

Characterization of activated *Acacia nilotica* seed pods for adsorption of Nickel from aqueous solution

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Abstract The use of low-cost adsorbent has been investigated in the removal of nickel ions from aqueous solution. The adsorption of nickel is strongly dependent on various parameters such as pH, dosage, contact time and initial concentration of metal. The optimum pH for nickel removal is found to be 7.0. The removal of nickel ions increases with time and attains saturation in about 60–120 min. The experimental data were analyzed with various isotherms such as Freundlich, Langmuir Temkin and Dubinin–Radushkevich adsorption isotherm. The experimental data were fitted into the following kinetic models: Lagergren pseudo-first order, the chemisorption pseudo-second order, Elovich kinetic model, and the intraparticle diffusion model. It was observed that chemisorption pseudo-second-order kinetic model described the sorption process with high coefficients of determination better than any other kinetic models. The results indicate that the second-order model best describes adsorption kinetic data. The adsorbent was characterized; functional group was analyzed by Fourier transform infrared spectroscopy and surface morphology by scanning electron microscope, and energy dispersive X-ray diffraction were analysed.

Keywords Adsorption · *Acacia nilotica* · Nickel · Isotherms · Kinetics

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Introduction

Water pollution is one of the most serious environmental problems faced by modern society. Most of heavy metal ions are toxic to living organisms. These metal ions are non-degradable and are persistent in the environment. Therefore, the elimination of heavy metal ions from wastewater is important to protect public health (Zhao et al. 2011). Attention has to be paid to the health hazards presented by existence of heavy metals in the environment, because of their accumulation in living tissue through the food chain. The problems associated with metal ions discharged in industrial effluents are considerable, due to both their toxic and carcinogenic properties (Hlihor et al. 2010). Nickel is also a common toxic pollutant. Nickel concentration in wastewaters is generally in the range of 0.0085–17 mmol/L. However, the average concentration of Ni(II) in the effluent from the plating plants is in the range of 0.17–1.36 mmol/L (Srivastava et al. 2009). The presence of Ni(II) ions above critical levels may cause various types of acute and chronic disorder in human health, such as severe damage of lungs and kidney, gastrointestinal distress (e.g., nausea, vomiting, and diarrhea), pulmonary fibrosis and renal edema, and skin dermatitis (Borba et al. 2006). Ni(II) is widely used in silver refineries, electroplating, zinc base casting, and storage battery industries (Repo et al. 2010).

The applicability of various methods developed so far for the removal of Ni(II) from effluents should be critically reviewed, and more suitable methods need to be proposed. Classical techniques of heavy metal removal from solutions include the following processes: precipitation, electrolytic methods, ion exchange, evaporation, and adsorption (Alyuz and Veli 2009). These techniques are economically expensive and have disadvantages such as

incomplete metal removal, generation of toxic sludge, and other disposable waste products (Vinoda et al. 2010). This may be due to the high cost and lack of eco-friendliness of the technological processes. To bridge this gap, more research is needed to capitalize some other methods such as adsorption, biological and ion exchange processes over the conventional methods. Adsorption techniques, among others, using a number of organic, inorganic, natural, synthetic, activated, or modified model adsorbents, are the most widely employed procedures in the waste treatment studies, and low-cost alternatives or cheaper and effective adsorbents are still needed. Recently, potential adsorbents for heavy metal removal include the following: sugarcane bagasse pith (Anoop Krishnan et al. 2011), coconut husk, teak tree bark (Kehinde et al. 2009), palmyra palm fruit seeds (Kannan and Thambidurai 2009), exhausted olive cake (Elouear et al. 2008), agricultural waste (Umesh et al. 2008), Coconut leaves (Gowda et al. 2012), ion exchange resins (Alyuz and Veli 2009), bottom ash and de-oiled soya (Mittal et al. 2009), (Mittal et al. 2010), industrial wastes (Jain et al. 2003), fruit wastes, sugar industry wastes, seafood-processing wastes, wood-type materials, petroleum wastes, fertilizer wastes (Ali et al. 2012), bagasse fly ash (Gupta et al. 2003), etc. Activated carbon, among a large variety of adsorbents, is still by far the most important one in current use in the environmental pollution control due to its large surface area, high adsorption capacity, porous structure, selective adsorption, and high-purity standards (Ucer et al. 2006). In an effort to evolve a useful, eco-friendly, and economical process, the present study was undertaken. The present study includes the adsorption studies on Ni(II) using *Acacia nilotica* acid activated carbon. The efficiency of this adsorbent was studied, and maximum adsorption and lowest equilibrium time for this adsorbent was recorded.

This study was planned to evaluate an indigenous *Acacia Nilotica* as a potential adsorbent for removal of nickel as primary, binary, and ternary. Many parameters including pH, adsorption capacity by varying adsorbent dosage, initial concentration of metal ions, effect of binary system, adsorption isotherm, and adsorption kinetics were studied. These parameters could be very useful in the understanding of removal of nickel ions from aqueous solutions.

