International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Neem Leaf Utilization for Copper and Zinc Ions Removal from Aqueous Solution

Reena Malik [1] Suman lata[2] Sushila Singhal[3]

[1]Department of Chemistry, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Haryana, India

2Department of Chemistry, Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Haryana, India

[3]Department of Chemistry, Desh Bandhu College, Delhi University, Delhi, India

Abstract: ***An adsorbent was developed from mature leaves of the Neem (Azadirachta indica) tree for removing copper and zinc from water. Adsorption was carried out in a batch process with several different concentrations of copper and zinc by varying pH. The uptake of metal was very fast initially, but gradually slowed down indicating penetration into the interior of the adsorbent particles. The data showed that optimum pH for efficient biosorption of copper and zinc by Neem leaves is5 and 4. Due to its outstanding zinc uptake capacity, the Neem tree was proved to be an excellent biomaterial for accumulating zinc from aqueous solutions.***

Keywords: Biosorption; Neem; Zinc; Waste water; Kinetics;Heavy metals Gibbs free energy

1. Introduction

In recent years, the development of biocomposites from biodegradable polymers and natural fibers have attracted great interests in the chemical science, because they could allow complete degradation in soil or by composting process and do not emit any toxic or noxious components[1-10]. A huge number of biodegradable polymers have been synthesized chemically or by microorganism and plants [11] Because of environmental pollution problems caused by using synthetic polymers based on petrochemicals [12], the development of environment Friendly polymeric material has attracted excessive interest [13]. Depending on the origin, different categories of biodegradable polymers have been proposed. To list a few, there are agro polymers, plant abstracted polymers(neem leaf aloe vera), polymers obtained by microbial production, for example, polyhydroxy alkanoates, and chemically synthesized polymers from monomers derived from agroresources (e.g., polylactic acid). Chemically synthesized polymers from monomers obtained commercially by chemical synthesis. Among these, starch is potentially useful material for biodegradable material because of its natural abundance and low cost [14,15]. Heavy metals are metallic elements that are present in both natural and contaminated environments. In natural environments, they occur at low concentrations. However at high concentrations as is the case in contaminated environments, they result in public health impacts. The elements that are of concern include lead, mercury, cadmium ,arsenic, chromium, zinc, nickel and copper. Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries, various consumer products and from burning of waste containing these elements. On release to the air, the elements travel for large distances and are deposited onto the soil, vegetation and water depending on their density. Once deposited, these metals are not degraded and persist in the environment for many years poisoning humans through inhalation, ingestion and skin absorption. Recent studies have shown that heavy metals can be removed using plantmaterials such as palm pressed fibers and coconut husk (Tan *et al*., 1993), water fern: *Azolla filiculoidis* (Zhao and Duncan, 1997), peat moss (Gosset *et al*., 2002), lignocellulosic substrate extracted from wheat bran (Dupont *et al*., 2003), *Rhizopus nigricans* (Bai and Abraham, 2001), cork and yohimbe bark wastes (Villaescusa *etal*.,2000), and leaves of indigenous biomaterials, *Tridax procumbens* (Freeland *et al*., 1974). Apart from the plant based materials, chemical modification of various adsorbents, phenol formaldehyde cationic matrices (Singanan *et al*., 2006), polyethylonamide modified wood (Swamiappan and Krishnamoorthy, 1984), sulphur containing modified silica gels(Freeland *et al*., 1974) and commercial activated charcoals are also employed (Verwilghen*et al*., 2004). The increasing awareness of the environmentalconsequences arising from heavy metal contamination of the aquatic environment has ledto the demand for the treatment of industrial wastewater before discharge into the aquaticenvironment (Fostner and Whittmann, 1979) A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion–exchange . Most of these methods suffer with high capital and regenerationcosts of the materials[16]. Therefore, there is currently a need for new, innovative and costeffective methods for the removal of toxic substances from wastewaters. Bio-sorption is aneffective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters.

The Neem tree is noted for its drought resistance. Normally it thrives in areas withsub-arid to sub-humid conditions, with an annual rainfall between 400 and 1200 mm. It can grow in regions with an annual rainfall below 400 mm, but in such cases it depends largely on ground water levels. Neem can grow in many different types of soil, but it thrives best on well drained deep and sandy soils. It is a typical tropical to subtropical tree and exists at annual mean temperatures between 21-32°C. It can tolerate high to very high temperatures and doesnot tolerate temperature below 4°C.Neem is a life giving tree, especially for the dry coastal, southern districts. It is one ofthe very few shade-giving trees that thrive in the drought prone areas. The trees are not at all delicate about the water quality and thrive on the merest trickle of water, whatever the quality. In Tamil Nadu it is very common to see neem trees used for shade lining the streets or in most people's back yards. In very dry areas like Sivakasi, the trees are planted in large tracts of land, in whose shade fireworks factories function. The aim of this work is to study the removal of toxic heavy metal ions by Neem leaves from synthetic waste water and to offer this biosorbent as local replacement for existing commercial adsorbent materials.

2. Material and Method

2.1 Preparation of Neem leaves

The Neem leaves were dried for a period of three days. The Neem leaves were cleaned with distilled water and dried at room temperature. The leaves were grounded with the grinding mill. The ground Neem leaves was sieved and was of particle size 0.25 to 0.5mm. This was to allow for shorter diffusion path, thus allowing the adsorbate (Neem leaves) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption [17].

2.2 Characterization of the neem leaf

The efficiency of biomass depends on factors such as number of sites on the biosorbent material, their accessibility and chemical state (i.e. availability), and the affinity between sites and metal (i.e. binding strength)[32-38] Characterization of biosorbent’s surface and structure hold keys to understanding the metal binding mechanism onto biomass. Fourier transform infra-red (FTIR), energy-dispersive X-ray spectroscopy and X-ray mapping were used here. FTIR spectroscopy technique was used to determine the functional groups available in neem leaf. FTIR spectrometer (Shimadzu 8400s) equipped with KBr window were used to analyze neem leaf powder (wave number range: 400–4000 cm_1). SEM were performed using JEOL JSM-6400F field emission SEM. The observation of samples was conducted at an accelerating voltage of 10 kV, aperture of 4, 37 mm working distance, and spot size of 8. Energy dispersive X-ray and X-ray elemental mapping analysis was performed on JEOL JSM-6460 LA low vacuum analytical SEM equipped with an integrated JEOL Hyper mini-cup, 133 eV resolution, SiLi crystal, ultra thin window (UTW) and energy dispersive X-ray spectrometer.

Scanning electron microscopy (SEM, JEOL JSM-35CF) of the Neem leaf powder (Fig. 1) showed that the powder was an assemblage of fine particles, which did not have regular, fixed shape and size. The particles were of various dimensions and all of them contained a large number of steps and kinks on the external surface, with broken edges.

2.3 Preparation of Synthetic Wastewater

The initial concentration used was 5.00mg/l for Copper, and 2.50mg/l for Zinc, and the contacting time was varied from 20 to 120 minutes .A stock solution of Copper and Zinc was prepared in distilled water with Zinc (II) Sulphate, and Copper (II) Sulphate. All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The pH of the effluent was adjusted to a pH of 5 to prevent hydrolysis. The concentration of metal ions in effluent was analyzed by Atomic Absorption Spectrophotometer. For quality control purpose, the diluted water were digested and analyzed with every sample group to track any possible contamination source. A duplicate analyzed for every sample to track experimental error and show capability of reproducing results [12].

