AZADIRACHTA INDICA (NEEM) AN ALTERNATIVE BIOSORBENT

M. S. Sulaiman

Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B 3011, Kano Nigeria.

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**ABSTRACT**

The selection of a potential biomass from the different types of low cost biomaterials that are readily available is a major challenge in the application of biosorption. Though the use of biomass for environmental purposes has been in practice for long, researchers are hopeful that the method will lead to an alternative economical method for the removal of heavy toxic substances from wastewater. Biosorption have been seen as a new technology, and has been put to use in various applications for a very long time. Neem tree (Azadirachta indica) is a distinctive mahogany tree among the Malecite family and is an inhabitant in the Southeast Asia regions and can also be found in different countries worldwide. For a very long time, its product have been widely used and proven to be effective in the biosorption of different metals, using either leaves, bark or the combination of both and also in other cases carry out chemical modifications using different modifying agents.

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1. INTRODUCTION

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials [1]. Biosorption is a physiochemical procedure that takes place in a certain biomass which allows it to accumulate and attach contaminants onto its cellular structure [2]. Though the use of biomass for environmental purposes has been in practice for long, researchers are hopeful that the method will lead to an alternative economical method for the removal of heavy toxic substances from wastewater. The efficiency of biomass depends on factors such as number of sites on the biosorbent material, their accessibility and chemical state, and the affinity between sites and metals [3]. Biosorption have been seen as a new technology, and has been put to use in various applications for a very long time. The most commonly used of biosorption is activated carbon filters. They have the ability to filter water and air by the process of binding the contaminants to their porous and surface area structure. Activated carbon structure is generated as the result of charcoal treatment with oxygen. Biosorption is a new alternative to other methods of heavy metal ions removal from wastewater especially industrial wastewater, due to their numerous disadvantages like high cost, partial metal removal and generation of sludge. Low cost, minimisation of sludge production, metal recovery, ability to regenerate the biosorbent and non-requirement of additional chemicals is what makes biosorption to have more advantages over other conventional methods [4]. Biosorbtents for metal removal comes under different types of categories such as fungi, bacteria, industrial wastes, algae and agricultural waste [5]. Hence, biosorption is a good applicant for the removal of toxic metals from large volume and lower concentration of aqueous solutions. The selection of a potential biomass from the different types of low cost biomaterials that are readily available is a major challenge in the application of biosorption. Neem tree (Azadirachta indica) is a distinctive mahogany tree among the Malecite family and is an inhabitant in the Southeast Asia regions and can also be found in different countries worldwide [6]. For a very long time, its product have been widely used and proven to be effective in solving variety of problems in relation to public health, agriculture, environmental pollution and also population control [7]. According to Neem foundation, [8], the fresh neem...
leaf has a moisture content of 59.4%, carbohydrates 22.9%, protein 7.1%, fibre 6.2%, minerals 3.4%, fats 1% and many other chemicals. Neem has certain powerful chemical ingredients; they are azadirachtin, salannin, meliantriol, nimbin and nimbidin. This chemical compounds were found to have a great metal binding capacity [9].

2. Heavy/Toxic Metal

“Heavy metals occur in immobilized form in sediments and as ores in nature” [10]. Heavy metals are within toxic substances attaining dangerous levels even at a low concentration [11]. Heavy metals (e.g. lead, copper, cadmium, zinc, chromium, etc.) are toxic even at low concentrations. As they are non-biodegradable, their threat is multiplied by their accumulation in the environment through the food chain [12]. This is due to their capability to attach with protein molecules and avoid reproduction of DNA and thus preventing the splitting of cells [13]. Urban industrial aerosols, animals waste, mining actions, agricultural and chemical substances are the most common sources of metals in environmental pollution. This metals can go into the water supply through industrial and drinking water or even from acid rain which has the ability to disintegrate soils and rocks, there by having their way into rivers, lakes and ground water [10]. Even though these metals have great application industrially, there is the issue of environmental concern, and the discharge limits of this toxic heavy metals have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/L [14]. As a result, it is necessary for industries to treat their industrial effluents before discharge into the environment.