The research involves the removal of Ni(II) by modification of *Acacia Nilotica* with H_2SO_4 and investigation of batch mode experimental conditions, such as pH of solution, contact time, adsorbent dosage, and initial concentration, as it relates the adsorption of the metal to the adsorbent. It also involved the use of Freundlich, Langmuir, Temkin and D–R adsorption isotherm model to fit in the data. Kinetic study using Lagergren pseudo-first order, the chemisorption pseudo-second order, Elvoich, and intraparticle was also used to investigate the mechanism of adsorption.

This research was carried out on December 1, 2012 at A.S.L Pauls College of Engineering and Technology, Coimbatore, Tamilnadu.

Materials and methods

Preparation of adsorbent: chemical activation of the adsorbent

Acacia nilotica seed pods were collected from surrounding area of Coimbatore, Tamilnadu. The seed pods were cut into small pieces and air-dried. The sample was soaked in conc. H_2SO_4 for 24 h at room temperature. The resulting material (*Acacia Nilotica* on sulphuric activation-ANS) was kept in air oven at 150 °C for 5 h. The adsorbent was soaked in 2 % $NaHCO_3$ solution to remove any remaining acid and pH of carbon. The activated carbon reached pH 7.0. The rinsed adsorbent was kept in an oven at 120 °C for the removal of moisture and dried and finally stored in a tight plastic container. The treatment of the adsorbent with H_2SO_4 aids to oxidize the adhering organic material, removal of any debris or soluble bio-molecules that might interact with the metal ions during the sorption. This process is called chemical activation. Sulphuric acid activation is an effort to obtain high yield, high surface area and high pore size of activated carbon.

Preparation of stock solution

All chemicals used were analytical reagents grade (AR) and prepared in distilled water. Stock solutions of Ni(II) at 1,000 mg/L concentration were prepared by dissolving nickel sulphate hexahydrate ($NiSO_4 \cdot 6H_2O$) (Analar Grade chemicals) in double distilled water. From the stock solutions, the solutions of desired concentrations were prepared for the studies.

Characterization of the adsorbent

The surface morphology of ANS was identified using SEM (Jeol JSM—6390). FTIR (SHIMADZU, Japan, and IR Affinity⁻¹) was used to identify the different chemical functional groups present in the modified ANS. FTIR analyses were also used to determine the functional groups that are responsible for the metal binding with ANS. The analysis was carried out using KBr pellet with spectral range varying from 4,000 to 400 cm^{-1} . Wide-angle X-ray diffraction of ANS was analyzed using SHIMADZU (Model XRD-6000).

Batch adsorption experiments

Batch experiments include the following: effect of pH, time, metal concentration, adsorbent dosage, adsorption

isotherms, and the kinetic studies. Adsorption experiments for the kinetic study were conducted as follows: A series of bottles containing 0.2 g/L ANS and metal ion of concentration 100 mg/L were kept in a shaker at room temperature. The solution pH was adjusted to 7.0 with 1 M HCl and 1 M NaOH. After shaking in different time intervals, the samples were collected and analyzed for residual concentrations. Batch adsorption experiments for the effect of initial pH on the adsorption process were conducted by preparing a series of 50 mL solutions containing 0.2 g/L of ANS and a fixed metal ion concentration of 100 mg/L in a series of 250-mL Erlenmeyer flasks at different pH (2.0–12.0). pH adjustment was in the range of 2.0–12.0 with 1 M HCl or 1 M NaOH. At the end of the mixing, the pH was measured. The adsorbent was separated from suspensions by filtration through a Whatman filter paper. The filtrate was analyzed spectrophotometrically to determine Ni(II) content. Ni(II) concentration was determined using an indirect UV–visible spectrophotometric method based on the reaction of Ni(II) and KCN, DMG, and NH₃, which forms colored complex. The absorbance of the colored complex was measured in a double-beam spectrophotometer. All experiments were conducted in three replicates, and the relative error between duplicates was less than 5 %.

The percentage removal in the effect of adsorbent dosage varied from 0.2 to 1.0 g/L of ANS to a 50 mL of solution containing 100 mg/L of metal ion concentration. Adsorption isotherm studies were conducted by adding 0.2 g of ANS to a 50-mL solution containing various metal ion concentrations (25, 50, 75, 100, 125, 150, 175, and 200 mg/L). The value of percentage removal and amount adsorbed (q in mg/g) were calculated using the following relationships:

$$\text{Percentage removal} = 100(C_i - C_e)/C_i \quad (1)$$

$$\text{Amount adsorbed } (q) = (C_i - C_e)/m \quad (2)$$

where C_i and C_e are initial and final equilibrium concentrations of Ni(II) ions (ppm), respectively, and ' m ' is the mass of adsorbent in g/L. From the batch mode experiments, the effects of initial concentration and contact time were employed in testing the applicability of isotherms and kinetic equations, respectively.

Zero point charge

The pH at the potential of zero point charge of the carbon (pH_{ZPC}) was measured using solid addition method. The experiments were done in 250-mL flasks each containing 50 ml of different initial pH-NaNO₃ solutions, and 0.2 g of adsorbent ANZ was added. The pH values were adjusted using 0.1 M HCl and 0.1 M NaOH (Makeswari and Santhi

2013). After stabilization, the final pH was recorded. The graphs of final pH versus initial pH were used to determine the zero point charge of the activated carbon.

