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Role of *Azadirachta indica* (neem) biomass in the removal of Ni(II) from aqueous solution

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ABSTRACT

The removal of nickel(II) from aqueous solution by different *Azadirachta indica* (Neem) biomass; neem leaves fresh (NLF), neem leaves activated (NLA), leaves ash (LA), neem bark fresh (NBF) and neem bark activated (NBA) were used for adsorption studies. Neem leaves and neem bark were activated by giving heat treatment and with the use of concentrated sulphuric acid. Batch adsorption technique was carried out as a function of contact time, pH of the solution, biosorbent dose, and metal concentration. The adsorption efficiencies were found to be pH dependent, which increase by increasing the pH of the solution in the range from 2 to 7. The equilibrium time was attained after 2 h and maximum removal was achieved at an adsorbent loading weight of 2 g. The decrease in the removal was attained by increasing metal concentration. Maximum biosorption capacity for Ni(II) was 95% at the pH of 7. FTIR spectroscopy confirmed neem biomass interaction responsible for Ni(II) adsorption. The equilibrium adsorption data were interpreted by using both Langmuir and Freundlich isotherms. The isotherm values fitted well with correlation coefficient (R^2) values.

Keywords: *Azadirachta indica* (Neem); Ni(II); Langmuir isotherm; Freundlich isotherm

1. Introduction

Environmental pollution is prevalent in many industrialized and developing countries. It results in contamination of the land, water, sediment, and air with which all living organisms interact. Metal contamination in aquatic environments has received huge concern due to its toxicity, abundance, and persistence in the environment and subsequent accumulation in aquatic habitats. Among heavy metals, nickel is an essential trace element, which originates from industries such as non-ferrous metal, mineral processing, paint formulation, electroplating, porcelain enameling, copper sulphate manufacturing, and steam-electric power plants [1].

Due to the increasing awareness of toxic metals contamination to the environment, studies of metal accumulation from the viewpoint of metal removal from contaminated water have been performed. Toxic action associated with nickel is the inhibition of oxidative enzyme activity. Acute poisoning causes nausea, vomiting, chest pain, and rapid respiration. Dermatitis or nickel itch is common among workers involved in making nickel containing jewelry and those who use nickel-plated watches and nickel containing detergents. It is highly carcinogenic and high levels of nickel induce the reduction of nitrogen and impaired growth. The deficiency of nickel in animals results in impaired growth and an increased fetal death rate [2].

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There has been an interest in research into the production of cheaper adsorbents to replace costly wastewater treatment methods such as chemical precipitation, reverse osmosis, electro flotation, membrane separation, electrodialysis, solvent extraction, ion-exchange, etc. Most of the methods suffer from draw backs like high capital and operational cost and problem in disposal of the residual metal sludges [3]. For this reason, the use of biological system for removing toxic metals from low metal solution has the potential to achieve greater performance at lower cost. Biosorption is one of the best processes that diverse biological materials for metal uptake or binding. This method is advantageous and non-polluting and can be highly selective, more efficient, easy to operate and hence cost effective. Agricultural waste materials such as sago waste [4]; rice husk [5]; rice husk ash [6]; fruit peel [7,8]; tree leaves [9]; sawdust [10]; lignocellulosic fibers [11]; and modified plant wastes [12] have been studied to investigate their affectivities in binding heavy metal ions. The major advantages of biosorption over conventional treatment methods include, low cost; high efficiency; minimization of chemical or biological sludge no additional nutrient requirement; possibility of regeneration of biosorbent and metal recovery [13], this approach is attracting more and more scientist and engineers. Metal binding through adsorption during this process involves the functional group associated with proteins, lipids, carbohydrates, lignin, and other biopolymers present in the cell and cell wall.

The present work deals with a series of experiments to assess the potential of *Azadirachta indica* (neem) biomass for the removal of nickel(II) from aqueous solution. Neem biomass was selected because it is a well known in India as one of the most versatile medicinal plants having a wide spectrum of biological activity. Adsorbents were prepared by neem leaves, bark, and leaves ash and studies were carried out for Ni(II) removal under different operating conditions, namely pH, biosorbent dose, initial metal concentration, and contact time. The adsorption isotherm like Langmuir, Freundlich, separation factor, and correlation coefficient (R^2) were deduced from the adsorption measurement.