2.1. Biosorption Mechanism

There are different mechanisms for biosorption which differ accordingly based on the adsorbent type used, biomass origin and the way it has been processed. “Metal sequestration follows complex mechanisms, mainly ion exchange, chelation, adsorption by physical forces and ion entrapment in inter- and intrafibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes”[15]. Basically different chemical active groups exist in the biomaterial that can sequester metals from the aqueous solution. The biomaterials present various molecular groups that can be exchanged with carboxyl, phosphate, amine and sulphate groups. These functional groups have the ability of metal complexation and some of the biosorbent materials are non-selective and attach to a wide range of heavy toxic metals without any particular priority, while other groups are specifically for certain metals depending on the chemical composition of the functional group [16]. Biosorption process by the range of functional groups and heavy metals complexation, ion exchange and physical adsorption have been studied by numerous researchers and all this mechanisms of biosorption can happen simultaneously.

Different adsorption peaks displayed by FTIR results indicates the presence of various functional groups on the surface of the Neem leaf powder. According to [17], 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 (1475.42 cm⁻¹), C=C, 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), sulphur compounds (1097.42 – 1339.47 cm⁻¹), alcohols and phenols, (1271 – 3627.85 cm⁻¹). Also, –OH (3597–3600cm⁻¹), –NH₂ (3399cm⁻¹), =CH (3297cm⁻¹), =C=N– (1656cm⁻¹), =C=C=, =C=N< and =C=O– (1160cm⁻¹), >C=O (1633, 1656, 1672, 1688, 1714cm⁻¹), >C=C< (1656cm⁻¹), and >C=S (1105cm⁻¹) as reported by [18]. After adsorption, in most researches carried out, there are shift in some certain cases in wave number indicating metal binding process on the Neem leaf powder surfaces. The relevance of a shift in the spectra is that there is an effect of metal adsorption on the functional groups [19].

The surface area of neem leaf powder was found to be higher and in some cases lower than other biosorbents. Surface areas of biosorbent have a greater influence on metal biosorption, especially when it is
higher. According to [20], found the specific surface area of neem leaf powder to be 21.45 m$^2$/g. Also the specific surface area is found to be 421 m$^2$/g by [21]. Based on the conclusion of many researchers, surface area and pore sizes might be involved in the biosorption mechanism and since neem leaf powder does not have a highly porous structure, biosorption might occur through chemical sorption with the presence of functional groups and ion exchange [22].

For evaluating the characteristics of adsorbent elements, SEM (Scanning electron microscope) and EDX (Energy-dispersive X-ray spectroscopy) are useful analytical equipment. Scanning electron microscopy (SEM) of the neem leaf powder showed that the powder was an assemblage of fine particles, which did not have regular, fixed shape and size [18]. EDX results according to [22] clearly indicate that Neem leaf powder consist of mainly C and O, and small amounts of, Ca, Mg, K, P and S.

![Figure 3 SEM images of Neem leaf powder](image3)

![Figure 4 EDX images of Neem leaf powder](image4)

2.2. Utilization of Neem Adsorbent

There are several researchers who studied the utilisation of *Azadirachta indica* leaf as an alternative adsorbent material for Cadmium (II) [20], Chromium (VI) [23], Lead (II) [18], and Copper (II) [17]. While [3] used the combination of neem leaves and stem bark. And also [20] use powdered neem leaf (*Azadirachta indica*) for the removal of Chromium (VI) from aqueous solution, batch process was used for the adsorption of Chromium (VI) process using metal ions of different concentration and also varying the adsorbent concentration, pH and temperature. Langmuir and Freundlich isotherms and various kinetic data were used for checking the suitability of the process. As low as 1.6 g dm$^{-3}$ of powdered neem leaf (*Azadirachta indica*) was able to remove up to 87% of Chromium (VI) in 300 minutes at a temperature of 27°C (300K), in the study, it was found out that the optimum pH ranges from 4.5-7.5.