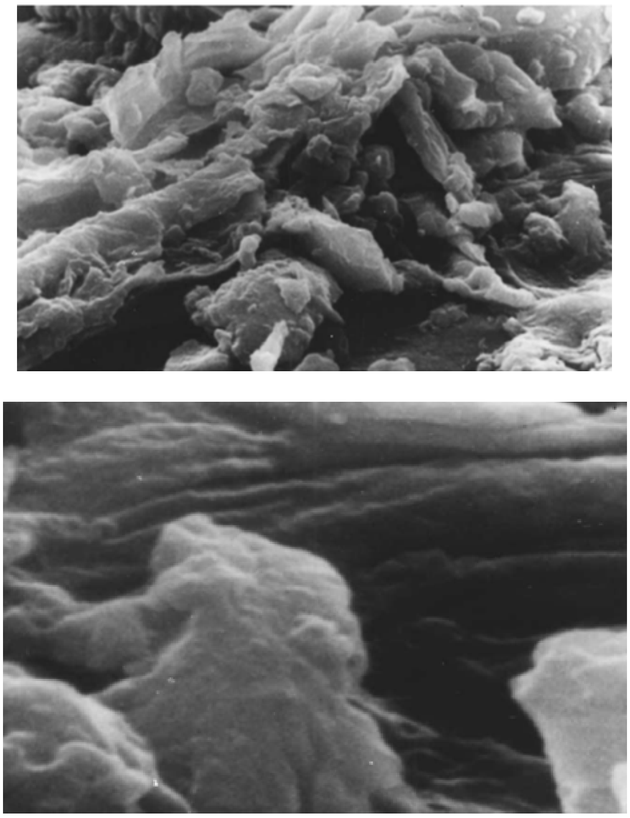
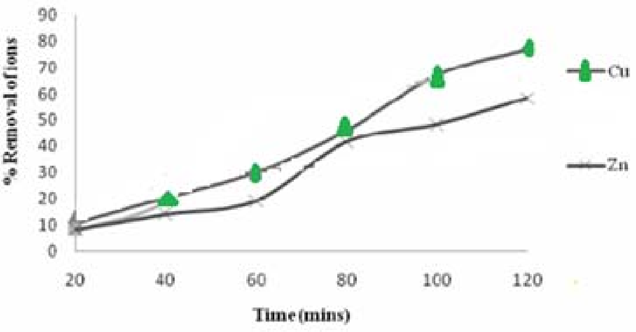


Figure 1: SEM photographs of neam leaf powder at 4000x (top) and 20000x (bottom) magnification

3. Adsorption Experiment

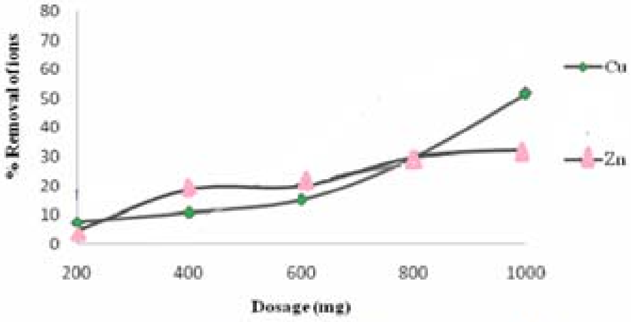
The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500ml capacity were filled with 50ml of the synthetic wastewater, and 1g of Neem leaves (ground). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 2 hours at 300 rpm. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS).



Variation of % removal of ions with Time

Figure 2

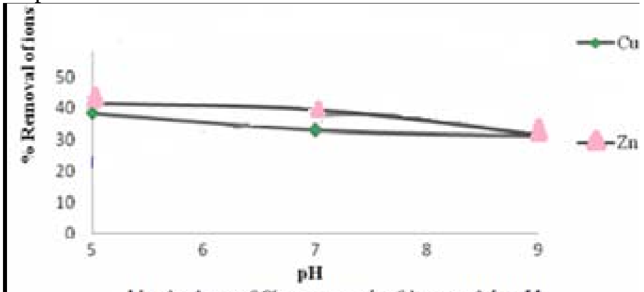
Figure 2 showed the percentage removal of the various metal ions by the Neem leaves adsorbent. For all the metal ions present in the synthetic wastewater, there was a progression in the percentage removal of metal ions present in the synthetic wastewater with time. From the result of the adsorption experiment Cu2+ ions had the highest percent removal of 76.8 at the end of 120 minutes, followed by Ni2+ ions, Zn2+ ions and Pb2+ ions with 67.5, 58.4 and 41.45 respectively. For Neem leaves, there was a progression in the rate of adsorption but it was not linear at any time. Also, from figure 2, it was observed that with increase in time, the adsorption rate of the Neem leaves increased. It was also observed that the rate of adsorption increased significantly for some of the metal ions present in the synthetic wastewater between 80 – 100 minutes of contact time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.



Variation of % removal of ions with Dosage

Figure 3

Figure 3, showed that, the adsorbent dose of 1.0g there was an increase in the adsorption rate. The larger the surface area, the larger the amount of metal ion adsorbed. This appears to be due to the increase in the available binding sites in the biomass for the complexation of the heavy metals [13]. This would probably explain the high percent removal of the heavy metals. The Neem leaves were able to achieve the percent removal of 51.8and 32.4 for Cu2+andZn2+ ions



Variation of % removal of ions with pH

Figure 4

Respectively Fig-4 showed that Neem leaves had a decrease in the adsorption rate for Cu2+ and Zn2+ ions and an increase in the adsorption rate when the pH of the synthetic waste water was between the value of 5 . When alkalinity increased that is from pH value of 7 to 9 there was a further decrease in the rate of adsorption by Neem leaves for Cu2+ , Zn2+ ions in the synthetic waste water . With the increase in pH from 5 to 9, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased. A close relationship between the surface basicity of the adsorbents and the anions is evident. This is similar to the findings of others, where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism [14,15,16].

4. Neem leaf utilization for copper ions removal from aqueous solution

Copper is a heavy metal widely found in polluted water, mostly comes from incomplete wastewater treatment. In this paper, neem leaf's performance to adsorb Cu from aqueous solution is probed. Surface structures of neem leaf remains stable during long time agitation treatment, highlighting its advantage as adsorbents.[22-25]. Characteristic of neem leaf before and after adsorption Functional groups on neem leaf powder were analyzed using FTIR. Diverse type of functional groups are available, namely C–H bending (985.56–1472.55 cm_1), C–H stretching (2845.77– 2909.42 cm_1), O–CH3 (1475.12 cm_1), C55C, ketone (1575.73–1748.35 cm_1), carboxylic (1319.22–1717.49 cm_1), amides (1575.73 cm_1), aromatic (754.12–762.79 cm_1), C–O–C stretching (1164.92 cm_1), sulfur compounds (1097.42–1339.47 cm_1), alcohols and phenols (1271–3627.85 cm_1). FTIR spectra are depicted in Fig. 5. After sorption, several functional groups which were initially present disappear, while some other had their position altered. For example, on alcohols and phenols group, O–H bending was not detected after Cu(II) sorption, while peaks characteristics of O–H bending and C–O stretching (chelating compounds) shifted from 2894.95 to 2882.42 cm_1. Same tendency were observed for carboxylic groups. Yet, several characteristic bonding such as C–H stretching and S55O stretching are not influenced by the adsorption process. Fig. 6(a) shows the SEM-EDX results for neem leaf after copper ion adsorption, on which copper's existence on the surface is confirmed from Cu K and L peaks. SEM and Cu elemental mapping on a particular surface spot after adsorption is also given in Fig. 6(b). Bright spots indicate copper's presence, of which the copper's distribution was not uniform. This would mean that only some functional groups on the surface were responsible for the copper uptake from the solution.