Adsorption isotherms and kinetics

Equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases. Three isotherms, Freundlich, Langmuir, Temkin and D–R isotherms, were employed to calculate the adsorption capacity. Adsorption kinetic study of Ni(II) was done by varying contact time around the optimum conditions obtained in the optimization adsorption procedures for ANS adsorbent and keeping the other parameters on their optimum conditions (pH, adsorbent dosage, initial metal ion concentration). The kinetics process were studied for contact times ranging between 5 and 120 min (pH = 7, dosage = 0.2 mg/L, metal ion 100 mg/L) by monitoring the percent removal of the heavy metals by the adsorbent. The data were then regressed against the Lagergren equation, which represents a first-order kinetic equation, and against a pseudo-second-order kinetic equation, Elovich, Ritchie's equation or intraparticle diffusion are tested with the experimental data.

Results and discussion

Characterization of the adsorbent

In order to observe the surface morphology (SEM & EDAX) of the adsorbent before and after adsorption, Ni(II) was shown in Fig. 1a, b. The surface functional groups of adsorbents were identified using Fourier transform infrared spectrophotometer. The FTIR spectra before and after adsorption of Ni(II) on ANS are shown in Fig. 2. The FTIR spectrum of ANS was used to identify functional groups present on the surface ANS that could be responsible for uptake of Ni(II) (ANNiS). The spectrum of the adsorbent was measured within the range of 4,000–600 cm⁻¹ wave number. The absorption peak around 3,468–3,749 cm⁻¹ could possibly be due to the presence of OH or NH₂ groups (Zvinowanda et al. 2009). The peaks observed at 2,499–1,983 cm⁻¹ can be assigned to stretching vibration of the C–H and C–C group. The absorption peaks at 1,629–1,506 are assigned to symmetric stretching vibration

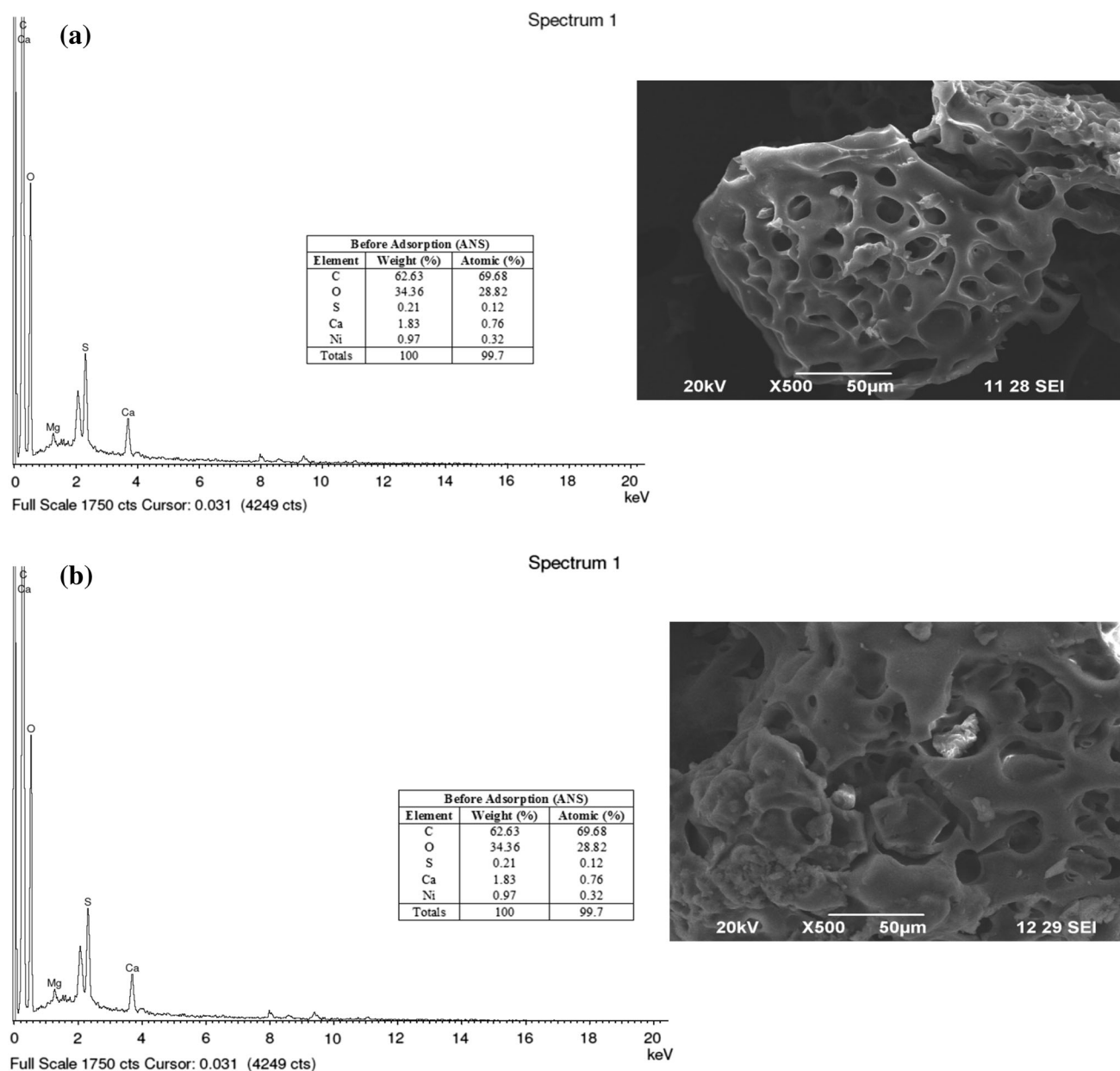


Fig. 1 EDAX & SEM analysis of **a** ANS (before adsorption), **b** ANS on Ni(II) (after adsorption of ANS on Ni(II))

