and seed adsorbents. The results are presented in Figure 4.

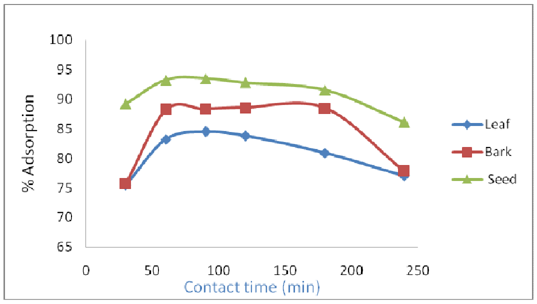

Figure 4. Effect of contact time for Ni(II) removal (30 mg/L, 1.5 g leaf, pH of 2.5, 250 rpm agitation speed and room temperature for leaf, at 20 mg/L, 2 g bark, pH of 2.5, 250 rpm agitation speed and room temperature for bark and also at 50 mg/L, 2.5 g seed, pH of 2.5, 300 rpm agitation speed and room temperature for seed).

From the results presented in Figure 4, the rate of percent removal is higher at the beginning because of large number of vacant surface sites available for adsorption. The maximum adsorption of Ni(II) was obtained at contact times of 90, 120 and 90 min for leaf, bark and seed adsorbents, respectively. After these equilibrium contact time, a decrease in the amount adsorbed was observed. Therefore, in a mixture of the adsorbents and metal ion, the metal ion competes for the adsorption sites on the adsorbent. This competition could affect the diffusion properties of the metal ions and also the adsorption capacity of the metal ions.

Effect of pH

The effect of pH on adsorption for Ni(II) was studied in the range of pH 2-8 with respect to leaf, bark and seed adsorbents. The results are presented in Figure 5. In the present investigation maximum adsorption of nickel ion was obtained at pH of 5, 6 and 6 for leaf, bark and seed adsorbents, respectively. The increase in percentage removal of metal ion due to increase in pH may be explained on the basis of a decrease in competition between proton (H^+) and positively charged metal ion at the surface sites and also by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ion and more negative groups for complexation of metal cations are provided. When alkalinity increased from pH value of 7 to 8, there was a further decrease in the rate of adsorption by the adsorbent for metal ions in the aqueous solution. At higher pH values, metal ions tend to hydrolyze and precipitate instead of adsorption and the adsorbent deteriorated with accumulation of metal ions, making true adsorption studies impossible.

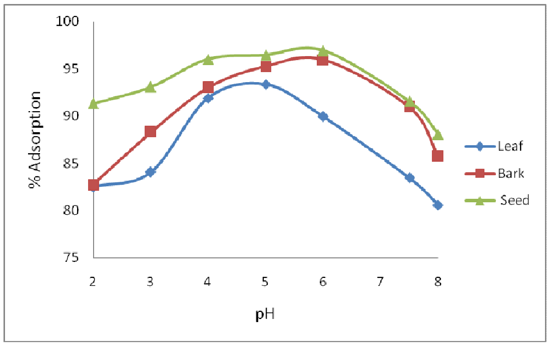

Figure 5. Effect of pH on Ni(II) removal (30 mg/L, 1.5 g leaf, 250 rpm agitation speed, 90 min. time and room temperature for leaf, at 20 mg/L, 2 g bark, 250 rpm agitation speed, 120 min. time and room temperature for bark and also at 50 mg/L, 2.5 g seed, 300 rpm agitation speed, 90 min. time and room temperature for seed adsorbent).

Effect of temperature

The effect of temperature on adsorption for Ni(II) was studied at 23, 30, 40, 50 and 60 °C with respect to leaf, bark and seed adsorbents. The results are presented in Figure 6. In the reported study, a slight increase in percent removal with increased temperature for the adsorbents was observed. The maximum adsorption of nickel ion was obtained at temperature of 40, 30 and 23 °C for leaf, bark and seed adsorbents, respectively. As the temperature increases the kinetic energy of metal ions in solution also increase to make the number of metal ions reaching to the adsorbent surface maximum. The observed decrease in Ni(II) percentage removal with increasing temperature suggests weak binding interaction between the active sites and the metal ions, which supports physisorption. Furthermore, physical adsorption reactions are normally exothermic; hence the extent of adsorption generally increases with a decrease in temperature. At optimum experimental conditions the percent adsorption of synthetic wastewater sample was found to be 93.90, 96.25 and 97.50 for leaf, bark and seed, respectively.

