

Biosorption of Pb (II) and Ni (II) Ions from Aqueous Solutions Using a Biomaterial

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Abstract: *An increase in population initiating rapid industrialization was found to consequently increase the effluents and domestic wastewater into the aquatic ecosystem. Heavy metals are major toxicants found in industrial wastewaters; they may adversely affect the biological treatment of wastewater. Conventional methods for the removal of heavy metals from waste waters are often cost prohibitive hence, there is a need for cheap methods for effluent treatment. Azadirachta indica leaves are converted to a fine powder for use as a biosorbent for the removal of metal ions in aqueous solution. In this work, the adsorptive interactions between Ni(II), Pb(II) and the powder were studied under a variety of conditions involving variations in pH, Pb(II), Ni(II) concentration, biosorbent amount, interaction time and temperature, all in single batch processes. The ability of Neem leaves to absorb metal ions as shown from the results can be used for the development of an efficient, clean and cheap technology for effluent treatment.*

Keywords: Neem leaves; Bioadsorbent; Effluents; Heavy metals; Wastewater.

1. Introduction

The increase in usage of heavy metals in industrial activities has caused the existence of them in waste water. For example lead and cadmium which the wastewater of industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp contains them [1, 2]. The inadequacy of our conventional methods of river dumping was further exposed by the death of fishes and even deforestation of nearby trees on the shore, affecting also, human and animal lives. Therefore, the study of the existing effluent disposal methods, facilities, and attitudes is essential in order to make a positive impact on our environmental hygiene. The discharge of metallic ions in industrial effluent is of great concern because their presence and accumulation have a toxic effect on living species [3]. Industrial wastewater containing metal ions such as nickel, lead, copper, zinc and aluminium are common because their metals are used in a large number of industries such as electroplating, batteries manufacture, mine, metal finishing, brewery, pharmaceutical, and so on. Heavy metals are toxic to aquatic organisms even at very low concentration. Most of these minerals were present in our environment only in minute amounts until recent centuries, when the orientation toward industrialization and production brought about our many technological advances. But technology, like medicine, has its side effects. At present, these toxic metals have polluted our atmosphere, our waters, our soil, and food chain. In the discharge of metal ions in industrial effluent using bio-adsorption process has been an area of extensive research because of the presence and accumulation of toxic carcinogenic effect on living species. The most common and harmful heavy metals are aluminium, lead, copper, nickel, chromium and zinc. They are stable elements that cannot be metabolized by the body and get passed up in the food chain to human beings. When waste is disposed into the environment, a further long-term hazard is encountered. There are possibly more problems from these metals, which

interfere with normal bodily function, than have been considered in most medical circles. Reviewing all of our vitamins and minerals has shown us that most every substance that is useful can be a toxin or poison, as well. Metals are known primarily and almost exclusively for their potential toxicity in the body, though commercially they may have great advantages. A conventional method for removing metals from industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion – exchange and adsorption. Most of these methods suffer with high capital and regeneration costs of the materials [4]. Therefore, there is currently a need for new, innovative and cost effective methods for the removal of toxic substances from wastewaters. Bio-sorption is an effective and versatile method and can be easily adopted in low cost to remove heavy metals from large amount of industrial wastewaters. Recent studies have shown that heavy metals can be removed using plant materials such as palm pressed fibers and coconut husk [5], waterfern *Azolla filiculoidis* [6], peat moss [7], duck weed *Wolffia globosa* [8], lignocellulosic substrate extracted from wheat bran [9], *Rhizopus nigricans* [10], cork and yohimbe bark wastes [11] and leaves of indigenous biomaterials, *Tridax procumbens* [12]. Apart from the plant based material chemical modification of various adsorbents, phenol formaldehyde cationic matrices [13], polyethylenamide modified wood [14], sulphur containing modified silica gels [12] and commercial activated charcoals also employed [15]. The Neem tree is noted for its drought resistance. Normally it thrives in areas with sub-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 does not tolerate temperature below 4°C. Neem is a life giving tree, especially for the dry coastal, southern districts. It is one of the 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 [16].