2. Materials and methods

2.1. Reagents

All the reagents used in this study were of analytical grade. $Ni(NO_3)_2 \times 6H_2O$, H_2SO_4, HCl, and NaOH were procured from S.D. Fine-chem Ltd., and atomic absorption spectrophotometer stock standard solution of 1,000 ppm nickel was purchased from Merck.

2.2. *Azadirachta indica* biomass

In the current study, three different parts of *A. indica* (neem) biomass were selected, which include leaves, bark, and LA. Neem biomass used in this work was collected from Jamia Millia Islamia, New Delhi, India; it was washed with double-distilled water (DDW) repeatedly to remove dust and soluble impurities, dried at 60°C for 72 h and ground to 40–45 mesh BSS screens in a mechanical grinder. The collected powder was washed with DDW to avoid the release of color in the aqueous solution during adsorption. The neem leaves and neem bark was activated by 0.1 M H_2SO_4 for 24 h and then they were washed with DDW until the pH of the adsorbents reached 5. Finally, they were air dried and used as final adsorbents. Leaves ash was prepared by heating 40–45 mesh size grounded neem leaves at 100°C to reach the constant weight and by burning this in muffle furnace at 550°C for 30 min [14]. These five adsorbents were stored in airtight plastic bags for further experiments. The ultimate and proximate analysis of all the five adsorbents was also carried out. The detailed characteristics are shown in Table 1.

2.3. Ni(II) solutions

A 1,000 ppm standard stock solution of Ni(II) was prepared from $Ni(NO_3)_2 \times 6H_2O$ in deionized distilled water, and the concentration range of Ni(II) varied from 25 to 100 ppm was prepared by dilution of the stock solution with deionized distilled water. Glassware used were immersed in 10% (v/v) HNO_3 overnight and washed thoroughly with deionized distilled water.

2.4. Determination of residual Ni(II) content in the solution

Flame atomic absorption spectrophotometer (FAAS), using PerkinElmer AAnalyst 3100 atomic absorption spectrophotometer equipped with an air-acetylene burner having 15 mA hollow cathode lamp

Table 1
Characteristics of *Azadirachta indica* (neem) biomass

Characteristics	NLF	NLA	LA	NBF	NBA
Bulk Density (g/cm^3)	0.286	0.226	0.438	0.396	0.34
Moisture content (%)	9.8	12.2	9.6	11.4	10.7
Ash content (%)	19	19.7	24.3	18.2	20.6
Volatile matter (%)	68.8	63.6	60.4	61.2	65.7
Carbon (%)	47.35	45.73	48.89	38.69	47.23
Hydrogen (%)	7.76	7.15	4.79	5.77	7.22
Nitrogen (%)	2.79	3.05	1.11	0.19	0.76
Oxygen (%)	42.1	44.07	45.21	55.35	44.79

at 232 nm wavelength, analyzed the residual Ni(II) in the solution before and after treatment.

2.5. Batch biosorption studies

In the batch biosorption experiment, 1 g of each adsorbent (40–45 mesh size) was placed in 250 ml plugged conical flask separately. For each experiment, 100 ml of Ni(II) standard solution having 100 ppm initial concentration was used. The pH was adjusted to 5 using 0.1 M HCl and 0.1 M NaOH solutions. These flasks were kept on a rotary shaker at 25 ± 1°C with 150 rpm up to 120 min. Samples were withdrawn at regular time intervals of 10 min (0–120 min) and the solutions were separated from the biomass through centrifuge at 4,000 rpm for 15 min. The preface experiment was performed at 25°C using an initial 100 ppm Ni(II) solution at pH 5 and 150 rpm for screening studies and then conditions were varied in order to see the maximum metal uptake by changing the pH, metal concentration, and biomass weight.

2.6. Metal uptake

The amount of metal ion adsorbed per gram of biomass of Ni(II) was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{1000m}. \tag{1}$$

The efficiency or percentage removal of metal ion of sorbents was calculated by using the following equation:

$$E = \frac{C_0 - C_e}{C_0} \times 100. \tag{2}$$

2.7. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to detect vibration frequency changes in the neem biomass. The spectrum was collected by PU420, JASCO spectrometer in the range 400–4,000 cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. Spectra were plotted using the same scale on the absorbance axis.