of the NO_2 group (Djomgoue et al. 2012). The FTIR of adsorption of ANS is shown in Fig. 2. This spectrum has less number of peaks compared with the before adsorption of ANS. The prominent absorption peaks in the adsorption of Ni(II) are observed at 3,749, 3,450.77, 2,499, 1,983, and $1,629 \text{ cm}^{-1}$. Wide-angle X-ray diffraction θ of ANS and ANNiS was shown in Fig. 3.

Effect of pH on Ni(II) removal

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface

charge of the adsorbent, the degree of ionization, and specification of the adsorbate.

The batch equilibrium studied at 50 mg/L of Ni(II) concentration with different pH values ranging from 2.0 to 12.0 was carried out under 303 K. Fig. 1 shows that maximum percentage of Ni(II) adsorption on ANS was observed at pH 7. An increase in the adsorption occurred in the pH range of 2.0 to 7.0 and slightly decreased at higher (8.0–10.0) pH values. Adsorption of Ni(II) on the ANS reached its maximum at pH 7.0 (84 % removal) shown in Fig. 4. After pH 7.0, cloudy precipitates of Ni(II) were visible in solution and thus were inaccessible for Ni(II)

adsorption. At lower pH, ANS could be ascribed to the hydrogen ions competing with Ni(II) for adsorption site. At higher H⁺ concentration, the adsorbent surfaces become more positively charged, thus reducing the attraction between adsorbent and metal ions. Therefore, adsorption of Ni(II) at lower pH range was not investigated in the present study. At higher pH, the adsorbent surface takes more negative charges, thus attracting more Ni(II) ions.

However, it was also observed that the adsorption capacity of metal ions decreased with further increases in pH due to the formation of anionic hydroxide, which reduced the concentration of free Ni(II) ions.

Zero point charge

Point of zero charge of an adsorbent surface is the pH at which that surface has a net neutral charge. The surfaces of metal oxides are generally covered with hydroxyl groups that vary in form at different pH levels. The zero point charges of the ANS were determined by using solid addition method. pH_{ZPC} values of the solution were measured before and after soaking with potassium nitrate. The experiments were done in 250-ml flasks each containing 50 ml of different initial pH NaNO₃ solutions and 0.2 g of ANS. The pH values were adjusted using either 0.1 M HCl or 0.1 M NaOH solutions, and the final pH of the supernatant liquid was plotted against initial pH (pH_i). Intersection point from the graph at which pH is given as pH_{ZPC}. The pH_{ZPC} of ANS is determined as 6.03 as shown in Fig. 5.

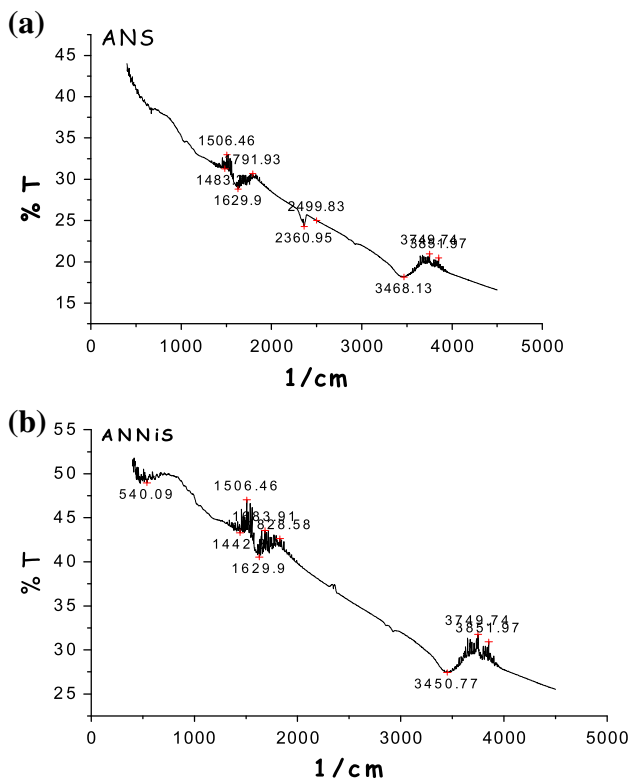


Fig. 2 FT-IR spectra—before and after adsorption of Ni(II) on ANS

Effect of agitation time on adsorption

The effect of contact time on Ni(II) removal was investigated at optimized adsorbent dose by varying the contact time (5–120 min), while other parameters were kept constant. Increase in percentage removal was observed with increase in contact time of adsorbent. Optimum time observed was 60 min. In adsorbent ANS, percentage removal was 57 and 78 for 5 and 60 min, respectively. There was no appreciable increase in percentage removal of Ni(II) after these optimum times. As shown in Fig. 6, the adsorption process took place in two stages. The first stage