Table 1: Low-cost adsorbents and their typical removal

Type	Typical removal Reference
Grindih coal and coconut shell	Cd(II)
Fly ash/wollastonite	Cr(VI)
Fly ash	Cu(II)
Peat	Cu(II), Cd(II), Ni(II), Zn(II)
Hydrous feric oxide	Cd(II)
Fly ash	Victoria Blue
Wollastonite	Fe(II)
Peat	Pb(II)
Fly ash and impregnated fly ash	Phenol, <i>o</i> -cresol, <i>m</i> -cresol, <i>m</i> -nitrophenol and <i>p</i> -nitrophenol
Fly ash	Fluoride
Peat	CN ⁻ , Cr(VI), Ni(II)
Wollastonite	Ni(II)
China clay	Ni(II)
Groundnut husk carbon	Cr(VI)
Banana pith	Acid Violet
Beech leaves	Cd(II)
Coconut shell	Cr(VI)
Biogas residual slurry	Congo red
Biogas residual slurry	Rhoda mine-B, Acid Brilliant Blue, Direct Red, 12B, Cr(VI), Pb(II)
Peanut hull carbon	Hg(II), Cd(II), Pb(II), Ni(II), Cu(II)
Waste tea, Turkish coffee, Exhausted coffee,	
Nut shell and Walnut shell	Cr(VI), Cd(II), Al(III)
Leaf mould	Cr(VI)
Water hyacinth roots	Methylene Blue
Moss and copper-coatedmoss	Cr(III), Cr(VI)
Algae	Lauryl benzyl sulphonate
Orange peel	Congo Red, Procion Orange,
Chrome sludge	Acid Blue 29, Reactive Blue 2
Chitin	Acid Blue 193, Acid Blue 40
Tree fern	Zn(II), Cu(II), Pb(II)
Used tea leaves	Pb(II)
Kaolinite	Mn(II), Co(II), Ni(II), Cu(II)
Soya cake	Cr(VI)
Crab shell	Pb(II), Cd(II), Cu(II), Cr(VI)
Goethite-coatedsand	Cd(II)

2. Experimental

2.1 Preparation of adsorbent

Mature Neem leaves, collected from a number of tall Neem trees were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature in a shade. The leaves were then kept in an air oven at 333–343K for 30 h till the leaves became crisp. The dried leaves were then converted into fine powder (Neem leaf powder, NLP) by grinding in a mechanical grinder. The powder was sieved and the 53–74 μ m fraction was separated. This fraction was washed several times with double-distilled water till the washings were free of color and turbidity. After drying for several hours at room temperature, the powder was preserved in glass bottles for use as an adsorbent.

2.2 Characterization of the adsorbent

The Neem tree (*Azadirachta Indica*) is well known in India and neighbouring countries for more than 2000 years. The Neem is a fast growing, usually evergreen plant, which reaches a height of 15–20m and a trunk girth of 1.5–3.5m [64]. The unpaired, pinnate leaves are 20–40 cm long containing about 30 leaflets on both sides. The leaflets are 5–8 cm long with dark green colour and are asymmetrical in nature. The importance of Neem has been recognized by the US National Academy of Sciences, resulting in a 1992 report entitled “Neem – a tree for solving global problems” [64]. The Neem tree survives in the city atmosphere contaminated with pollutants emitted by vehicles [65]. The tree helps growing of other trees in barren land by improving soil fertility [64,66] and it prevents the loss of valuable topsoil by wind erosion, especially during the winter. The main chemical ingredients, present in various segments of the Neem tree, consist of a few related compounds belonging to the “triterpene”, or more specifically “limonoid” group of natural products. The main components in Neem are azadirachtin, salannin, meliantriol, nimbin and nimbidin. The structure of azadirachtin, which was the first active ingredient isolated from Neem and which has been projected as the main agent in Neem for fighting insects, is shown in Fig. 1 [63]