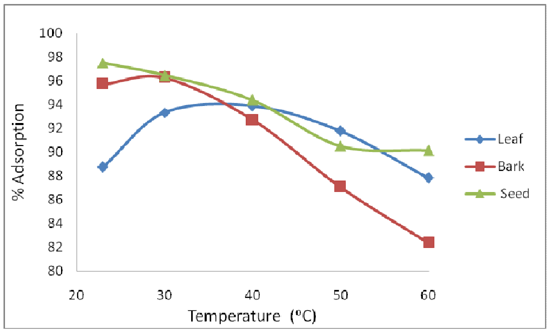

Figure 6. Effect of temperature on Ni(II) removal (30 mg/L, 1.5 g leaf, 250 rpm agitation speed, 90 min time and pH of 5 for leaf, at 20 mg/L, 2 g bark, 250 rpm agitation speed, 120 min time and pH of 6 for bark and also at 50 mg/L, 2.5 g seed, 300 rpm agitation speed, 90 min time and pH of 6 for seed).

In summary, adsorption efficiency of the adsorbents in the optimization process were observed in the order of seed > bark > leaf. Even though the adsorption efficiency of leaf is also good for further study, it was observed that the water after adsorption process by leaf was so colorful and had bad odor that makes another waste for the environment. Therefore more studies regarding adsorption models and industrial wastewater were made for bark and seed adsorbents of *M. stenopetala.*

Investigation of adsorption kinetics

Adsorption kinetic study for nickel was studied by varying contact time around the optimum conditions obtained in the optimization adsorption procedures for bark and seed of *M. stenopetala* adsorbents and keeping the other parameters on their optimum conditions.
The kinetic models used in this study are explained as follow:

Pseudo-first-order model. $\log(q_e - q) = \log q_e - \frac{k_f}{2.303} t$ (1)

and: $q = \frac{(C_o - C_e)V}{m}$

where C_o and C_e are the initial and equilibrium adsorbate concentrations in solution (mg/L) respectively, V is volume of solution (L) and m is mass of dry adsorbent (g), q_e is the maximum adsorption amount of adsorbent in equilibrium at optimum condition (mg/g), k_f is rate constant of pseudo-first-order model (1/min) and t is the time [2, 5, 14].

Pseudo-second-order model. $\frac{t}{q} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t$ (2)

where k_s is rate constant of pseudo-second-order model (g/mg min). Initial sorption rate in mg/gmin, as $t \rightarrow 0$ can be defined as: $(\frac{dq}{dt})_{initial} = k_s q_e^2$

The initial sorption rate, the equilibrium adsorption capacity (q_e), and the pseudo-second-order rate constant k_s can be determined from plot of t/q versus t [2, 14].

Elovich model. $$q_t = \frac{In(\alpha\beta)}{\beta} + \frac{Int}{\beta} \quad (3)$$

where, α is the initial adsorption rate (mg/g min), β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg). A plot of q_t versus lnt gives a linear trace with a slope of (1/β) and an intercept of 1/β ln(αβ) [15-17].

Intraparticle diffusion model. $$\ln q = \ln K_{id} + a \ln t \quad (4)$$

where t is the contact time, in min, a is a dimensionless constant and K_{id} is the intraparticle diffusion rate constant, in min^{-1}. According to this model, the plot of "lnq" versus "lnt" should be linear if intraparticle diffusion is involved in the adsorption process [18]. The results of kinetic parameters determined using contact time variation of Ni(II) are given in Table 1.

From Table 1, the R^2 values suggest that the pseudo-second order ($R^2 \geq 0.98$) and pseudo first order ($R^2 \geq 0.87$) model kinetics provide a good model for the adsorption of nickel ion on bark and seed of *M. stenopetala* adsorbents. The experimental q_e values were closer to the calculated q_e values obtained from the second order kinetic plots compared to those of the first order kinetic plots which indicate better applicability of pseudo-second order than pseudo first order model kinetics. These suggest that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption that the rate limiting step of metal adsorption on the adsorbents may be chemical sorption or chemisorption [2, 3].