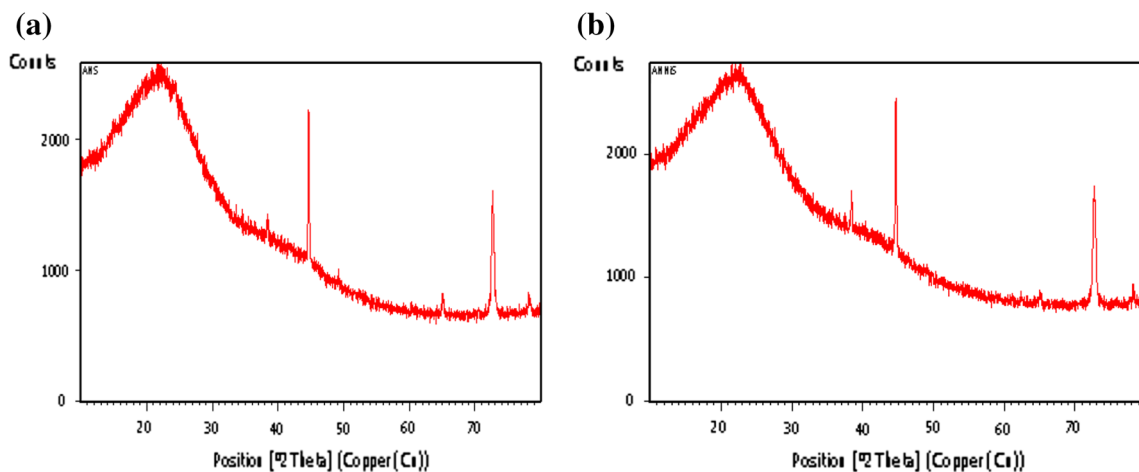


Fig. 3 X-RD spectra—before and after adsorption of Ni(II) on ANS

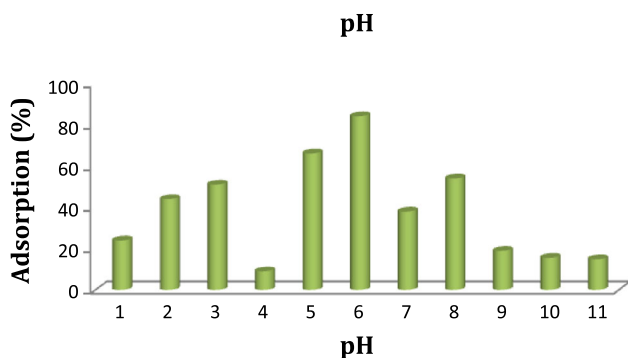


Fig. 4 Effect of pH (pH 2.0–10.0, initial concentration of Ni(II) is 100 mg/L, adsorbent dose 0.2 mg/L at 303 K)

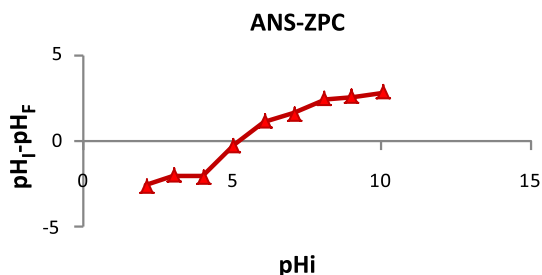


Fig. 5 Zero point charge of ANS

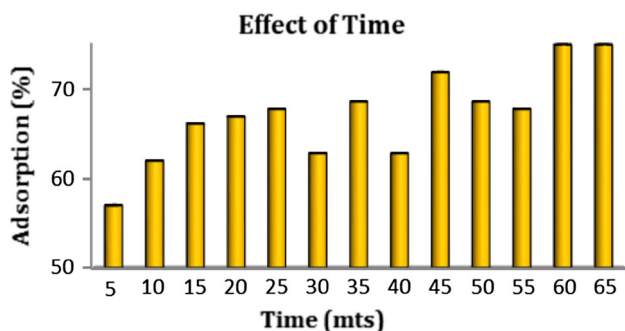


Fig. 6 Effect of agitation time (time 5–120 min, pH 7.0, initial concentration of Ni(II) is 100 mg/L, adsorbent dose 0.2 mg/L at 303 K)

was rapid, where about 68 % adsorption was completed within first 20 min. The second stage represented a slower progressive adsorption. The rapid initial adsorption may be attributed to the accumulation of metals on to the surface of adsorbent, due to its large surface area. With the progressive occupation of these sites, process became slower in the second stage. Moreover, the initially deposited metal ions penetrate into the interior of the sorbent through intraparticle diffusion, which was a slower process. The adsorption process attained equilibrium in 1 h. Based on the results of kinetics experiments, a time of 1 h was considered to be adequate for remaining experimentations. It may be