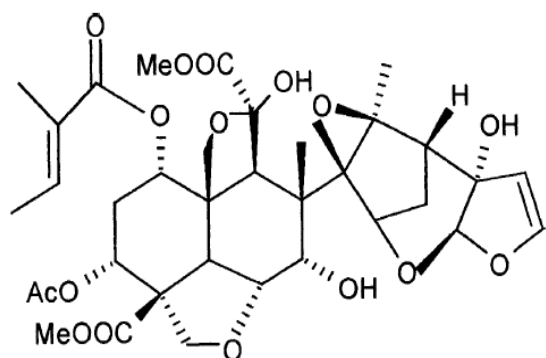


Figure 1: Structure of azadirachtin.

Other important constituents of Neem include a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc. [67]. The presence of polar groups on the surface [2,9,11] is likely to give considerable cation exchange capacity to Neem leaf powder. The physicochemical

characteristics of fresh Neem leaves have been reported [68] as follows

Moisture (%)	59.4
Fat (%)	1.0
Carbohydrates (%)	22.9
Calcium	510 mg/100 g
Iron	17 mg/100 g
Niacin	1.40 mg/100 g
Carotene	1998 μ g/100 g
Glutamic acid	73.30 mg/100 g
Aspartic acid	15.50 mg/100 g
Prolime	4.00 mg/100 g
Proteins (%)	7.1
Fiber (%)	6.2
Minerals (%)	3.4
Phosphorous	80 mg/100 g
Thiamine	0.04 mg/100 g
Vitamin C	218 mg/100 g
Calorific value (kcal/kg)	1290
Tyrosine	31.50 mg/100 g
Alanine	6.40 mg/100 g
Glutamine	1.00 mg/100 g

FTIR measurements (Perkin Elmer Spectrum RX I) for the Neem leaf powder showed the presence of a large number of functional groups, notably $-\text{OH}$ (3597–3600 cm^{-1}), $-\text{NH}_2$ (3399 cm^{-1}), $\equiv\text{CH}$ (3297 cm^{-1}), $>\text{C}=\text{N}-$ (1656 cm^{-1}), $\equiv\text{C}-\text{C}\equiv$, $\equiv\text{C}-\text{N}<$ and $\equiv\text{C}-\text{O}-$ (1160 cm^{-1}), $>\text{C}=\text{O}$ (1633, 1656, 1672, 1688, 1714 cm^{-1}), $>\text{C}=\text{C}<$ (1656 cm^{-1}), and $>\text{C}=\text{S}$ (1105 cm^{-1}). This is in conformity with the presence of various constituents of Neem leaves. Further, it was observed that if NLP was agitated with water for 6–8 h, dried and IR spectra taken again, no significant change in peak distribution and intensity was observed. The surface structure of the NLP particles thus remained stable through long periods of agitation with water. XRF analysis of the dried Neem leaf powder (Philips PW 1480, Rh anode and LiF 200 Crystal Analyzer) showed the presence of Ca, Cu, Fe, K, and Mn. However, due to absence of suitable standard, quantitative estimation could not be done. Determination of the surface area of the Neem leaf powder by the methylene blue adsorption method [69] yielded a value of 21.45 $\text{m}^2 \text{g}^{-1}$ for the specific surface area (average monolayer capacity for methylene blue adsorption on Neem leaf powder was 8.76 mg g^{-1} , cross-sectional area of the dye molecule $1.30 \times 10^{-18} \text{m}^2$). With respect to Pb(II) (average monolayer capacity 300 mg/g on Neem leaf powder at 300 K, cross-sectional area of Pb(II) ion $5.56 \times 10^{-20} \text{m}^2$ [70]), the specific surface area was computed to be 48.50 $\text{m}^2 \text{g}^{-1}$. Scanning electron microscopy (SEM, JEOL JSM-35CF) of the Neem leaf powder (Fig. 2) 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 Desorption and Regeneration