Table 1. Kinetic parameters determined using contact time variation of Ni(II).

Kinetic models	Parameters	Bark	Seed
Pseudo-first-order	k_f (1/min)	0.047	0.038
	q_{cal}.(mg/g)	2.828	0.0033
	R^2	0.9664	0.9228
Pseudo-second-order	K_s (g/mg.min.)	0.075	0.087
	q_e(mg/g)	0.560	0.753
	R^2	0.9952	0.9837
Elovich model	α (mg/g min.)	0.191	5.44×10^{-6}
	β (g/mg)	12.034	6.313
	R^2	0.8922	0.6202
Intraparticle diffusion	k_{id} (min^{-a})	0.1966	2.01536
	a	0.1806	0.17576
	R^2	0.8899	0.6254

Investigation of adsorption isotherms

In this study, adsorption isotherm models were evaluated using three parameters such as temperature variation, contact time variation and also using adsorbate concentration variation. The adsorption isotherm models used for this study are given as follow:

Langmuir isotherm. $\frac{C_e}{q} = \frac{C_e}{Q} + \frac{1}{bQ}$ (5)

"Q" and "b" in this case can be determined from the plot of C_e/q versus C_e. "Q" indicates the maximum sorption up on complete monolayer saturation. Higher value of "b" indicates the adsorbent has high affinity for the adsorbate and vice versa. The essential characteristics of the Langmuir isotherm can be expressed by: $R_L = \frac{1}{(1 + bC_o)}$

where C_o (mg/L) is the initial concentration of adsorbate, and b (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm which is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [2, 19].

Freundlich isotherm. $q = K_F C_e^{1/n}$ Or $\log q = \log K_F + \frac{1}{n} \log C_e$ (6)

where "n" is heterogeneity factor representing the deviation from linearity of adsorption, "K_F" indicates the adsorption capacity of adsorbent related to the bonding energy, mg/g$(L/mg)^{1/n}$. For 1/n less than unity, adsorption is the predominant process take place otherwise desorption becomes predominant [14, 19].

Tempkin isotherm. $q = B_1 InK_T + B_1 InC_e$ (7)

where $B_1 = \frac{RT}{b_T}$

Regression of *q* versus lnCe enables the determination of isotherm constants K_T and B_1. K_T is equilibrium binding constant (L/g) corresponding to maximum binding energy and constant B_1 is related to the heat of adsorption, R the gas constant (8.314 J/mol K), b_T is Temkin isotherm constant that indicate adsorption potential of adsorbent and T is the absolute temperature (K) [2, 5, 15-17].

Dubinin–Radushkevich (D–R) Isotherm. $Inq = InQ_m - K\varepsilon^2$ (8)

where *K* is a constant related to the adsorption energy, Q_m the theoretical saturation capacity, ε the Polanyi potential can be calculated by: $\varepsilon = RTIn(1 + \frac{1}{C_e})$

The plot of Inq versus ε^2 gives slope, *K* (mol^2/J^2) and the intercept yields the adsorption capacity, Q_m (mg g^{-1}). The mean free energy of adsorption (*E*) can be expressed by: $E = \frac{1}{\sqrt{2K}}$ It has been reported that physiosorption processes usually have adsorption energies < 40 kJ/mol and above this value sorption is of chemisorption mechanism. If the mean adsorption energy value is between 8 and 16 kJ/mol, the adsorption process follows chemical ion exchange and if "E" < 8 kJ/mol the sorption process is physical in nature [9, 20].

The results of isotherm parameters determined using concentration variation, temperature variation and contact time variation for nickel ion are given in Table 2, 3 and 4, respectively. From the isotherm parameter results (Table 2, 3 and 4), the Langmuir model yielded the best fit with R^2 value higher as compared to the other three models. The R^2 value is greater than 0.895 in Table 2 and also R^2 value is greater than 0.998 in both Table 3 and 4 using both adsorbents. The value of dimensionless constant separation factor (R_L) was obtained between 0 and 1 on the three parameters under study using both bark and seed adsorbents, this implies the adsorbate is favorably adsorbed by the adsorbents.