3. Results and discussion

3.1. Effect of pH

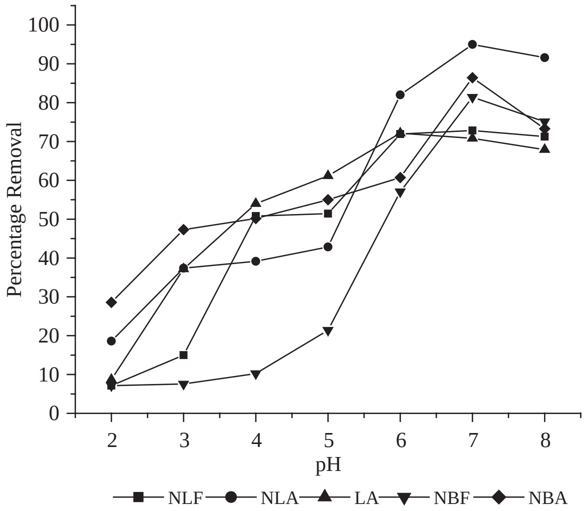

Fig. 1. Effect of pH on biosorption of Ni(II) by different neem biomass.

pH is an important parameter on biosorption of metal ions on biomass from the solution, as pH affects the solubility of metal ions and concentration of the functional groups of the biomass. The results obtained by varying the pH of metal solution from 2 to 8 are shown in Fig. 1, which shows the variation in biosorption in terms of the metal ion removal percentage. Minimum Ni(II) removal was recorded at pH of 2. It is due to the presence of abundant H$^+$ ions in the solution that competes with the metal ion for the adsorption site of the biomass as a consequence of the repulsive forces resulting in lower removal efficiency. The adsorption percentage of free Ni(II) ion increases with the increase in pH and attained maximum value in the pH range of 6–7. This increase in the adsorption can be justified on the basis of reduction of H$^+$ ion concentration in the solution resulting in decreased repulsive forces. At pH 7, the binding site is free from the H$^+$ ion that was competing with Ni(II) ion. The adsorption decrease at pH greater than 7 is probably due to negatively charged by adsorbing hydroxyl ions on surface or by ionization of very weak acidic functional groups of the adsorbents, or both [15]. A repulsive force may develop between the negatively charged surface and the anions. This results in decreased percentage metal removal at higher pH. This can also be explained on the basis of functional groups present. FTIR analysis has suggested the presence of aromatic structures, nonaromatic double bonds, –OH, C–O, C=O, –COO gps in the neem biomass. At pH 6–7, the ionic state of ligands of functional groups, which are mostly the chemical structures of the surface cell walls of the neem, would promote a reaction with metal ions. This reaction would occur through electrostatic attraction between positively charged metal cations and negatively charged binding sites on the biomass. As the pH is

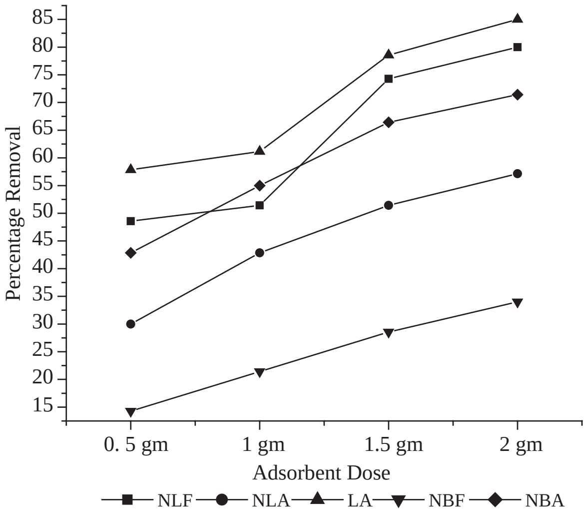

Fig. 2. Effect of neem biosorbent dose on the removal of Ni (II).

increased, the measured surface charge on the biomass would become more positive, leading to a weakening of the electrostatic interaction of metal ions with neem biomass. The decrease in the metal removal in basic medium can be accounted for the metal precipitation.