In another different study by [23] the neem leaf (*Azadirachta indica*) physical structure and surface chemistry were modified by an activation process, this is to enhance the adsorption capacity. Another study by [20] also considered neem leaves as a potential adsorbent for Cadmium.
The biosorption of Chromium (VI) from Industrial Effluent using neem leaf powder was conducted by [24]. The equilibrium studies are systematically carried out in a batch process covering various process parameters that include agitation time, adsorbent dosage, temperature and initial concentration of chromium. The percentage removal was found to be 100% after 180 minutes agitation time, 29°C temperature, a concentration of 100mg/L and 1.00g of adsorbent dosage. The adsorption behavior was found to follow the Freundlich Adsorption isotherm. Also [25] uses neem leaves for the adsorption of Chromium (VI) from aqueous environment. Maximum removal efficiency of 85% was achieved at the optimum values of parameters. Also, [26] carries out a comparative study to remove Chromium (VI) using neem leaves and activated charcoal. The equilibrium studies were systematically carried out in a batch process covering various process parameters that include agitation time, adsorbent dosage, initial concentration of Chromium, volume of aqueous solution and pH of aqueous solution. Adsorption behaviour was found to follow the Freundlich’s Adsorption Isotherm in case of both the adsorbents but the Neem powder was proved to be more promising than Charcoal in the removal of Chromium.

The adsorption of Copper in a batch and continuous mode using neem leaves has been carried out [17]. The maximum adsorption capacity of neem leaf powder was found to be 18.29 mg/g. Langmuir equation represents the adsorption equilibria better than Freundlich. Also thermodynamics data indicated that the adsorption process is spontaneous, irreversible and endothermic. In another study conducted by Sulaiman and Garba [22], neem leaves powder was investigated for the removal of Copper (II) ions from aqueous solution. Characterisation of the Neem leaf powder was conducted, and the effects of contact time, particle size, Copper (II) ion concentration as well as effect of chemical treatment were studied. Batch biosorption experiments were carried out at a fixed adsorbent dosage of 1.0 g/L, initial ion concentration of 100 mg/L, a temperature of 333K and a pH range of between 5-6. Adsorption isotherms were modelled by the Langmuir and Freundlich isotherm equations, with the former providing a better fit for the data. Also a research carried out by [9], uses biosorption technology to remove Copper (II) ions from aqueous solutions. Mature leaves of neem (Azadirachta indica) were developed into powder form of size 32–45 μm and used as the biosorbent. Parameters varied include Copper (II) ion concentration and adsorption temperature. Thermodynamic studies showed that the system is spontaneous and endothermic in nature, based on the parameters of Gibbs free energy (ΔG°), biosorption enthalpy (ΔH°) and biosorption entropy (ΔS°) obtained, which gave values of −2.74, 26.70 and 0.07 kJ mol⁻¹ K⁻¹, respectively. The adsorption mechanism was found to be predominantly chemisorptions.

Neem leaf serves as a potential alternative adsorbent to remove copper ions from wastewater solution, this is due to the fact that the surface structures of neem leaf remains stable during long time agitation treatment and also can be obtained without excessive cost, highlighting its advantage as adsorbents [18].

The efficiency of neem leaf and stem bark powder in the removal of Zinc ions from waste water was conducted by [3]. The metal uptake was initially very fast, but gradually slows down indicating penetration into the interior of the adsorbent particles. The data showed that the optimum pH for efficient biosorption of zinc by neem leaves and stem bark was 4 and 5 respectively. Due to its outstanding zinc uptake capacity, the neem tree was proven to be an excellent biomaterial for accumulating zinc from aqueous solution. Also [27] uses neem bark for the removal of zinc ions from aqueous solution. The biosorption isothermal data were well interpreted by Langmuir model with maximum biosorption capacity of 33.49 mg/g on zinc ions. It was found out that the kinetics of the biosorption was better described with second- order kinetic and also suggested that inter-particle diffusion might also have a significant role in the biosorption process, slowing down the approach toward equilibrium.