For carrying out desorption and regeneration studies, NLP was first saturated with Pb(II) by taking 4 g of NLP in a pyrex glass column (1.5 cm internal diameter) and continuously passing a solution of Pb(II) (60 mg/L) through it while keeping a constant head of 2 cm till the concentration at the outlet equaled the initial concentration. Desorption was carried out by passing successively (i) deionised water (pH 7.0) and (ii) dilute nitric acid (pH 4.0) through the column till Pb(II) could not be detected in the outlet in each case. For Ni- Ni(II) stock solution of strength 1000 mg/L was made by dissolving 4.953 g of the Nickel nitrate hexa-hydrate [Ni (NO₃)₂·6H₂O] in 1 L double distilled water. The pH of the Ni(II) solution was 5.6. All other solutions of various concentrations were made from this solution

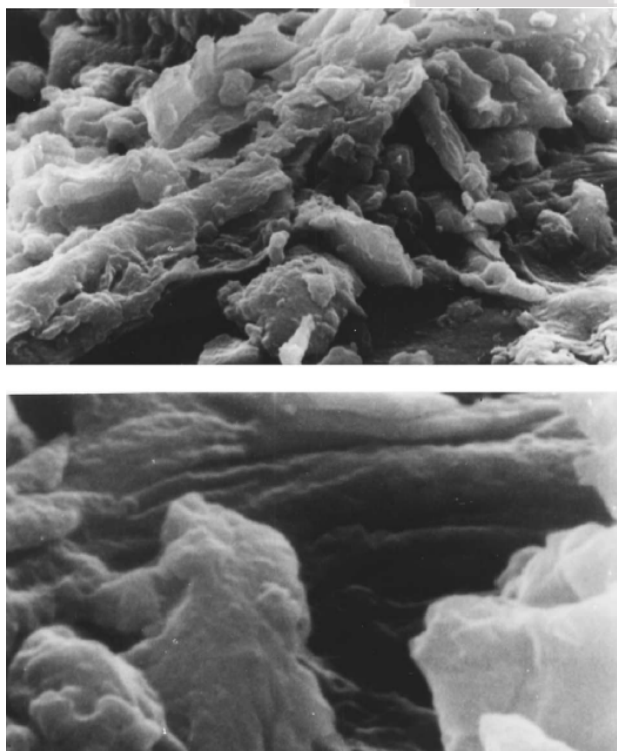


Figure 2: SEM photographs of Neem leaf powder at 4000× (top) and 20 000× (bottom) magnification.

3. Adsorption of Pb (II) from aqueous solution by Neem leaf powder

The health hazards due to the presence of lead in water are of extreme concern to the public, government and industry. Lead has toxic effects on the neuronal system and on the function of brain cells [17,18]. This underlines the need for developing methods for effective removal of lead from water at least below the regulatory level. Heavy metals in aqueous solution are usually removed by adsorption, ion exchange, coagulation, floatation, hyper-filtration, chemical precipitation, reverse osmosis, etc. Use of ion exchange resins requires considerable cost and adsorption on activated carbon is beset with problems related to regeneration of the adsorbent and recovery of the contaminants. These technologies, apart from being expensive, create secondary problems with metal-bearing sludge [19]. This has initiated research in new, low-cost materials for possible use as