Table 2. Isotherm parameters determined using concentration variation of Ni(II).

Isotherm Models	Parameters	Bark	Seed
Langmuir isotherm	Q (mg/g)	0.9960	1.2834
	b (L/mg)	0.6903	1.6519
	R_L	0.046-0.127	0.010-0.015
	R^2	0.9359	0.9806
Freundlich isotherm	$K_{F,}$ mg/g(L/mg)$^{1/n}$	0.3750	0.833
	n	2.0325	4.6860
	R^2	0.8052	0.6678
Temkin isotherm	b_T	1184.38	11929.8
	$K_T \times 10^{-6}$ (L/g)	6.5715	56.0454
	R^2	0.8954	0.7147
Dubinin–Radushkevich isotherm	Q_m (mg/g)	0.7114	1.123
	$K \times 10^{-8}$(mol^2/J^2)	17.1630	11.64
	E (kJ/mol)	1.705	2.076
	R^2	0.9319	0.6051

Table 3. Isotherm parameters determined using temperature variation of Ni(II).

Isotherm Models	Parameters	Bark	Seed
Langmuir isotherm	Q (mg/g)	0.399	0.441
	b (L/mg)	6.180	15.75
	R_L	0.0082	0.0013
	R^2	0.9985	0.9998
Freundlich isotherm	$K_{F,}$ mg/g(L/mg)$^{1/n}$	0.4726	0.4730
	n	10.31	16.98
	R^2	0.9591	0.9806
Temkin isotherm	b_T	0.044	0.028
	$K_T \times 10^{-6}$ (L/g)	1.9×10^{-5}	3.82×10^{-8}
	R^2	0.9662	0.9825
Dubinin–Radushkevich isotherm	Q_m (mg/g)	0.423	0.455
	$K \times 10^{-8}$(mol^2/J^2)	261.82	98.73
	E (kJ/mol)	0.044	0.071
	R^2	0.8152	0.8798

Table 4. Isotherm parameters determined using contact time variation of Ni(II).

Isotherm Models	Parameters	Bark	Seed
Langmuir isotherm	Q (mg/g)	0.423	0.82
	b (L/mg)	9.48	3.23
	R_L	0.0053	0.006
	R^2	0.9995	0.9991
Freundlich isotherm	$K_{F,}$ mg/g(L/mg)$^{1/n}$	0.473	1.02
	n	12.87	11.63
	R^2	0.9771	0.9667
Temkin isotherm	b_T	70400	31568
	$K_T \times 10^{-6}$ (L/g)	1.808	2.29
	R^2	0.9804	0.9714
Dubinin–Radushkevich isotherm	Q_m (mg/g)	0.4379	1.156
	$K \times 10^{-8}$(mol^2/J^2)	2.32	9.00
	E (kJ/mol)	4.6	2.38
	R^2	0.8941	0.7701

The confirmation of the experimental data into Langmuir isotherm equation may be due to formation of monolayer adsorption on a uniform surface with a finite number of adsorption sites [9, 21, 22]. The applicability of the four isotherm models in Table 3 and 4 were consistently obtained within the decreasing order of: Langmuir > Temkin > Freundlich > Dubinin-Radushkevich isotherm model using bark and seed adsorbents.

Study on adsorption thermodynamics

In this study, the values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ were determined from classical Van't Hoff equation [23]:

$$\Delta G^0 = -RTInK_c \quad \text{and} \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{9}$$

$$InK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

where R is universal gas constant (8.314 J/mol K), T (K) is the absolute temperature and K_c is the single point or linear sorption distribution coefficient defined as: $K_c = C_o/C_e$ in which C_o and C_e are the initial adsorbate concentrations added to the solid phase adsorbent and equilibrium adsorbate concentrations remained in the liquid phase (mg/L), respectively. The results for adsorption thermodynamic parameters of Ni(II) are given in Table 5.