3.2. Effect of biosorbent dose

Biosorbent dose seemed to have a great influence in biosorption process. It determines the sorbent–sorbate equilibrium of the system. The effect of biosorbent dosage on the adsorption of Ni(II) was studied by varying the amount of biomass from 0.5 to 2 g/100 ml, while keeping other parameters, namely pH, initial metal concentration, and contact time, constant. It is clear from Fig. 2 that as the amount of biosorbent increases, the percentage of the removal of Ni(II) also increases. With increasing adsorbent dosage more surface area is available for adsorption due to increase in active sites on the adsorbent. This increased amount of biosorbent caused the sorbent capacity, q_e, to reduce. The drop in adsorption capacity is due to the sites remaining unsaturated during the adsorption process.

3.3. Effect of initial metal concentration

Ni(II) biosorption is significantly influenced by the initial concentration of Ni(II) in aqueous solutions. The result obtained by increasing the initial metal ion concentration from 25 to 100 ppm reveals that there is a decrease in percentage removal due to diminishing loading capacity of biosorbent (Fig. 3). As the metal ion/adsorption ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency.

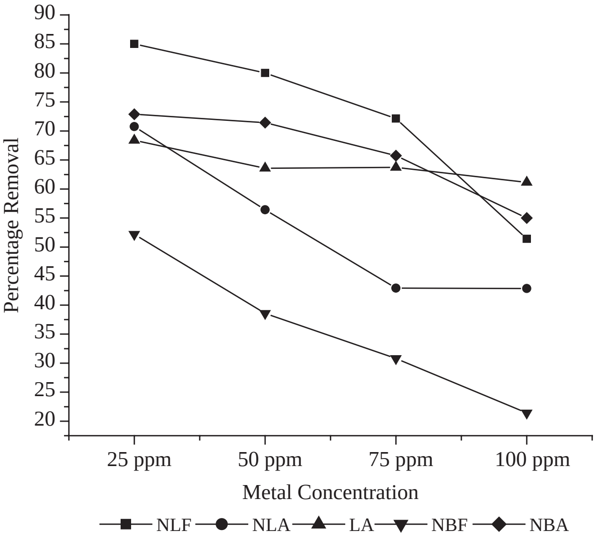

Fig. 3. Effect of initial concentration of Ni(II) on their removal by the neem biomass.

3.4. Effect of contact time

The effect of contact time was studied for removal of Ni(II) from the solution containing 100 ppm of Ni(II) at 25 ± 1°C, pH 5, and 1 g biosorbent. A gradual increase in the extent of adsorption was observed when the agitation time was varied from 10 to 120 min at 10 min interval in each case. In spite of some differences between the five biosorbents, the results reveal that their behaviors are rather similar toward Ni(II) ions, that is, the adsorption capacity increases with time (Fig. 4). In the beginning under the chosen conditions, the adsorption was quick. Then, the process gradually slows down and attains maximum around 90 min. beyond this time; the total capacity of adsorption does not change indicating that all the active sites were saturated.

3.5. Fourier transform infrared studies

Because the strength of the adsorption is proportional to the concentration, FTIR was used for some quantitative analysis. In Figs. 5(a)–(e), FTIR spectra of fresh neem leaves, there is a strong band at 3,423 cm^{-1} representing the –OH stretching. The band at 2,924 and 2,857 cm^{-1} were assigned to C–H stretches of methylene groups on the surface and chelates H-bridges. The bands at 1,729 and 1,644 cm^{-1} indicates the presence of C=O stretching and C=C stretches (aromatic) whereas at 1,447 cm^{-1} band due to CH_2 bending was observed. Small band observed at 1,320 cm^{-1} was due to OH bending. Bands at 1,250 and 1,037 cm^{-1} in the FTIR spectrum of fresh neem leaves can be due to C–O stretching.

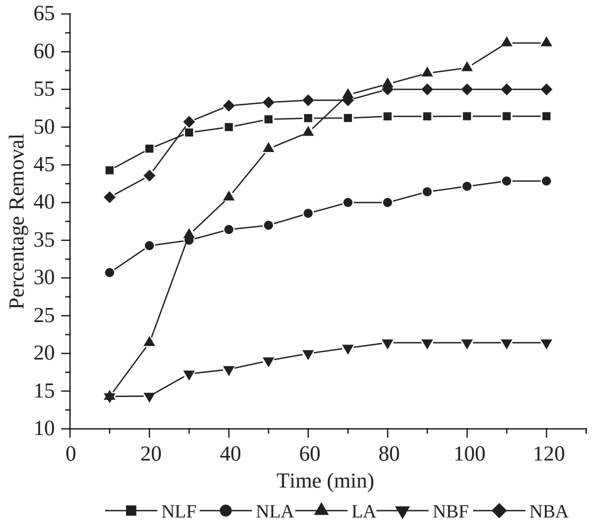

Fig. 4. Effect of contact time on the removal of Ni(II) by neem biomass.