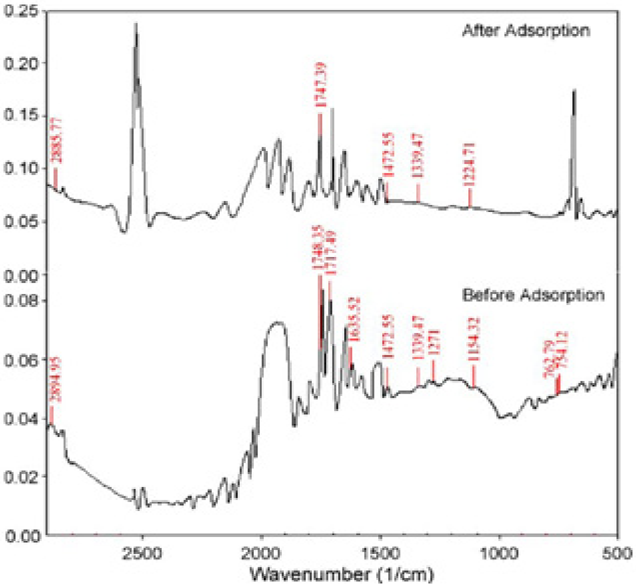


Figure 5: Fourier transform infra-red (FTIR) spectra leaf powder before and after adsorption

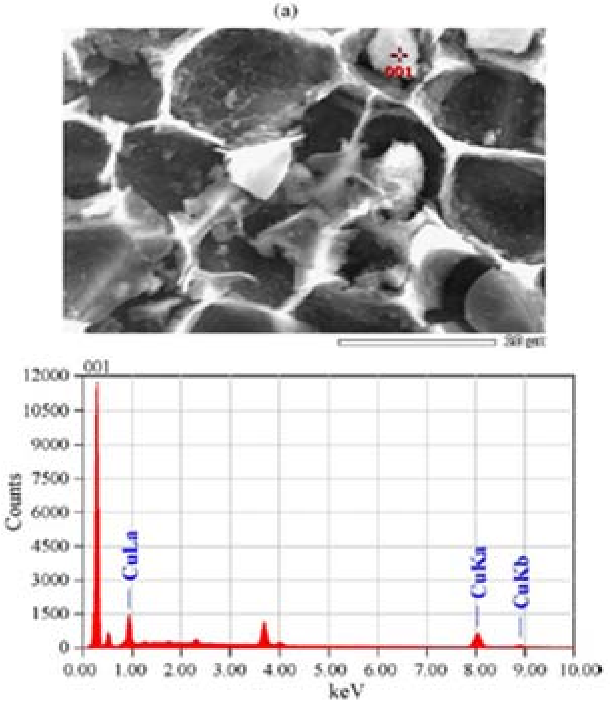


Figure 6 (a): SEM and EDX spectra of Cu loaded neem leaf powder

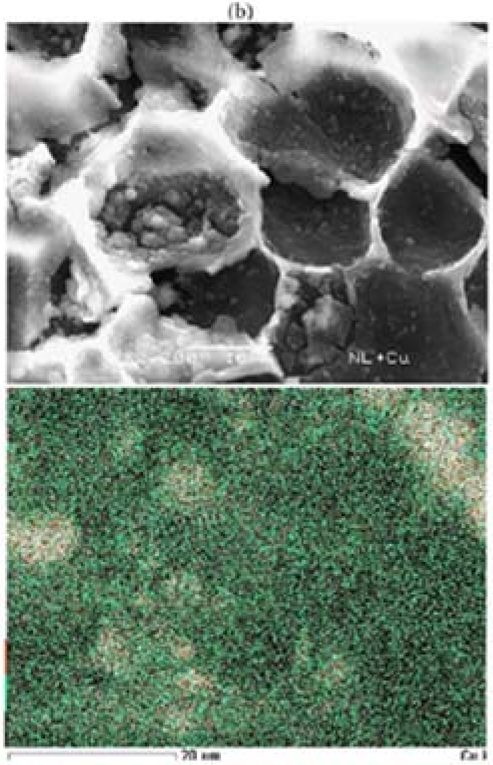


Figure 6 (b): SEM and EDX elemental mapping for Cu on Cu-loaded neem leaf powder

At low pH the amount of Cu(II) uptake was also low and enhanced with increasing pH from 2.0 to 5.0. The highest percentage removal of Cu(II) on neem leaf were observed between the pH 4.0 and 6.0. At pH < pHpzc, the acidic water donates more protons than hydroxide groups and the surface charge of neem leaf is positive, causing the protons presents in the solution to compete strongly with Cu(II) ions for the active sites on the surface of neem leaf, resulting in lower amount of Cu(II) uptake. With pH rise, electrostatic repulsion between Cu(II) and surface sites as well as the competing effect of protons decreased which proves to be more beneficial toward Cu(II) ions uptake. To correlate the adsorption equilibria data, Langmuir and Freundlich models are employed. Langmuir model has the form of qe ¼ qmax KLCe 1 þ KLCe (1) And Freundlich has the form of qe ¼ K f C1=n e (2) where qe is the amount adsorbed at equilibrium condition, qmax is the Langmuir constant which is equal to adsorption capacity. KL represents Langmuir sorption equilibrium constant while Ce is equilibrium concentration. KF and n on the other hand are Freundlich constants. Langmuir and Freundlich fitting plots are shown in Fig. 7(a). Its parameters and correlation coefficient values (R2) are summarized in Table 1. It is obvious that Langmuir equation fits the data better that Freundlich equation, which is also evidenced by better correlation coefficient value in Table 1. Freundlich equation fails to predict the adsorption experimental data at high equilibrium concentration due to the inavailability of saturation capacity term in its equation. While qmax (maximum adsorption capacity) increased from 2.85 _ 10_4 to 2.88 _ 10_4 mol/g, KL (Langmuir equilibrium constant) was enhanced from 2567 to 5223 (L/mol) along with temperature rose. The enhancement of maximum adsorption capacity (qmax) as a function of temperature is a strong indication that the chemisorption is the control mechanism. One of the distinct features of the chemisorption is the increase of adsorption capacity with temperature. Another indication is the high value of KL. The KL value can be correlated with adsorption enthalpy change (DH8). Due to the endothermic nature of chemisorption, DH8 value would be positive. Therefore, in parallel to temperature increase, KL value should also rise. Fig. 7(b) shows the breakthrough curve for a fixed initial concentration of 500 mg/L and flow rate 8.5 mL/min with different bed height of 4, 5 and 6 cm. Fig. 7(c), on the other hand displays the breakthrough curve for fixed bed height of 5 cm and flow rate 8.5 mL/min with different initial copper concentration of 400, 500 and 600 mg/L. The dynamic column data were fitted by Thomas model to determine the equilibrium specific uptake of copper (q0) and also its rate constant (KTH).

5. Adsorption studies

Table 1

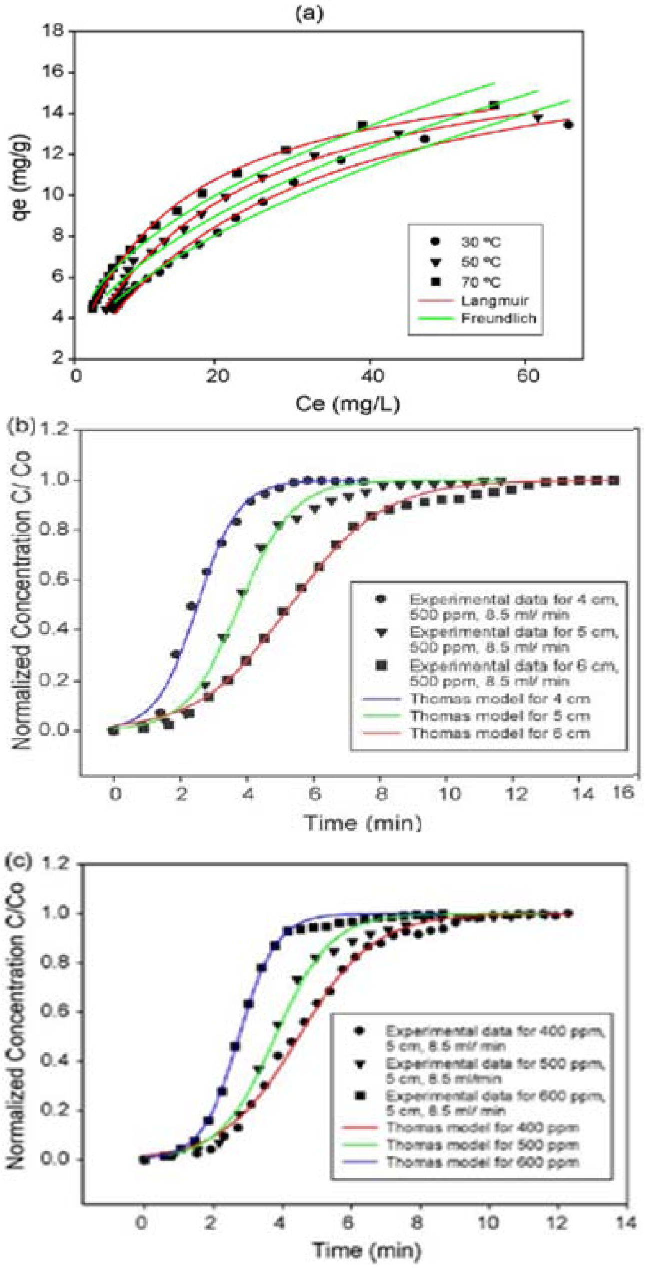
Isotherm constants of Freundlich and Langmuir models for sorption process.