adsorbents (Table 1) [20-61]. Such materials can be broadly classified into three categories: (i) natural minerals and similar materials like coal, peat, clays (kaolinite, wollastonite, sepiolite, etc.), red mud, sand, hydrous ferric oxide, etc., (ii) industrial wastes like fly ash, saw dust, biogas slurry, chrome sludge, electric furnace slag, etc., and (iii) biological materials like coconut shell, banana pith, beech leaves, orange peel, waste tea, water hyacinth, moss, algae, chitin, bagasse, tree fern, soya cake, olive cake, almond shells, cactus leaves, fly larva, cypress, chinchona and pine leaves, and in many cases their carbonized products. The efficiency of various bacteria, yeast, fungi, algae and bioadsorbents for heavy metal uptake has been observed over two decades [61]. The interesting features of the newly developed bioadsorbents are their high versatility, metal selectivity, high uptake, no concentration dependence, high tolerance for organics and regeneration [62]. These properties coupled with rapid kinetics of the biosorption systems have allowed engineering of new and highly effective yet simple industrial biosorbents for heavy metal removal processes. The present work has used an easily available plant-based renewable resource, dry Neem leaf powder, as an adsorbent for removal of toxic heavy metals such as Pb(II).

4. 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).

5. Results and Discussions

AAS showed the good percentage removal of the ions by the Neem leaves adsorbent. For the metal ions present in the water, 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 Pb²⁺ ions approximately 67. For Neem leaves, there was a progression in the rate of adsorption but it was not linear at any time. 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.

6. Effect of pH

pH is an important factor controlling the process of adsorption. In the present work, adsorption could not be carried out beyond pH 7.0 due to precipitation of Pb(OH)₂ and therefore, the experiments were done in pH range 2.0–7.0. For a typical experiment with Pb(II) solution of

concentration 100 mg/L, adsorbent dose of 0.4 g/L, and agitation time of 3 h, the extent of adsorption at 300K increased from 0.92 to 78.56% in the pH range of 2.0–7.0 (Fig. 3). It was seen that adsorption increased continuously with decrease in acidity till it reached an almost constant value between pH 4.5 and 5.5, after which the extent of removal of Pb(II) again showed an increase which might be due to onset of precipitation. Low pH depresses adsorption of Pb(II), which may be due to competition with H⁺ ions for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and Pb(II) ions replace H⁺ ions bound to the adsorbent or forming part of the surface functional groups such as OH, COOH, etc. It is also possible that the adsorption of the metal ion may take place through binding of both Pb²⁺ and Pb(OH)⁺ ions to the adsorbent surface [71]. Similar trend was reported for adsorption of Pb(II) on silica gel [72] when the extent of adsorption 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.

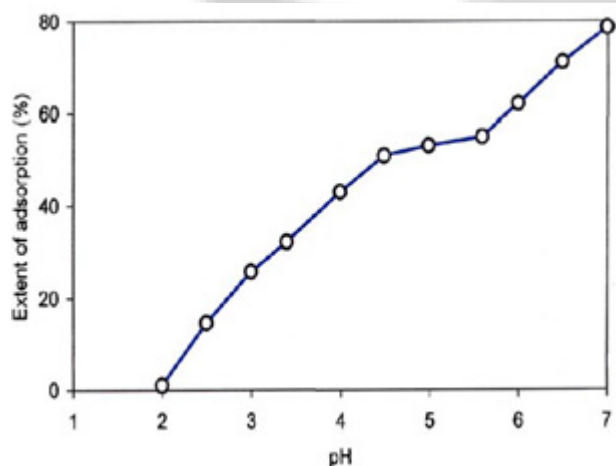


Figure 3: Effect of pH on adsorption of Pb(II) on Neem leaf powder at 300K (Pb(II): 100 mg/L, adsorbent: 0.4 g/L, agitation time: 3 h).

7. Effect of adsorbent amount and Pb(II) concentration

The variation in the extent of adsorption with the amount of adsorbent for a constant Pb(II) concentration (100 mg/L) at 300K is presented in Table 3. The adsorption increased rapidly as more and more of the adsorbent was added. The adsorption increased from 16.1 to 67.7% when the adsorbent amount was increased from 0.2 to 1.2 g/L for an agitation time of just 20 min. Increasing the amount of the adsorbent makes a large number of sites available leading to an increase in adsorption. With an increase in the concentration of Pb(II) at constant amount of adsorbent, the adsorption came down for the same agitation time (Table 4). The extent of adsorption decreased from 88.0 to 50.9% (time: 120 min) as Pb(II) concentration was increased from 50 to 150 mg/L for NLP amount of 0.8 g/L. Considering the heterogeneities of NLP surface and the possibility of multi-layer adsorption, these results could be explained on the basis of water–Pb(II), Pb(II)–NLP, and water–NLP interactions