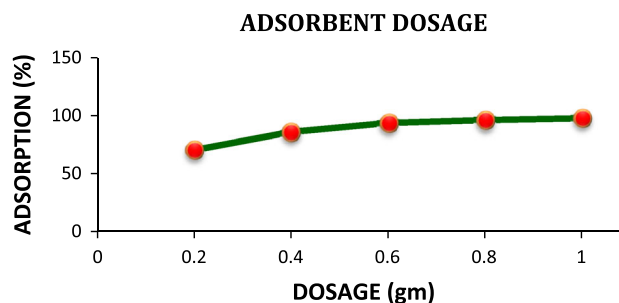


Fig. 7 Effect of adsorbent dosage: Concentration of Ni(II) is 100 mg/L, at pH 7.0, adsorbent dosage 0.2 to 1.0 mg/L at 303 K)

explained as initial adsorbent showed the fast adsorption, which gets slowed down later on, because initially large number of vacant surface sites may be available for adsorption, and after some time, the remaining vacant surface sites may be exhausted due to repulsive forces between the solute molecules of solid and bulk phase (Djougoue et al. 2012). As a result of the experimental studies, it is seen that high efficiency for nickel adsorption can be obtained at short time periods.

Effect of sorbent dose

The adsorbent dosage effect on the percent removal at equilibrium conditions was investigated. The dependence of Ni(II) adsorption was studied by varying the amount of adsorbents from 0.2 to 1.0 g, while keeping other parameters (pH = 7, initial metal concentration 100 mg/L and contact time 60 min) as constant. From Fig. 7, it can be observed that the removal efficiency of the adsorbent was generally improved by increasing its dosage. This is expected due to the fact that the higher the dose of adsorbents in the solution, the greater is the availability of exchangeable sites for the ions. Results showed that the maximum percentage removal of Ni(II) was about 97 % at the dosage of 1.0 g. This result also suggest that after a certain dose of adsorbent, the maximum adsorption sets in, and hence, the amount of metal ions adsorbed to the adsorbent due to increasing ANS surface area and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent.

Effect of initial metal ion concentration

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: The effect of adsorbate concentration on the removal of Ni(II) from aqueous solutions is shown in Fig. 8. Adsorbate concentrations were varied from 25 to 200 mg/L. The equilibrium concentration of Ni(II) increased with increasing adsorbate concentration, because of decreasing surface area per unit



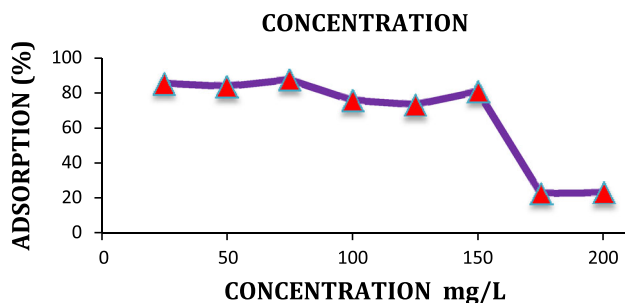


Fig. 8 Effect of initial concentration: concentration of Ni(II): 25–200 mg/L, at pH 7.0, adsorbent dose 0.2 mg/L at 303 K

adsorbent. At lower concentration, almost all the metal ions could interact with binding sites, facilitating maximum adsorption (88 %) at 75 mg/L of Ni(II) solution. At higher concentration (23 % at 200 mg/L), more Ni(II) ions are left unadsorbed in the solution due to saturation of adsorption sites.

Competitive adsorption in binary metal system

Effect of Cu(II) ions and Cr(VI) ions on adsorption of Ni(II) ions

From the results, it is indicated that the equilibrium uptake of Ni(II) ions decreased with increasing concentration of Cu(II) and Cr(VI) ions from 10 to 40 mg/L; in the single ion situation, the maximum uptake obtained at initial concentration of Ni(II) ions 100 mg/L at pH 7.0 was found to be 84 %, while the uptake obtained in the binary (Ni–Cu and Ni–Cr) metal solution at the same initial concentration of Ni(II) ions was found to be 89.23, 82.69, 76.08, and 53.12 % with Cu(II) ions and 93.10, 80.00, 79.31, and 74.19 % with Cr(VI) ions as shown in Fig. 9, when the binary metal ions concentration was 10, 20, 30, and 40 mg/L, respectively. The results suggested that in competitive adsorption of the binary mixture solution, the adsorption capacity of the primary heavy metal often dropped with the introduction of the secondary heavy metal. The total adsorption capacity was also found to decrease for the cases of binary adsorption. It is indicated that the functional groups on the surface of ANS had a relatively stronger affinity. It has been reported that the greater the atomic weight, electronegativity, electrode potential and ionic size, the greater will be the affinity for sorption. It is clear that the electronegativity is a dominant factor for adsorption (Makeswari and Santhi 2013).