Heavy metal ion	Temperature (°C)	Freundlich			Langmuir		
		K_F (mg/g)	N	R^2	Q_{max} (mol/g)×10^4	K_L (L/mol)	R^2
Cu^{2+}	30	1.78	1.99	0.975	2.84	2567	0.991
	50	2.24	2.16	0.961	2.86	3545	0.995
	70	2.78	2.35	0.978	2.88	5223	0.997

Thomas model (Thomas, 1944) is defined as

$$\frac{C_t}{C_o} = \frac{1}{1+\exp[K_{TH}(q_e m - C_o V_{eff}/v)]} \qquad (3)$$

where KTH is Thomas rate constant, while Ct and Co are the concentration of metal in the effluent and influent, respectively. In addition, Veff is the volume of effluent and m is the mass of biosorbent in the column. Bed height effect on the breakthrough curves can be clearly seen in Fig. 7(b). The breakthrough time increase as the bed height increases. Furthermore, the amount of cooper ions adsorbed also increases for larger bed height. Accordingly, at larger bed height, the distance for mass transfer zone is longer, resulting in higher value of breakthrough time which is mainly caused by the higher contact time between metal ions solution and neem leaves powder surface. The effect of influent concentrations on the breakthrough curves is also shown in Fig. 7(c). Increasing the influent concentration enhances the total adsorption capacity, hence the breakthrough curve become steeper as the feed concentration increase.



(a) Biosorption isotherms of copper on neem leaf powder, (b) effect of bed height on the breakthrough curve, (c) effect of concentration on the breakthrough curve.

Figure 7

6. Thermodynamic of adsorption

Free energy change (DG8) is a fundamental criterion of process spontaneity which can be estimated from

$$\Delta G^{\circ} = -RT \ln K_L \qquad (4)$$

where KL is equilibrium constant obtained from Langmuir model (L/mol), T is the absolute temperature (K) and R is the gas constant (8.314 J/mol K). The correlation between free energy change, enthalpy change (DH8) and entropy change (DS8) is given by

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (5)$$

The values of DG8 obtained at 30, 50 and 70 8C are -19.78, _21.96, and _24.42 kJ/mol, respectively. Negative values of DG8 denotes the spontaneity nature of the adsorption. A positive DH8 value (15.43 kJ/mol) indicates that the process is endothermic as well as suggesting the high probability for chemisorption as the controlling mechanism. Additionally, positive value of DS8 (0.116 kJ/mol K) indicates that the process is irreversible which again is the characteristic of chemisorptions [26-31]

7. Conclusion

This study probes the performance of neem leaf biomass waste to sequester copper from aqueous solution. Neem leaf serves as a potential alternative adsorbent to remove copper ions from copper containing solution. The adsorption experiments were conducted in batch and dynamic modes at optimum pH of 5. Adsorption equilibria data were also fitted by the well-known adsorption models, Freundlich and Langmuir. Langmuir equation represents the adsorption equilibria better than Freundlich. Thermodynamics data indicated that the adsorption of copper ion onto neem leaf is endothermic. Chemisorption can be pointed out as the controlling mechanism. Carboxylic groups, alcohols and phenols were involved in the binding process. Lastly, the dynamic data was also provided in the form of breakthrough curve along with Thomas model representation.

7.1 Neem leaf utilization for Zinc ions removal from aqueous solution

Zinc is widely used in coating iron and other metals, in wood preservatives, catalysts, photographic paper, accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments and batteries , and as a consequence it is often found in the wastewaters arising from these processes. The most significant industrial sources arise from electroplating, mining industry effluents and acid mine drainage. For instance zinc concentrations of over 620 mg/L have been recorded in drainage from abandoned copper mines in Montana, USA [39-44].

7.2 Influence of initial pH

The solution pH is one of the parameters having considerable influence on the biosorption of metal ions [45], because the surfaces charge density of the adsorbent and the charge of the metallic species present on the pH. In the present work, the extent of zinc biosorption was investigated in the pH range 1.0–6.0 with a constant amount of Neem leaves powder 0.15 g/100mL and Neem stem bark 0.15 g/100mL for a zinc solution of concentration 100 mg/L. The results are shown in Fig. 4. The biosorptionof zinc was maximum at pH 5.0 for Neem leaves powder. The maximum zinc biosorption for Neem leaves powder was 86.48% (pH 5). Biosorption could not be carried out beyond pH 6.0 due to the precipitation of Zn(OH)2 and therefore experiments were done in pH range 4–5. At pH value above optimum pH, there is a net negative charge on the biomass cells and the ionic state of ligands is such to promote the uptake of metal ions. As the pH lowered, however the over all surface charge on the biomass cells become positive, which will inhibit the approach of positively charge metal cations. It is likely that protons will then compete with metal ions for ligands and thereby decreases the interaction of metal ions with the cells [46]. Whereas at higher pH (above 5), then ligands (–COOH, –NH2) attract positively charged metal ions and binding occurs, indicating that the major process is an ionexchange mechanism that involve an electrostatic interaction between the positively charged groups in cell walls and metallic cations [47–48]. Similar trend was reported for biosorption of Zn(II) on silica gel [49] when the extent of biosorption increased from 0 to 90% in pH range of 2.0–6.0. The authors interpreted the process as due to ion-exchange and the large discrepancies at higher pH were attributed to metal removal by other possible mechanisms such as precipitation. According to the results of this initial experiment, the further biosorption investigations were performed at pH 5 for Neem leaves powder as an optimal value.

7.3 Effect of adsorbent particle size and adsorbent dose

The effect of altering the adsorbents particle size on the q (mg/g) showed that there was a more dominant removal of zinc by the smaller particles. This was most probably due to the increase in the total surface area, which provided more biosorption sites for the metal ions. At smaller particles the removal efficiency for Neem leaves particle was more than stem bark. This was not the case with the biosorption of zinc for the larger particle size. The enhanced removal of sorbate by smaller particles has been noted previously during a study for the color removal by silica [50]. The maximum biosorption was occurred with 0.250mm adsorbent particle size for Neem leaves powder .Adsorbent dose in aqueous solution seemed to influence the adsorption capacity q, for lower values of biomass doses there was an increase in the adsorption capacity q [51]. It was suggested that an increase in adsorbent dose interferes between the binding sites and caused electrostatic interaction between cells. Adsorbent dose added into the solution determines the number of binding site available. An increase in adsorbent quantities strongly affects the quantities of zinc removed from aqueous solutions to a certain limit and than decreases. This effect was also reported in literature for biosorption phenomenon of heavy metals [52,53].