Table 3: Variation in the extent of adsorption of Pb(II) at 300K on different amounts of Neem leaf powder (Pb(II) concentration 100 mg/L)

Time (min)	Extent of adsorption (%) for a adsorbent amount				
	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.2 g/L
20	16.1	29.4	38.2	48.5	67.7
40	22.6	38.2	44.7	54.8	72.5
60	30.0	45.2	50.8	62.8	76.6
120	44.7	58.0	65.7	77.6	85.6
180	56.7	63.7	75.7	84.8	89.4
240	60.5	66.9	78.3	88.9	92.3
300	60.8	67.3	78.8	90.7	93.0

Table 4: Variation in the extent of adsorption of Pb(II) at 300K for different concentrations of Pb(II) (Neem leaf powder 0.8 g/L)

Time (min)	Extent of adsorption (%) for Pb(II) concentration of				
	50 mg/L	75 mg/L	100 mg/L	125 mg/L	150 mg/L
20	74.9	62.2	48.5	34.9	21.6
40	80.5	68.6	54.8	38.6	27.9
60	82.3	76.7	62.8	46.8	36.1
120	88.0	84.4	77.6	61.6	50.9
180	92.7	89.6	84.8	68.7	58.1
240	96.6	94.1	88.9	72.8	62.2
300	99.7	96.9	90.7	74.7	64.1

8. Regeneration of the adsorbent

Desorption experiments showed that 80% of Pb(II) could be recovered simply by washing Pb(II)-loaded NLP with deionised water (pH 7.0) and the rest with dilute nitric acid (pH 4.0). The washed NLP after being thoroughly dried first in air and then in an air oven at 333K for 4 h could be reused as an adsorbent with nearly equal activity. The results of desorption are an indication that most of Pb(II) were held on NLP surface by comparatively weak adsorptive interactions while the rest might be held through strong chemisorptive or ion-exchange type of binding.

9. Adsorption of Ni (II) from aqueous solution by Neem leaf powder

Nickel is moderately abundant and is the twenty-second most abundant element by weight in the earth's crust [74]. It is mostly found along with sulphides of iron or copper [75]. Nickel is a common pollutant arising from many electroplating and vegetable fat producing industries, metal mining and processing as well as other industrial, urban and agricultural activities. Primary base metal smelters are major sources of Ni. The permissible limit of Ni(II) in drinking water is 0.5 mg/L [76]. Ni(II) can cause dermatitis, dizziness, headache, nausea and carcinogenesis. It is also toxic to the plants. Daily intake of nickel from food is 100–300 µg/day in most countries. Critical organs for nickel exposure in humans are the respiratory system, especially the nasal cavities, sinuses and the skin. Exposure to nickel has been known to cause occupational asthma in metal-plating workers [76,77]. Many other respiratory effects due

to exposure to nickel are reported, like chronic sinusitis and bronchitis, nasal septal erosions, decreased pulmonary residual capacity, increased respiratory frequency. Nickel and nickel compounds have a strong sensitizing potential on the skin, which is manifested by irritation, eczema and allergic contact dermatitis. Nickel carbonyl is the most acutely toxic nickel compound. Poisoning can lead to headache, vertigo, nausea, vomiting and severe pneumonia. Chronic irritative effects observed in nickel refinery and nickel plating workers include rhinitis, sinusitis, perforations of the nasal septum and bronchial asthma. High risks have been reported in nickel refinery workers and workers involved in processes with exposure to soluble nickel e.g. nickel sulphate [78], often combined with some exposure to nickel oxide. Various physicochemical and biological methods are in use for the removal of toxic metal ions from water and the practical application of these methods are dependent on their operational costs as well as difficulties associated with disposal of wastes generated [73,74–76]. These methods are required to address the inadequacy of the conventional treatment methods of chemical precipitation, evaporation, etc., for treating effluents at low metal loadings [73,77–79] and must represent a cost effective remediation technology [80–84].