FTIR spectrum of acid-treated neem leaves (activated) indicates that the main functional groups of fresh neem leaves remain unchanged after acid treatment. There is a slight shift in the values with the additional band at 1,159 cm^{-1}, which may be due to C–O–C stretching.

NBF shows the decline in the number of bands than the leaves. Band at 3,411 cm^{-1} is because of –OH stretching. The appearance of band at 2,925 cm^{-1} indicates the presence of –CH$_2$ stretching. C=C stretching band has shifted from 1,644 to 1,621 cm^{-1} from leaves to bark. There was a single band for C–O stretching at 1,259 cm^{-1}.

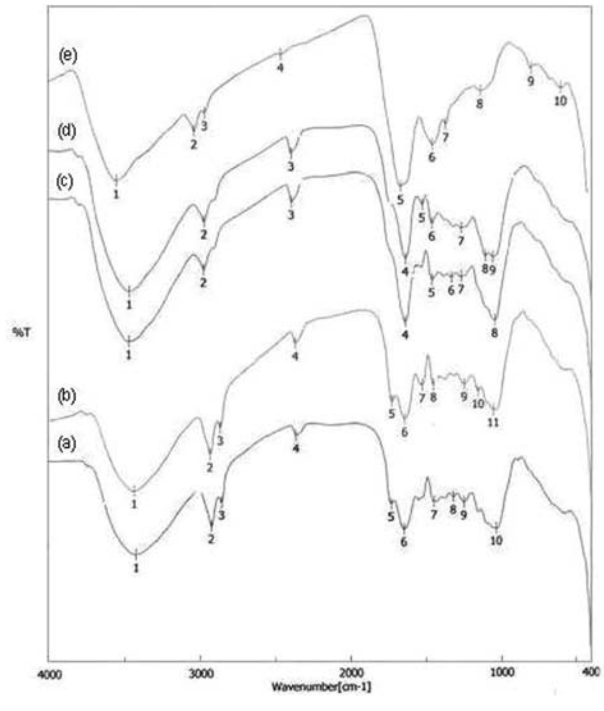

Fig. 5. FTIR Spectrum (a) NLF (b) NLA (c) NBF (d) NBA (e) LA.

In activated neem bark, two peaks appeared for C–O stretching at 1,105 and 1,057 cm^{-1}. The shift of –CH$_2$ band was observed in the same way while the rest remains unchanged for fresh neem bark.

An FTIR spectrum of LA also follows the same trend as for fresh neem leaves with the variation in few bands. There was clear band shift of C=C and CH$_2$ bending from 1,644 to 1,604 cm^{-1} and 1,454 to 1,409 cm^{-1}, respectively. 1,200–1,100 cm^{-1} band of C–O stretches has disappeared but there was an additional band at 776 and 587 cm^{-1} due to CH bending and deformation, respectively.

FTIR spectra indicate the presence of ionizable functional groups; their ionization leaves vacant sites that can be replaced by metal ions. This gives an indication that these materials could be used as adsorbents for the removal of heavy metals.

3.6. Adsorption isotherm

Heavy metal adsorption data are usually described, analyzed, and modeled using adsorption isotherms, which related to the metal uptake per unit of adsorbent and equilibrium metal concentration of the bulk phase. There are several isotherm models such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Brunaur, Emmett, Teller (BET) models available in literature [16]. In this current study, only the Langmuir and Freundlich isotherm models were examined [17,18] using initial metal ion concentration between 25 and 100 mg/l. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

3.6.1. Langmuir isotherm

The Langmuir adsorption isotherm is interpreted in Eq. (3) as:

$$q_e = \frac{q_m b C_e}{1+bC_e}. \tag{3}$$

The Langmuir isotherm parameters can be determined from a linearized form of equation represented as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right)C_e. \tag{4}$$

The adsorption isotherm corresponds to the relationship between the mass of the solute adsorbed per unit