7.4 Biosorption profile

Previous experimental studies showed that biosorption is dependent on different time intervals. Batch biosorption experiments were carried out at optimum conditions. Kinetic studies revealed that maximum adsorption capacities and metal removal efficiencies for zinc were achieved generally in first 15 min biosorption takes place very rapidly and then it continues at slower rate upto maximum biosorption. Equilibrium was reached in a contact time of 6 h. Fig. 8 showed the time course of biosorption, when the initial metal concentrations (Co) were 100 mg/L. In first 15 min biosorption is sharp due to decrease in pH of solution because protons were released by biosorbent. Kinetic study revealed that biosorption take place in two phases, rapid surface biosorption within 15 min and slow intracellular biosorption upto end time agrees with pervious experimental studies [54,55,56].

7.5 Effect of initial metal concentration

The experimental data shown in Fig. 8 indicates that the adsorption capacity increased with increase in initial metal ion concentration for metal on the biomass upto 100 ppm but furthermore adsorption capacity becomes saturated. The increase in metal zinc concentration increased the uptake affinity (*q*) and decreased the percentage removal of zinc, except 100 mg/L at which there was percentage removal, i.e. 88.66% for Neem leaves powder . This biosorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, biosorption sites took up the available metal more quickly. However, at higher concentrations, metal ions need to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate [57].

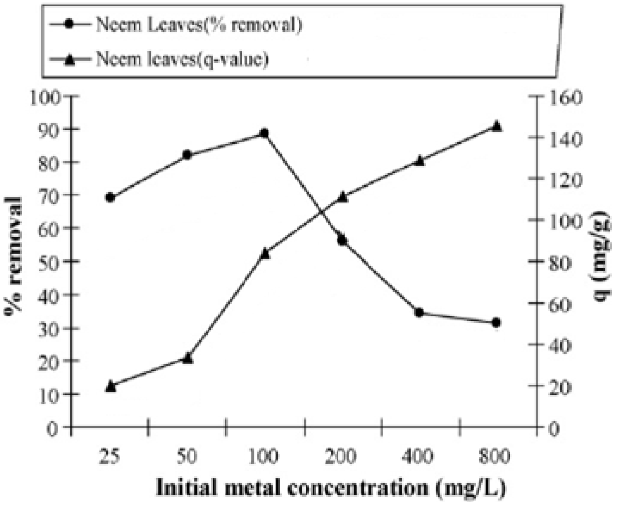


Figure 8: Effect of initial metalconcentration on biosorption of zinc (for neem leaves, pH 4, absorbent dose= .15g/100mL; for neem bark, pH 5, absorbent dose=0.20g/100mL.

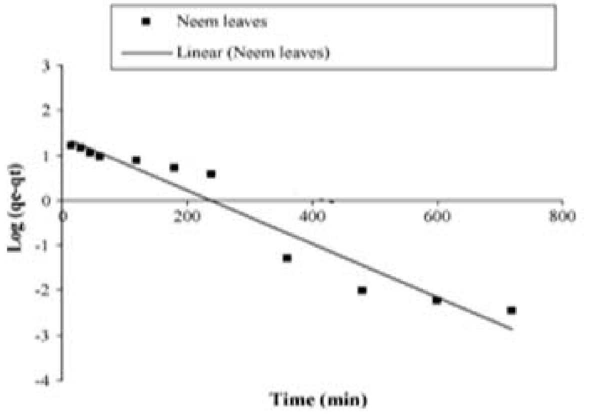
8. Kinetics modeling

The order of adsorbate–adsorbent interactions has been described by using various kinetic models. Traditionally, the pseudo-first-order model derived by Lagergren and Sven [58] has found wide application. On the other hand, several authors [59–62] have shown that second-order kinetics can also very well describe these interactions in certain specific cases. The pseudo-first-order rate equation of Lagergren:

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,\mathrm{ad}}\, t}{2.303} \qquad (1)$$

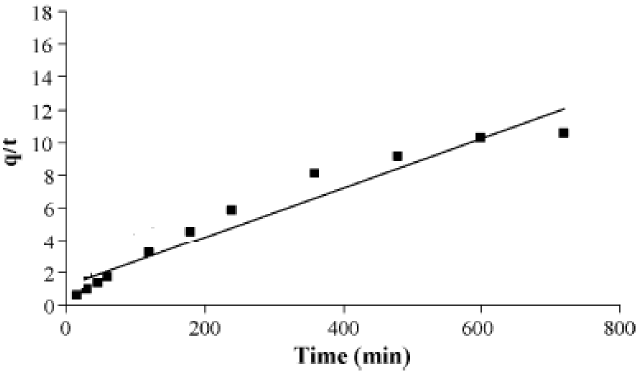
where *qt* and *q*e (mg/g) are the amount adsorbed at time *t* and at equilibrium, and *k*1,ad (min−1) is the Lagergren rate constant of the pseudo-first-order adsorption process. Plot of log(*q*e −*qt*) versus *t* gives a straight line for first-order kinetics (Fig. 9), which allows computation of the adsorption rate constant, *k*1,ad. The Lagergren first-order rate constant *k*1,ad, *q*e and *R*2 determined from the model indicate that this model had failed to estimate *q*e since the experimental value of *q*e differs from estimated one. The best fit for the experimental data of this study was achieved by the application of pseudo-second-order kinetic equation. The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism. So, the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [63]:

$$\frac{t}{q_t} = \frac{1}{k_{2,\mathrm{ad}}\, q_e^2} + \frac{t}{q_e} \qquad (2)$$



The pseudo-first-order (Lagergren) plot (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL.: pH 5, adsorbent dose = 0.20 g/100 mL.).

Figure 9



The pseudo-second-order plot

Figure 10

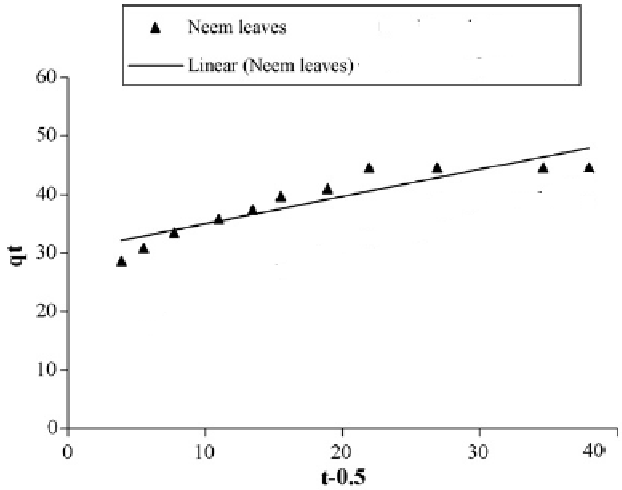
where *k*2 ,ad (g/mg min) is the second-order rate constant. The plot of *t*/*qt* versus *t* gives a linear relationship (Fig. 10), which allows computation of *q*e, *k*2,ad and *h* without having to know any parameter beforehand. The coefficient of correlation for second-order kinetic model was equal to 0.9447 (Neem leaves) and the estimated value of *q*e also agreed with the experimental one. Both factors suggest that the biosorption of zinc ions followed the second-order kinetic model, indicating that the rate-limiting step was a chemical biosorption process between zinc and Neem biosorbents. The above two equations cannot identify the diffusion mechanism. To identify the diffusion mechanism, Weber and Morris model is thus applied [64]. According to this theory:

$$q_t = k_i t^{0.5} + C \qquad (3)$$

where *k*i is the intraparticle diffusion rate constant (mg/g h1/2) and *C* (mg/g) is a constant that gives an idea about the thickness of the boundary layer. If theWeber–Morris [65] plot of *qt* versus *t*0.5 gives a straight line, then the biosorption process is controlled by intraparticle diffusion only. The *k*i and *C* can be calculated from slope and intercept of the plots *qt* versus *t*0.5. It can be seen from Fig. 11 that the regression was linear, but the plot did not pass through the origin, suggesting that biosorption involved intraparticle diffusion, but that was not the only rate-controlling step. Other kinetic models may control the biosorption rate. The pseudo-first-order Lagergren model, pseudo-secondorder model and Weber–Morris model parameters are given in Table 1.