10. Adsorption Experiments

Batch adsorption experiments were carried out in 100ml Erlenmeyer flasks by mixing a pre-weighed amount of AILP and 50 ml of aqueous Ni(II) solution of fixed concentration. The flasks were kept in a thermostatic water bath shaker and were agitated for a predetermined time interval at a constant temperature. The parameters such as pH, time of contact, adsorbent amount, metal concentration, and temperature were varied during different sets of batch experiments (Table 1). After adsorption, the

mixture was allowed to settle and centrifuged. Ni(II) remaining unadsorbed in the supernatant layer was measured with atomic absorption spectrophotometry (Varian SpectraAA 220). All experiments were repeated several times till reproducible results were obtained at least thrice.

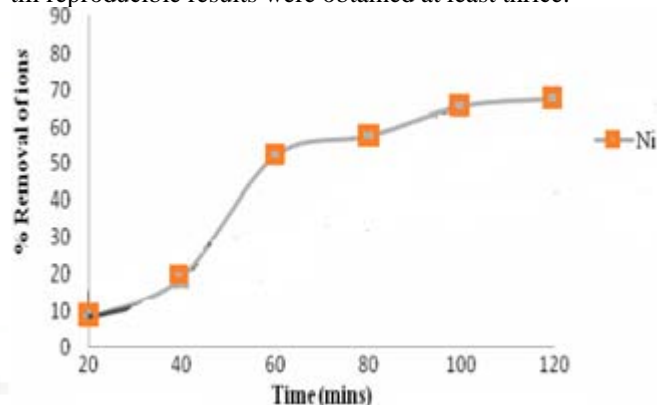


Figure 4: Variation of % removal of ions with Time

Figure 4, 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 Ni²⁺ ions with 67.5. For Neem leaves, there was a progression in the rate of adsorption but it was not linear at any time. Also, from figure 1, 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.

Table 5: Experimental conditions for the adsorption study

Type of study	AILP amount (g/L)	Ni(II) concentration (mg/L)	pH	Temperature(K)	Interaction time(min)
Effect of pH	1.0, 1.5, 2.0, 3.0, 4.0	50	2.0, 2.5, 3.0, 3.5, 4.0, 5.0	303	150
Influence of AILP Amount	1.0, 1.5, 2.0, 3.0, 4.0	10, 20, 30, 40, 50	5.6	303	150
Influence of Ni(II) concentration	1.0, 1.5, 2.0, 3.0, 4.0	10, 20, 30, 40, 50	5.6	303	150

11. Results and Discussion

11.1 Influence of Ph

The solution pH is one of the parameters having considerable influence on the adsorption of metal ions [86,87] because the surface charge density of the adsorbent and the charge of the metallic species present depend on the pH. In this work, the extent of Ni(II) biosorption on AILP was investigated for different amounts of AILP at constant Ni(II) concentration (50 mg/L) from pH 2.0 to 5.0 [fig.6]. Adsorption experiments were not carried out at pH higher than 5.6 (pH of Ni(II) aqueous solution) as precipitation of Ni(II)-hydroxide starts around pH 7.0, which introduces uncertainty into the interpretation of the results. The extent

of adsorption (%) of Ni(II) increased in the pH range, 2.0–5.0. At very low pH, the adsorbent surface will be covered with H₃O⁺ ions, and Ni(II) ions will have to compete with them for adsorption sites. That the uptake of nickel(II) is pH-limited has also been observed by other workers. For example, the adsorption capacity of Ni(II) on deactivated protonated yeast was shown to reach a maximum value at pH 6.75 [88]. Metal biosorption has been shown to be the result of ionization of negative functional on the basis of Ni(II) ions competing with the hydronium ions for the sorption sites. At low pH values, the concentration of H₃O⁺ far exceeds that of Ni(II) ions and hence, the surface will be covered with H₃O⁺ ions, leaving Ni(II) ions unbound. With the pH increasing, the number of hydronium ions come down making some of the sites available for Ni(II) ions and