Sorption isotherms

Heavy metal ion concentrations ranged from 25 to 200 mg/L with a fixed adsorbent dosage (0.2 g) and pH (7.0). As

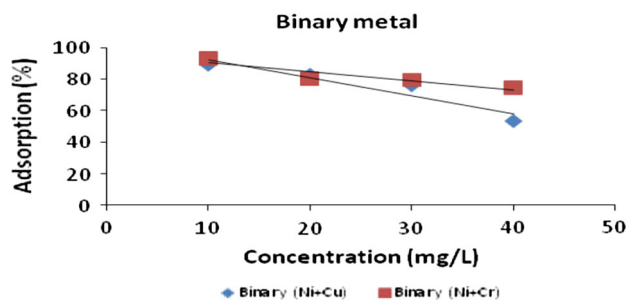


Fig. 9 Effect of binary metal adsorption of Ni(II) on ANS

metal concentrations increased, the removal efficiencies decreased for Ni(II) adsorption on adsorbent ANS. Thus, increasing the initial heavy metal concentration in the solution decreased the removal efficiency. It is likely that a given mass of adsorbent material has a finite number of adsorption sites and that as metal concentrations increase, these sites become saturated, that is, there is some metal concentration that produces the maximum adsorption for a given adsorbent dosage, because addition of more metal cannot increase adsorption because no more sites are available: All are occupied. Another cause may have been a progressive decrease in the proportion of covalent interactions and an increase in the proportion of electrostatic interactions at sites with a lower affinity for heavy metals as the initial heavy metal concentrations increased. The resulting data are applied to Freundlich, Langmuir, Temkin and D–R isotherms.

The Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface. The Freundlich isotherm is expressed as follows:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (3)$$

where Q_e is the amount of nickel ion adsorbed (mg/g), C_e is the equilibrium concentration of nickel ion in solution (mg/L), and K_f and n are constants, the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of $\log Q_e$ versus $\log C_e$ show that the adsorption of nickel ion obeys the Freundlich adsorption isotherm. The Freundlich adsorption isotherm was obtained by plotting C_e/q_e versus C_e for the adsorption of Ni(II) on ANS at the different concentrations. The K_f and ‘ n ’ values were found to be 2.7058 and 1.5121, respectively. The values of $1 < n < 10$ shows favorable adsorption of Ni(II).

The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as the monolayer adsorption on a surface contains a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm has an assumption that the adsorption occurs within adsorbent at specific homogeneous sites. The



Table 1 Isotherms and kinetic results

Langmuir (Q_m, b, R_L, R^2)		Freundlich (n, K_f, R^2)		Temkin (α, β, b, R^2)		D–R (K_L, Q_m)	
Q_m (mg/g)	10.4167	n	1.51217	α	0.173	K_L	1
b (L/mg)	0.14355	K_f (L/g)	2.7058	β	7.4512	Q_m (mg/g)	12422.9
R_L	0.06513	–	–	b (J/mol)	326.927	E (kJ/mol)	0.2302
R^2	0.9724	R^2	0.8795	R^2	0.9192	R^2	0.7513
Kinetic models		R^2	Rate constants and calculated values				
First order	0.641		K_1 (1/min) = 2.07×10^{-2}			Q_e (mg/g) = 5.0118	
Second order	0.981		K_2 (g/mg min) = 2.08×10^{-2}			Q_e (mg/g) = 18.45	
Intraparticle	0.6401		K_{diff} (mg/g min ^{1/2}) = 0.6462			C_e = 13.277	
Elovich	0.6103		A_E (mg g ⁻¹ min ⁻¹) = 0.6658			B_E (g mg ⁻¹) = 2676.6	

linear form of the Langmuir equation is expressed as follows:

$$C_e/q_e = 1/Q_m b + C_e/Q_m \quad (4)$$

where C_e is the equilibrium concentration of nickel ion in solution (mg/L), q_e is the amount of nickel ion adsorbed, and Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms. Q_m and b , respectively, were determined from the Langmuir plots and found to be 10.416 mg/g and 0.1435 mg/L. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy, and no diffusion of adsorbate in plane of the adsorbent surface. To confirm the favorability of the adsorption process, the separation factor (R_L) was determined. The essential characteristics of Langmuir isotherms were expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where b is the Langmuir constant and C_0 is the initial concentration of Ni(II). The parameter indicates the isotherm shapes as shown in Table 1. The R_L value is 0.0651. R_L values observed between 0 and 1 confirm that the ongoing adsorption of Ni(II) process is favorable. The mean values of the regression coefficient (R^2) are found to be 0.9724 and 0.8795 in Langmuir and Freundlich isotherm equations, respectively. The result shows that the experimental data best suit Langmuir isotherm than the Freundlich isotherm. The results are shown in the Table 1.

S. no	Separation factor (R_L)	Types of isotherm
1	$R_L > 1$	Unfavorable
2	$R_L = 1$	Linear
3	$0 < R_L < 1$	Favorable
4	$R_L > 0$	Irreversible

Temkin adsorption isotherm was developed assuming that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate interactions; adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The linear form of Temkin isotherm is expressed as follows:

$$q_e = RT \ln K_T + (RT/b_T) \ln C_e \quad (6)$$

where b_T is the Temkin constant related to heat of sorption (J/mol) and K_T is the Temkin isotherm constant (L/g). These constants were obtained from plotting q_e versus $\ln C_e$. The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The Temkin constants are calculated from the slope and intercepts of q_e versus $\ln C_e$. Correlation coefficient of R^2 value is 0.9192.