9. Equilibrium modeling

To examine the relationship between sorbed (*q*e) and aqueous concentrations (*C*e) at equilibrium, biosorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data, initial zinc concentrations were varied while the biomass weight in each sample was kept constant. Six hours of equilibrium periods for biosorption experiments were used to ensure equilibrium conditions. This time was chosen considering the results of kinetics of zinc removal by Neem biosorbents, which will be further presented. If the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the



The Weber Morris plot.

Figure 11

biosorption of the next ion, then the biosorption process would follow the Langmuir adsorption isotherm equation [66], which was linearised to the form:

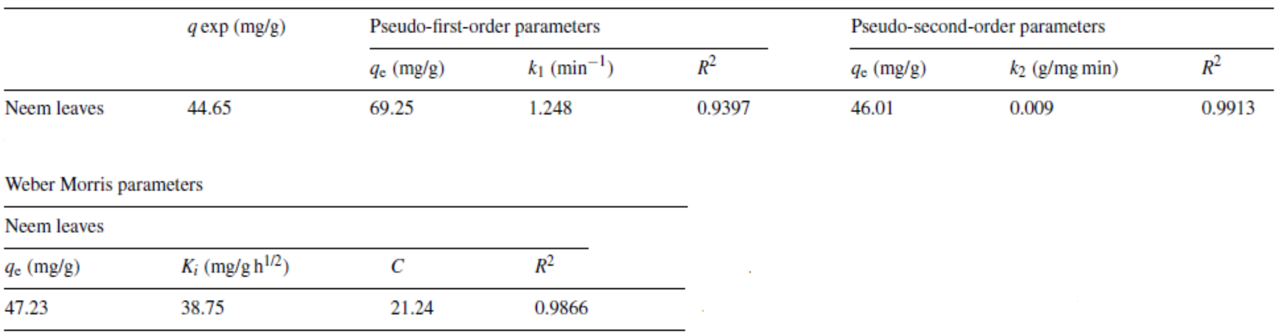
$$\frac{C_e}{q_e} = \frac{1}{(q_o\,K_L)} + \frac{C_e}{q_o} \qquad (4)$$

The capacity of Neem biomass in binding with zinc was determined by plotting *C*e/*q*e against *C*e using the above equation showed the data linearised to fit the Langmuir equation. The plots of specific biosorption (*C*e/*q*e) against equilibrium concentration (*C*e) gave the linear isotherm parameters of *q*o, *K*L and the coefficient of determination and these are presented in Table 2. The *R*2 values suggested that the Langmuir isotherm provided a good model of the biosorption system The adsorption capacity, *q*o which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the Neem biomass had a mass capacity for zinc (147.08 mg Zn/g for Neem leaves).The Freundlich equation is another model which has been commonly used to describe adsorption isotherms. Its linearised form is represented by the equation [68]:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \qquad (5)$$

where *q*e is the amount adsorbed per unit mass of adsorbent and *C*e is the equilibrium concentration (mg/L) The plot of log *q*e versus log*C*e was linear (Fig. 8) and constants *K*F and *n* can be evaluated from the slopes and intercepts. The Freundlich constants are shown in Table 2. It was found that the adsorption equilibrium datawas better fitted by the Langmuir isotherm, although it can also be modelled by the Freundlich isotherm, in the concentration range studied, since it presented the greater coefficient of correlation. The apparent Gibbs free energy of the biosorption processes (_*G*◦ads) corresponding to zinc ion on the biomass was evaluated using the Bockris-Swinkel’s adsorption isotherm equation as reported by Rudresh and Mayanna [69]. The equation is

Table 1
The pseudo-first-order (Lagergren), pseudo-second-order and Weber Morris parameters (for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL:



	q exp (mg/g)	Pseudo-first-order parameters			Pseudo-second-order parameters		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
Neem leaves	44.65	69.25	1.248	0.9397	46.01	0.009	0.9913

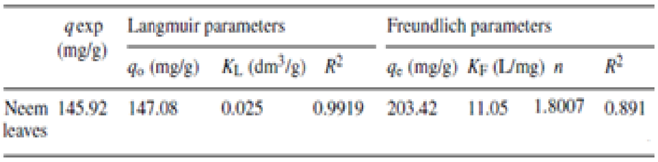
Weber Morris parameters

Neem leaves			
q_e (mg/g)	K_i (mg/g h$^{1/2}$)	C	R^2
47.23	38.75	21.24	0.9866

Expressed as:

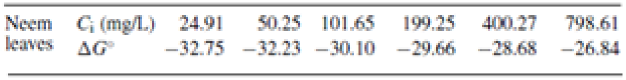
$$G^{o}_{ads} = -2.30RT\,\log\left[\frac{55.4\theta}{C_o(1/\theta)}x\frac{\theta + n(1-\theta)^{n-1}}{n^n}\right] \qquad (6)$$

Table 2 The Langmuir isotherm and Freundlich isotherm parameters for Neem leaves, pH 4, adsorbent dose = 0.15 g/100 mL:



	$q$exp (mg/g)	Langmuir parameters			Freundlich parameters			
		q_o (mg/g)	K_L (dm^3/g)	R^2	q_e (mg/g)	K_F (L/mg)	n	R^2
Neem leaves	145.92	147.08	0.025	0.9919	203.42	11.05	1.8007	0.891

Table 3 Apparent Gibbs free energy
ΔG°ads (kJ/mol) of the metal ions between the biomass and aqueous phase



Neem leaves	C_i (mg/L)	24.91	50.25	101.65	199.25	400.27	798.61
	ΔG°	−32.75	−32.23	−30.10	−29.66	−28.68	−26.84

where *C*o is the initial concentration of zinc ion in the solution. The values of _*G*◦ads were then evaluated at various initial metal ion concentrations. The data is presented in Table 3. The negative values of _*G*◦ indicated the spontaneous biosorption nature of zinc ion by the Neem adsorbents and suggested strongbiosorption of zinc ions on the biomass surface. In general, it is of note that up to −20 kJ/mol are consistent with electrostatic interaction between charged molecules and surface indicative of physical adsorption while more negative than −40 kJ/mol involve chemisorption. The order of magnitude of the valuesindicates a physicochemical mechanism for the bio sorption of metal ions on to the Neem biosorbents .Zinc uptake by biomass, as quantified in this study from batch experiments, was compared with literature values of other biosorbents (Table 4 [70-81]). Although the data collated in Table 4 may not represent equivalent or optimised conditions or with various zinc removal mechanisms in each case, it still provides a useful comparison for engineers in their decision of suitable biosorbent selection in engineering practice.biomass in this study is comparable with these data. Indeed zinc uptake by Neem biomass in this study was significantly higher than most of the selected biosorbents.

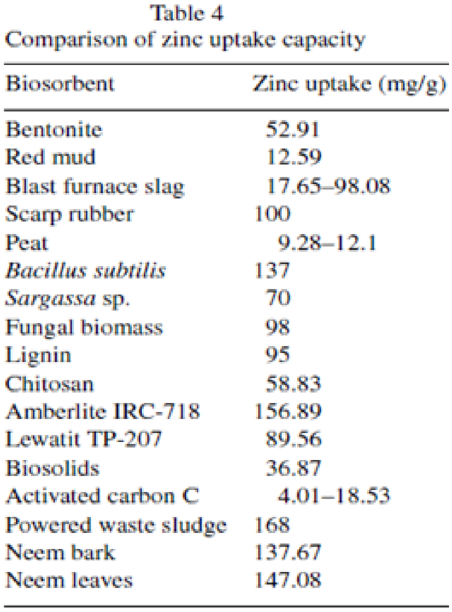


Table 4
Comparison of zinc uptake capacity

Biosorbent	Zinc uptake (mg/g)
Bentonite	52.91
Red mud	12.59
Blast furnace slag	17.65–98.08
Scarp rubber	100
Peat	9.28–12.1
Bacillus subtilis	137
Sargassa sp.	70
Fungal biomass	98
Lignin	95
Chitosan	58.83
Amberlite IRC-718	156.89
Lewatit TP-207	89.56
Biosolids	36.87
Activated carbon C	4.01–18.53
Powered waste sludge	168
Neem bark	137.67
Neem leaves	147.08

10. Conclusions

The removal of metal ions in synthetic wastewater by using biosorption technology was studied. Based on the results, the following conclusions can be drawn. The ground Neem leaves was very effective in removal of Cu and Zn ions from the synthetic waste water. Neem leaves are efficient biomaterial for removal of some heavy metals from industrial wastewater. This process can be effectively used in the heavy metals removal in industrial wastewater.