sorption increases till Ni(II) starts binding with OH⁻ ions. The pH dependency of metal ion uptake by a biomass can also be justified by the association–dissociation of certain functional groups, such as the carboxylic groups. At low pH, the carboxylic groups remain in undissociated form and therefore, cannot bind the metal ions in solution, although they may take part in complexation and ion exchange processes [89].

11.2 Effect of adsorbent mass and adsorbate concentration

Ni(II) adsorption was influenced by the amount of AILP. With the amount of AILP varied from 1 to 4 g/L (Ni(II) 50 mg/L), adsorption increased from 75.2 to 88.4% for a constant agitation time of 150min at 303 K. On the other hand, for AILP amount of 1 g/L, the adsorption decreased from 98 to 75% when Ni(II) concentration was increased from 10 to 50mg/L with the same agitation time and adsorption temperature. The amount adsorbed per unit mass (q_e) increased gradually with increase in Ni(II) concentration for any AILP amount. This may be due to an increase in the number of Ni(II) per unit mass of AILP leading to higher uptake of the metal ions. The q_e values decreased with the increase in the adsorbent amount for any concentration of Ni(II) due to availability of less number of Ni(II) ions per adsorbent unit mass AILP has a larger adsorption capacity than a number of unconventional adsorbents [90] and this may be attributed to easily accessible surface functional groups for metal ion uptake. The chemicals in AILP contain a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc. [91] and FTIR measurements have shown the presence of a large number of functional groups, like OH, COOH, CO, etc., in AILP which might have contributed to the excellent sorption properties of AILP [90].

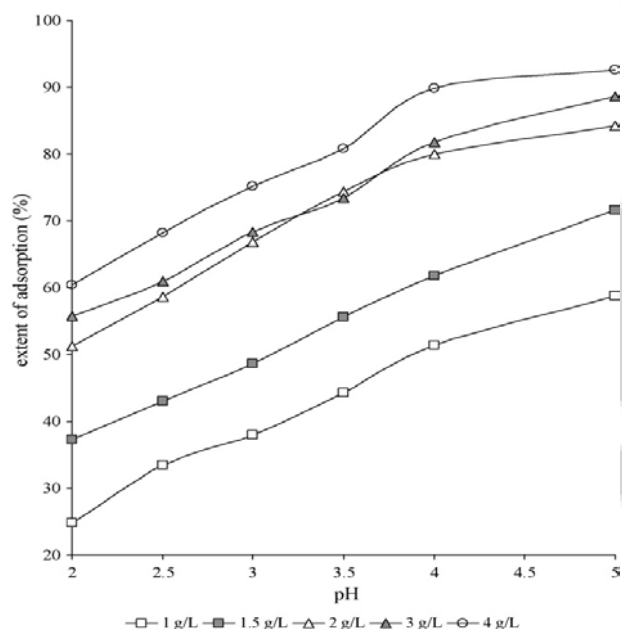


Figure 6: Variation of the extent of adsorption of Ni(II) on different amounts of AILP at 303K with pH (Ni(II) 50 mg/L, interaction time 150 min).

12. Conclusion

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 Ni²⁺ ions from the synthetic waste water. Neem leaves are efficient biomaterial for removal of some heavy metals from industrial wastewater. The percent removal of Ni²⁺ ions was 68.75 with an effective dose of 1.0 g of bioadsorbent (Neem leaves). This process can be effectively used in the heavy metals removal in industrial wastewater. It is found from this study that the powder made from mature, dried leaves of the tree, *A. indica*, could be a useful biosorbent for the removal of toxic metal ions from aqueous medium.

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