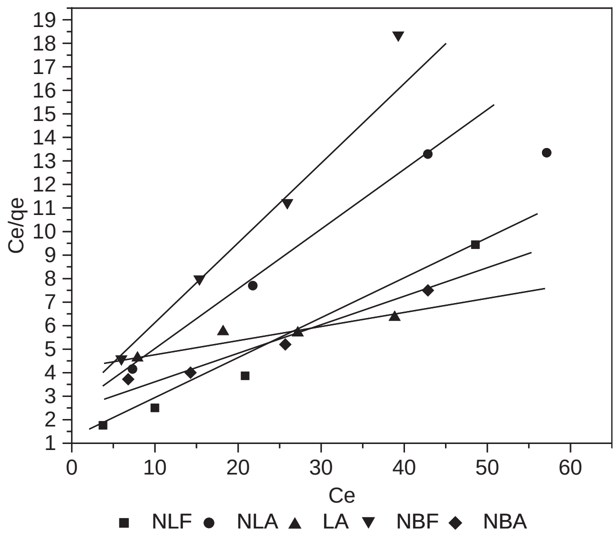

Fig. 6. Langmuir isotherm model of Ni(II) onto neem biomass.

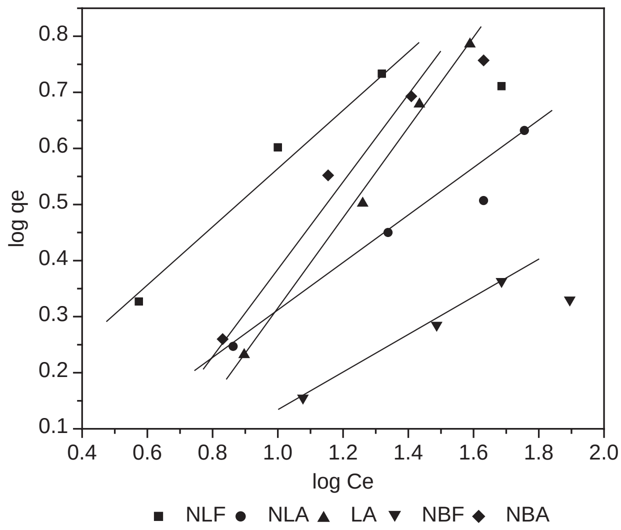

Fig. 7. Freundlich isotherm model of Ni(II) onto neem biosorbent.

mass of adsorbent q_e and the solute concentration for the solution at equilibrium $C_{e.}$ Plots of C_e/q_e against C_e should be linear if the Langmuir equation is obeyed by the adsorption equilibrium (Fig. 6). The corresponding calculated Langmuir constants, q_m, b with correlation coefficients (R^2) are given in Table 2.

3.6.2. Freundlich isotherm

The Freundlich isotherm is the earliest known relationship describing the sorption equation in aqueous system and is represented below:

$$q_e = K_f C_e^{1/n}. \tag{5}$$

The Freundlich equation is modified in logarithmic form as

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log K_f. \tag{6}$$

The corresponding linear plots of log q_e against log C_e (which indicate that the adsorption of the nickel also follows the Freundlich isotherm) are omitted here too (Fig. 7). The values of Freundlich constants, K_f, n with correlation coefficient (R^2) are given in Table 3. The values of $1/n$ less than 1 (n between 1 and 10) represent a favorable adsorption.

3.6.3. Separation factor (R_L)

The shape of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is represented as:

$$R_L = \frac{1}{1 + bC_e}. \tag{7}$$

The magnitude of R_L gives an idea about the nature of adsorption equilibrium: favorable ($0< R_L<1$); Unfavorable ($R_L>1$); Linear ($R_L=1$); and irreversible ($R_L=0$). The dimensionless parameter, R_L, for neem biomass were noted between 0.0534 and 0.7285 ($0< R_L<1$) consistent with in the requirement for a favorable adsorption process.