From the results given in Table 5, the values of ΔG^0 calculated are negative for the adsorption of metal ion onto the adsorbents at all temperatures which confirms the feasibility of the process and the spontaneous nature of the adsorption. The obtained $\Delta G°$ value of nickel was less than -10 kJ/mol which indicate physical adsorption as the predominant mechanism in the sorption process. The values of ΔH^0 obtained for Ni(II) was within the range of -22.981 to -41.936 kJ/mol using bark and seed adsorbents under the studied temperature range. A negative value of ΔH^0 implies that the adsorption phenomenon is exothermic and its magnitude less than 42 kJ/mol implies formation of physical adsorption. A negative value of ΔS^0 suggests that the adsorption process involves an associative mechanism rather than dissociative. Adsorption leads to order through the formation of an activated complex between adsorbate and adsorbent. Also negative value of ΔS^0 reflects that no significant change occur in the internal structures of the adsorbent during the adsorption process.

Table 5. Adsorption thermodynamic parameters of Ni(II).

Thermodynamic Parameter	Adsorbents	Temperature (K)				
		296.15	303.15	313.15	323.15	333.15
$\Delta G°$ (kJ/mol)	Bark	-8.263	-7.612	-6.684	-5.755	-4.826
	Seed	-9.172	-8.569	-7.709	-6.848	-5.988
$\Delta H°$ (kJ/mol)	Bark	-35.770				
	Seed	-34.653				
$\Delta S°$ (J/molK)	Bark	-92.884				
	Seed	-86.042				

Application of the developed method in real samples

In order to apply the method on industrial wastewater sample, characterization of the wastewater is important to determine the effect of interfering substances present. Therefore, the levels of some physicochemical characteristics of industrial wastewater samples were studied and the obtained results are given in Table 6.

Following the optimum conditions of six adsorption parameters obtained in synthetic wastewater, removal of Ni(II) was studied on the real wastewater. Since the pH of industrial wastewater sample is 7.8, the adsorption procedure was also maintained at this pH for check up and the results are given in Table 7.

The experimental studies showed that the bark and seed of *M. stenopetala* adsorbents could be used as an alternative, inexpensive and effective material to remove toxic Ni(II) ion from real wastewater. The results obtained are therefore very encouraging for the industrial application of the technique, which brings the concentration of Ni(II) below the industrial limit in waste water.

Table 6. Some physicochemical characteristics of tannery industrial wastewater.

Parameters	Values
Temperature	28 ± 2 °C
pH	7.8 ± 2
Salinity	6.4
Conductivity	10.07 ms/cm
Total dissolved solid	8,595 mg/L
Total solids	12,452 mg/L
Total suspended solids (TSS)	3,857 mg/L
Alkalinity	1,320 mg/L
Acidity	30 mg/L
Dissolved oxygen (DO)	5.6 mg/L
Chemical oxygen demand (COD)	292 mg/L
Sulfate	1,659.85 mg/L
Ni(II)	5.83 mg/L

Table 7. Adsorption studies on removal of Ni(II) from real wastewater.

Adsorbent	pH	C_o (mg/L)	C_e ± SD (mg/L)	% Adsorption
Bark	6	5.83	1.01 ± 0.027	82.68
	7.8	5.83	1.12 ± 0.021	80.79
Seed	6	5.83	0.86 ± 0.032	85.25
	7.8	5.83	0.97 ± 0.024	83.36

where C_o and C_e are initial and final adsorbate concentrations in solution respectively.

CONCLUSION

Optimum conditions of metal ion concentration, adsorbent dose, agitation speed, contact time, pH and temperature using leaf, bark and seed of *Moringa stenopetala* adsorbents on Ni(II) removal in synthetic wastewater were obtained. At optimum experimental conditions the percent adsorption of synthetic wastewater sample was found to be 94, 96 and 98 for leaf, bark and seed, respectively. From the adsorption models point of view the adsorption mechanism of nickel ion using bark and seed adsorbents was attributed to a physico-chemical adsorption process under the studied range of experimental parameters. The adsorption studies in industrial wastewater collected from Modjo Tannery Share Company reveal that for removal of Ni(II) 83% and 85% was found using bark and seed adsorbents of *M. stenopetala* tree, respectively. The method of adsorption developed in this study is cheap, fast and environmental friendly.

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