References

[1] Mohanty AK, Misra M, Hinrichsen G. Biofibers, biodegradablepolymers and biocomposites: an overview. Macromol Mater Eng2000;276/277:1–24.
[2] Gatenholm P, Mathiasson A. Biodegradable natural composites I(processing and properties) and II (synergistic effects of processingcellulose with PHB). J Appl Polym Sci 1992;45:1667–77.1994;51:1231–1237.
[3] Keller A. Compounding and mechanical properties of biodegradablehemp fiber composites. Compos Sci Technol 2003;63(9):1307–16.
[4] Puglia D, Tomassucci A, Kenny JM. Processing, properties andstability of biodegradable composites based on Mater-Biwandcellulose fibres. Polym Adv Technol 2003;14:749–56.
[5] Shibata M, Oyamada S, Kobayashi S, Yaginuma D. Mechanical properties and biodegradability of green composites based on biodegradable polyesters and lyocell fabric. J Appl Polym Sci 2004;
[6] 92:3857–63.
[7] Shibata M, Ozawa K, Teramoto N, Yosomiya R, Takeishi H.Biocomposites made from short Abaca fiber and biodegradablepolyesters. Macromol Mater Eng 2003;288:35–43.
[8] Zini E, Baiardo M, Armelao L, Scandola M. Biodegradable polyesters reinforced with surface-modified vegetable fibers. Macromol Biosci 2004;4:286–95.
[9] Raghavan D, Emekalam A. Characterization of starch/polyethylene and starch/polyethylene/poly (lactic acid) composites. Polym Degrad Stability 2001;72:509–17.
[10] Shogren RL, Doane WM, Garlotta D, Lawton JW, Willett JL.Biodegradation of starch/polylactic acid/poly(hydroxyester-ether) composite bars in soil. Polym Degrad Stability 2003;79:405–11.
[11] Rosa DS, Rodrigues T, Guedes CG, Calil MR. Effect of thermal aging on the biodegradation of PCL, PHBV and their blends with starch in soil compost. J Appl Polym Sci 2003;89:3539–46.
[12] S. S. Umare, A. S. Chandure, and R. A. Pandey, "Synthesis,characterization and biodegradable studies of 1,3-propanediolbased polyesters," *Polymer Degradation and Stability*, vol. 92,no. 3, pp. 464–474, 2007
[13] Shah, F. Hasan, A. Hameed, and S. Ahmed, "Biological degradation of plastics: a comprehensive review," *Biotechnology Advances*, vol. 26, no. 3, pp. 246–265, 2008.
[14] S. Bhattarjee, L. Besra, and B. P. Singh, "Effect of additives on the microstructure of porous alumina," *Journol of European Ceramic Society*, vol. 27, no. 1, pp. 47–52, 2007. M. Movveale, R. Scaffaro, A. Maio, and F. P. La Mantia,
[15] "Effect of adding wood flour to the physical properties of a biodegradable polymer," *Applied Science and Manufacturing*, vol. 39, no. 3, pp. 503–513, 2008.
[16] Aksu, Z. and O. Tunc, ''Application of Biosorption for Penicillin G Removal: Comparison with Activated Carbon,'' Process Biochem., 40, 831 (2005).
[17] Huang, C. P. and Wu, M. H. Chromium removal by carbon adsorption. J. Water. Pollut. Control Fed., 47, 2437-2445, 1975.
[18] Adeyinka, A., Liang, H. and Tina, G. "Removal of Metal Ion form Waste Water with Natural Waste" School of Engineering and Technology. 1-8. 33. Ibid 4, 2007.
[19] Marshall, W. E. and Champagne, T.E. Agricultural Byproducts as Adsorbents for Metal Ions in Laboratory Prepared Solutions and in Manufacturing Wastewater, Journal of Environmental Science sand Health, Part A: Environmental Science and Engineering. Vol. 30, No. 2, 241 – 261, 1995.
[20] Gong, R., Ding, Y., Liu, H., Chen, Q. and Liu, Z. Lead biosorption and desorption by intact and pretreated *Spirulina maxima* biomass. *Chemosphere*.58(1): 125-130, 2005
[21] Leon, Y., Leon, C.A. Solar, J.M. Calemma, V. and Radovic, L.R. Evidence for the protonation of basal plane sites on carbon. *Carbon*.30. 797–811, 1992.
[22] Radovic L.R., Silva, I.F. , Ume, J.I., Menendez, J.A., Leon, C.A., Leon, Y and Scaroni, A.W. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. *Carbon*, 35. 1339-48, 1997.
[23] Faria, P.C.C., Orfao, J.J.M. and Pereira, M.F.R. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Research, 38. 2043-2052, 2004.
[24] S. S. Umare, A. S. Chandure, and R. A. Pandey, "Synthesis,characterization and biodegradable studies of 1,3-propanediolbased polyesters," *Polymer Degradation and Stability*, vol. 92,no. 3, pp. 464–474, 2007