Table 2
Langmuir isotherm parameters

Biosorbent	Linear regression equation	q_m (mg/g)	b(l/mg)	R^2
NLF	Y = 0.17x + 0.96	5.8997	0.1770	0.9872
NLA	Y = 3.5x + 0.19	5.1813	0.0551	0.9302
LA	Y = 0.06x + 4.19	16	0.0149	0.8632
NBF	Y = 0.39x + 4.48	2.5595	0.0872	0.9832
NBA	Y = 0.12x + 2.57	8.3263	0.0466	0.9653

Table 3
Freundlich isotherm parameters

Biosorbent	Linear regression equation	K_f (l/mg)	1/n	R^2
NLF	Y = 0.32x + 0.35	2.2331	0.3214	0.8168
NLA	Y = 0.23x + 0.28	1.9262	0.2270	0.9502
LA	Y = 0.3x + 0.32	2.0975	0.2976	0.9962
NBF	Y = 0.12x + 0.15	1.4171	0.1185	0.8747
NBA	Y = 0.3x + 0.33	2.1439	0.3049	0.9289

4. Comparison of the present study with literature

Table 4 shows various adsorbents previously studied for Ni(II) removal. Although the data collected in this table may or may not represents equivalent or optimized conditions or with various nickel removal mechanisms in each case, it still provides a useful comparison in decision of selection of suitable biosorbent. The percentage removal of nickel by neem biomass in this study is comparable with these data. Indeed nickel removal by neem biomass in this study was significantly higher than most of the selected biomass.

5. Conclusion

In this study adsorption of Ni(II) ion on different neem biomass has been investigated. Adsorption of Ni(II) was found dependent on initial concentration of metal ion, pH, biosorbent dosage, and agitation time. NLA was the most effective for which the removal reached 95% at concentration of 100 ppm at pH of 7. Increase in biosorbent dose and contact time up to 2 h favor the adsorption of Ni(II), whereas increase in the metal ion concentration does not favor the adsorption. This is because removal percentage decreases with the increase in metal ion concentration. Langmuir and Freundlich isotherm models in the examined concentration range satisfactorily explain the equilibrium adsorption data. The Langmuir isotherm is followed better for NLF, NBF and NBA with R^2 values 0.9872, 0.9832, and 0.9653, respectively. Freundlich isotherm is fitted well for NLA and LA with R^2 0.9502 and 0.9962, respectively. The calculated value of dimensionless separation factor (R_L) confirms favorable Langmuir adsorption isotherm for Ni(II). FTIR spectroscopic analysis describes well the metal uptake by functional groups in the biomass. Based on the results of the present study and due to easy

Table 4
Summary of work done by various researchers using variety of agricultural waste materials for the removal of Nickel

Adsorbent used	Metal ion	Results	Ref.
Hazelnut shell activated carbon	Ni (II)	Effective removal	[19]
Casia fistula biomass	Ni (II)	100%	[20]
Maple saw dust	Ni (II)	75%	[21]
Sugarcane bagasse	Ni (II)	>80%	[22]
Tea waste	Ni (II)	86%	[23]
Defatted rice bran, chemically treated soybean & cottonseed hulls	Ni (II), Zn (II), Cu (II)	57%, 87%	[24]
Waste tea leaves	Ni (II), Pb (II), Fe (II), Zn (II)	92%, 84%, 73%	[25]
Saw dust of oak and black locust hard wood (modified & unmodified)	Ni (II), Cu (II), Zn (II)	70–90%	[26]
Dye loaded groundnut shells and saw Dust	Ni (II), Zn (II), Fe (II)	>70%	[27]
Coir fiber chemically modified with hydrogen peroxide	Ni (II), Cu (II), Zn (II)	Up to 90%	[28]
Modified & unmodified kenaf core, kenaf bast, sugarcane bagasse, cotton, coconut coir, spruce	Ni (II), Cu (II), Zn (II)	Up to 88%	[29]
Agro waste of black gram husk	Ni (II), Pb (II), Cd (II), Cu (II), Zn (II)	Up to 93%	[30]

availability and high efficiency for removal of Ni(II), it is concluded that the NLA are an ideal adsorbent for the removal of Ni(II) from aqueous solutions. Thus, neem biomass can be effectively used for the removal of Ni(II) ion from aqueous solution.

Notation

R^2	Correlation coefficient
q_e	Amount adsorbed per unit mass of adsorbent
C_0	Initial metal ion concentration
C_e	Final metal ion concentration
V	Volume of the reaction mixture
m	*Weight* of biomass in the reaction mixture
E	Efficiency or percentage removal of metal ion of sorbents
q_m	Adsorption capacity for Langmuir adsorption isotherm
b	Langmuir constants
K_f	Adsorption capacity for Freundlich adsorption isotherm
n	Freundlich intensity constant
R_L	Separation factor or equilibrium parameter

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