The Dubinin–Radushkevich (D–R) isotherm is valid at low concentration ranges and can be used to describe sorption on both homogeneous and heterogeneous surfaces. The D–R isotherm equation in the linear form is as follows (Al-Meshragi et al. 2008),

$$\ln q_e = \ln q_{m\max} - \beta \varepsilon^2 \quad (7)$$

where $q_{m\max}$ is the Dubinin–Radushkevich monolayer capacity (mg/g), β is a constant related to sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows, which is equal to

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (7.1)$$

$$E = 1/(2B)^{1/2} \quad (7.2)$$

where R is ideal gas constant (8.3145 J/mol K) and T is the absolute temperature (K). The saturation limit q_{\max} may represent the total specific micropore volume of the sorbent. The value of β is the activity coefficient related to mean sorption energy (mol^2/kJ^2). It is related to the adsorption mean free energy, E (kJ/mol), defined as the free energy change. Based on this energy of activation, we can predict whether an adsorption is physisorption or chemisorption. The adsorption energy (E) given by D–R model suggested the physical nature of the removal mechanism in most cases ($E < 8$ kJ/mol). If the energy of activation is < 8 kJ/mol, the adsorption is physisorption, and if the energy of activation is 8–16 kJ/mol, the adsorption is chemisorption in nature (Sivakumar and Palanisamy 2009). From this statement, adsorption of Ni(II) on ANS is physisorption in nature.

Sorption kinetics

One of the most important characteristics in evaluating adsorption efficiency is kinetics. In order to clarify the adsorption kinetics of Ni(II) ions onto ANS, the kinetic models, Lagergren equation, which represents a first-order kinetic equation and against a pseudo-second-order kinetic equation, Elovich, Ritchie's equation or intraparticle diffusion, were used. The experimental data are shown in Table 1. Lagergren equation (Moghadam et al. 2013):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (8)$$

where q_e is the amount of metal ions adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_t is the amount of metal ions (mg/g) adsorbed at specific time t , and K_1 (1/min) is the rate constant. The value of K_1 (1/min) was calculated from the slopes of the linear plot of $\log(q_e - q_t)$ versus time (t).

The equation applicable to experimental results generally differs from a true first-order equation in two ways, (Ho and McKAY 1998)

1. The parameter K_1 ($q_e - q_t$) does not represent the number of available sites.
2. The parameter $\log(q_e)$ is an adjustable parameter, and often it is found unequal to the intercept of a plot of $\log(q_e - q_t)$ against t , whereas in a true first order, $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t .

If the rate of the sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \quad (9)$$

where t is the contact time (min), and q_e (mg/g) and q_t (mg/g) are the amounts of the solute adsorbed at equilibrium at any time t . If pseudo-second order is applicable, the plot of t/q_t against t should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot, respectively. Table 1 shows the pseudo-second-order rate and the linear regression correlation coefficient value R^2 . Linear model gave a good fit to the experimental data. It was observed from the table that q_e values 18.45 mg/g, K_2 is 2.08×10^{-2} . Corresponding linear regression correlation coefficient R^2 is 0.981. The pseudo-second-order model is based on the assumption that the sorption of a metal by an adsorbent may involve a chemisorption which can be the rate controlling step.

The Elovich model equation is generally expressed as (Ho and McKay 2002)

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (10)$$

where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$). β is the desorption constant (g mg^{-1}) during any experiment. If the adsorption process fits the Elovich model, a plot of qt against $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The conformity between experimented data and the model-predicted values was expressed by the correlation coefficients (R^2 , value close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the adsorption kinetics.

The mechanism of sorption is either film diffusion controlled or particle diffusion controlled. Before adsorption takes place, several diffusion processes are known to affect the adsorption process that takes place. The sorbate will have to diffuse through the bulk solution into the film surrounding the adsorbent and then into macropores of the adsorbent. The intraparticle diffusion model is expressed as follows: (Ho 2006)

$$q_t = k_{id}(t)^{0.5} \quad (11)$$

where q_t is the amount of Ni(II) sorbed at a time t and k_{id} is the intraparticle diffusion rate constant ($\text{mg/g min}^{-0.5}$). The k_{id} values under different conditions were calculated from the slopes of the straight line portions of the respective plots. Higher values of the intraparticle rate constants (K_{id}) illustrate an enhancement in the rate of adsorption, whereas larger values illustrate a better adsorption mechanism. If intraparticle diffusion is rate limited, then plots of adsorbate uptake q_t versus $t^{0.5}$ would result in a linear relationship. Values of k_{id} were found to be $0.6462 \text{ mg/g min}^{0.5}$ with a R^2 value of 0.6401. If the plot of q_t versus $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting



step. However, the linear plot in our study did not pass through the origin. This indicates some degree of boundary layer control and also that the intraparticle diffusion was not the only rate-controlling step (Al-Souod 2012).

Conclusion

The objective of this paper is utilization of agricultural waste material *A. Nilotica* seed pods used as modified low-cost adsorbent for the removal of Ni(II) from aqueous solution. It has excellent adsorption capacities compared with non-conventional adsorbents. The monolayer (maximum) adsorption capacities (q_m) were found 10.41 mg for 0.2 g/L of ANS. Langmuir and Freundlich isotherms confirmed that the adsorption is favorable. D–R isotherm shows nature of adsorption is physisorption. Lagergren pseudo-second-order kinetic model was found to be the best-fitting kinetic model. Adsorption was found to increase on increasing pH, dosage, and decreasing concentration. A modified *A. Nilotica* seed pod is a low-cost, attractive, and alternative adsorbent.

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