[25] Shah, F. Hasan, A. Hameed, and S. Ahmed, “Biological degradation of plastics: a comprehensive review,” *Biotechnology Advances*, vol. 26, no. 3, pp. 246–265, 2008.
[26] S. Bhattarjee, L. Besra, and B. P. Singh, “Effect of additives on the microstructure of porous alumina,” *Journol of European Ceramic Society*, vol. 27, no. 1, pp. 47–52, 2007. M. Movveale, R. Scaffaro, A. Maio, and F. P. La Mantia,
[27] “Effect of adding wood flour to the physical properties of a biodegradable polymer,” *Applied Science and Manufacturing*, vol. 39, no. 3, pp. 503–513, 2008.
[28] N. Tzankova Dintcheva and F. P. La Mantia, “Durability of a starch-based biodegradable polymer,” *Polymer Degradation and Stability*, vol. 92, no. 4, pp. 630–634, 2007.
[29] Aksu, Z. and O. Tunc, ‘‘Application of Biosorption for Penicillin G Removal: Comparison with Activated Carbon,’’ Process Biochem., 40, 831 (2005).
[30] Aksu, Z. and G. Donmez, ‘‘Binary Biosorption of Cadmium(II) and Nickel(II) onto Dried Chlorella vulgaris: Co-Ion Effect on Mono-Component Isotherm Parameters,’’ Process Biochem., 41, 860 (2006).
[31] Al-Rub, F. A. A., ‘‘Biosorption of Zinc on Palm Tree Leaves: Equilibrium, Kinetics, and Thermodynamics Studies,’’ Sep. Sci. Technol., 41, 3499 (2006).
[32] Bhattacharyya, K. G. and A. Sharma, ‘‘Adsorption of Pb(II) from Aqueous Solution by Azadirachta indica (Neem) Leaf Powder,’’ J. Hazard. Mater., B113, 97 (2004).
[33] Ho, Y. S. and A. E. Ofomaja, ‘‘Biosorption Thermodynamics of Cadmium on Coconut Copra meal as Biosorbent,’’ Biochem. Eng. J., 30, 117 (2006).
[34] Kang, S., J. Lee, and K. Kima, ‘‘Biosorption of Cr(III) and Cr(VI) onto the Cell Surface of Pseudomonas aeruginosa,’’ Biochem. Eng. J., 36, 54 (2007).
[35] Mungasavalli, D. P., T. Viraraghavan, and Y. C. Jin, ‘‘Biosorption of Chromium from Aqueous Solutions by Pretreated Aspergillus niger: Batch and Column Studies,’’ Colloids Surf. A: Physicochem. Eng. Aspects, 301, 214 (2007).
[36] Sharma, A. and K. G. Bhattacharyya, ‘‘Azadirachta indica (Neem) Leaf Powder as a Biosorbent for Removal of Cd(II) from Aqueous Medium,’’ J. Hazard. Mater., B125, 102 (2005).
[37] Thomas, H. C., ‘‘Heterogeneous Ion Exchange in a Flowing System,’’ J. Am. Chem. Soc., 66, 1664 (1944).
[38] Wibowo, N., L. Setyadhi, D. Wibowo, and J. Setiawan, ‘‘Adsorption Benzene and Toluene from Aqueous Solutions onto Activated Carbon and Its Acid and Heat Treated Forms: Influence of Surface Chemistry on Adsorption,’’ J. Hazard. Mater., 146, 237(2007).
[39] B. Volesky, Biosorption and Biosorbents, Biosorption of Heavy Metals, CRC Press, Boston, USA, 1990, pp. 3–5.
[40] R.H. Crist, K. Oberholser, N. Shank, M. Nguyen, Nature of bonbing between metallic ions and algal cell walls, Sci. Technol. 15 (1981) 1212– 1217.
[41] T.A. Davis, B. Volesky, R.H.S.F. Vieira, Sargassum seaweed as biosorbent for heavy metals, Water Res. 34 (2000) 4270–4278.
[42] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
[43] J.T. Matheickal, Q. Yu, Biosorption of lead (II) and copper (II) from aqueous solution by pre-treated biomass of Australian marine algae, Bioresour. Technol. 69 (1999) 223–229.
[44] Y. Sag, A. Kaya, T. Kutsa, The simultaneous biosorption of Cd (II) and Zn (II) on *Rhizopus arrhizus*; application of adsorption modals, Hydrometallurgy 50 (1998) 297–314.
[45] N.C.M. Gomes, V.R. Linardi, Removal of gold, silver and copper by living and nonliving fungi from liquor obtained from the gold mining industry, Revista. de. Microbiologia 27 (1996) 67–75.
[46] The Council of the European Communities, Directive 76/464/EEC—on pollution caused by certain dangerous substances discharged into the aquatic environment of the community, Off. J. Eur. Commun. (1976), No. L 129/23.
[47] USDHHS, Toxicological Profile for Zinc, US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta, GA, 1993.
[48] B.Volesky, in: B.Volesky (Ed.), Sorption and Biosorption,BVSorbex Inc., Montreal, St. Lambert, Que., Canada, 2003.
[49] C.E. Janson, R.E. Kenson, L.H. Tucker, Treatment of heavy metals in wastewaters, Environ. Prog. 1 (1982) 212–216.
[50] D.W.G. Grosse, A review of alternative treatment processes for metal bearing hazardous waste streams, Air Pollut. Control Assoc. 36 (1986) 603–614.
[51] B. Volesky, Biosorption and Biosorbents, Biosorption of Heavy Metals, CRC Press, Boston, USA, 1990, pp. 3–5.
[52] M. Sanches-Polo, J. Rivera-Utrilla, Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonized activated carbons, Environ. Sci. Technol. 36 (2002) 3850–3854.
[53] Y. Sag, D. Ozer, T. Kutsal, A comparative study of the biosorption of lead (II) ions to *Z. ramigera* and *R. arrhizus*, Process Biochem. 30 (1995) 169–174.
[54] M.H. Jnr, A.I. Spiff, Studies on the effect of pH on the sorption of Pb2+ and Cd2+ ions from aqueous solutions by *Calacdium biocolor* (Wild Cocoyam) biomass, Eur. J. Biotechnol. 7 (2004) 313–323
[55] B. Cordero, P. Loderio, R. Herrero, M.E.S. de-Vicente, Biosorption of cadmium by *Fucus spiralis*, Environ. Chem. 1 (2004) 180–187.
[56] H.H. Tran, F.A. Roddick, J.A. O’Donnel, Water Res. 33 (1999) 2992.
[57] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of color from effluent using various adsorbents—III. Silica: rate processes, Water Res. 14 (1980) 15–20.
[58] E. Fourest, B. Roux, Contribution of sulfonate groups and alginate to heavy metal sorption by dry biomass of *sargassum fluitans*, Environ. Sci. Technol. 30 (1) (1996) 277–282.
[59] V. Padmavathy, P. Vasudevan, S.C. Dhingra, Biosorption of Ni(II) ions on Baker’s yeast, Process Biochem. 38 (2003) 1389–1395.
[60] S.Y. Quek, D.A.J. Wase1, C.F. Forster, The use of sago waste for the sorption of lead and copper, Water SA 24 (1998) 251–256.

[61] J.P. Chen, S. Yiacaumi, Biosorption of metal ions from aqueous solutions, Sci. Technol. 32 (1–4) (1997) 51–69. C. Sing, J. Yu, Copper adsorption and removal from water by living

[62] mycelium of white-rot fungus *Phanerochaete chrysosporium*, Water Res. 32 (9) (1998) 2746–2752.

[63] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250

[64] M.H. Jnr, A.I. Spiff, Studies on the effect of pH on the sorption of Pb2+ and Cd2+ ions from aqueous solutions by *Calacdium biocolor* (Wild Cocoyam)biomass, Eur. J. Biotechnol. 7 (2004) 313–323.

[65] S. Lagergren, K. Sven, Vetenskapsakad Handl. 24 (4) (1898) 1–39.

[66] Y.S. Ho, Adsorption of Heavy Metals from Waste Streams by Peat, The University of Birmingham, UK, 1995.

[67] T. Gosset, J.L. Trancart, D.R. Thevenot, Water Res. 20 (1986) 21.

[68] D.C. Sharma, C.F. Foster, Bioresour. Technol. 49 (1994) 31.

[69] C.T. Tien, C.P. Huang, J.P. Vernet (Eds.), Trace Metals in the Environment, Elsevier, Amsterdam, 1991, p. 295.

[70] W.J. Weber, J.C. Morris, Proc. Int. Conf. on Water Pollution Symposium 2, Pergamon, Oxford, 1962, pp. 231–266.

[71] W.J.Weber, J.C. Morris, J. Sanitary Eng., Div. ASCE 89 (SA2) (1963) 31.

[72] Langmuir, J. Am. Chem. Soc. 38 (11) (1916) 2221–2295.

[73] H.M.F. Freundlich, Z. Phys. Chem. 57 (A) (1906) 385–470.

[74] H.B. Rudresh, S.M. Mayanna, Adsorption of *n*-Decylamine on zinc from acidic solution, J. Environ. Sci. Technol. 122 (1977) 251–256.

[75] Mellah, S. Chegrouche, The removal of zinc from aqueous solutions by natural bentonite, Water Res. 31 (1997) 621–629.

[76] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste, Water Res. 36 (2002) 2304–2318.

[77] Agrawal, K.K. Sahu, B.D. Pandey, Removal of zinc from aqueous solutions using sea nodule residue, Colloids Surf. A 237 (2004) 133–140.

[78] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[79] Z. Reddad, C. Gerente, Y. Andres, L.P. Cloire, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[80] L. Norton, K. Baskaran, T. McKenzie, Biosorption of zinc from aqueous solutions using biosolids, Adv. Environ. Res. 8 (2004) 629–635.

[81] K.H. Chu, Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics, J. Hazard. Mater. B90 (2002) 77–95.

[82] F. Kargi, S. Cikla, Determination of model parameters for zinc (II) biosorption onto powered waste sludge (PWS) in a fed-batch system, J. Environ. Manage. 85 (4) (2007) 883–890.