Azadirachta indica (Neem) leaf powder was used as a biosorbent for removal of Cadmium (II) from aqueous medium by [20]. Adsorption increased from 8.8% at pH 4.0 to 70.0% at pH 7.0 and 93.6% at pH 9.5, the higher values in alkaline medium being due to removal by precipitation. The adsorption was very fast initially and maximum adsorption was observed within 300 min of agitation. The kinetics of the interactions was tested with pseudo first order Lagergren equation (mean k1 = 1.2×10⁻² min⁻¹), simple second order kinetics (mean k2 = 1.34×10⁻³ gmg⁻¹ min⁻¹), Elovich equation, liquid film diffusion model (mean k = 1.39×10⁻² min⁻¹) and intra-particle diffusion mechanism. The adsorption data gave good fits with langmuir and freundlich isotherms and yielded langmuir monolayer capacity of 158 mg g⁻¹ for the neem leaf powder and freundlich adsorption capacity of 18.7 L g⁻¹. A 2.0 g of Neem leaf powder could remove 86% of Cadmium (II) at 293K from a solution containing 158.8 mg Cadmium (II) per liter. The study on performance of low-cost adsorbent such as Neem leaves powder in the removal of Cadmium (II) and Lead (II) ion from aqueous solution was performed by [28]. The adsorbent material adopted was found to be an efficient media for removal of Cadmium (II) and Lead (II) ion with different parameter like Adsorbent dosages, Concentration and contact time etc. Also column studies were conducted with different contact time.
and the reduced concentration was determined using Atomic Absorption Spectrophotometer (AAS). It was found that the metal uptake capacity (amount of removal) of Cadmium (II) and Lead (II) ion decreased, but the adsorption capacity (percentage of removal) increased with the decrease in the concentration of Cadmium (II) and Lead (II) in the initial sample solution. Correlation coefficient and isotherm constant was also calculated from isotherm studies with different parameter.

The most widely and dangerous substance that has a great effect on the environment and human health is Lead (II). A batch adsorption process with several different concentrations of Lead (II) by varying amount of adsorbent, pH, agitation time and temperature was reported by [18]. The uptake of the metal was very fast initially, but gradually slowed down indicating penetration into the interior of the adsorbent particles. Both first-order and second-order kinetics were tested and it was found that the latter gave a better explanation. The experimental data closely followed both Langmuir and Freundlich isotherms. The adsorbent had a considerably high Langmuir monolayer capacity of 300 mg/g. A small amount of the adsorbent (1.2 g/L) could remove as much as 93% of Lead (II) in 300 min from a solution of concentration 100 mg/L at 300 K.

A chemically and physically pretreated neem leaves biomass was used for possible application in the removal of Lead (II) from wastewater by [29]. Neem leaves biomass was pretreated chemically with HgCl2, CH3COOH, CH3CHO, and Oxalic acid and heating, autoclaving, ultrasonic bath, and boiling were used for physical pretreatment. The Langmuir isotherm model was found to be useful to explain sorption mechanism. Sorption system followed second-order kinetic model, which indicates that the rate-controlling step is chemisorptions.

The ability of neem leaves to adsorb different metal ions from aqueous solution was carried out by [30]. The results obtained after contacting for 120 minutes showed that neem leaves achieved the percent removal of 76.8, 67.5, 58.4 and 41.45 for Copper, Nickel, Zinc and Lead ions respectively.

Like metals also, colored materials (dyes) contributes to the potential danger of bioaccumulation in the food chain [31]. Biosorption using neem material is among the different techniques used in the removal of these harmful dyes from the industrial effluents. A research carried out by [31] investigates the possibility of using neem bark and mango bark. The results indicated the feasibility of using neem and mango bark in the removal of malachite green (dye) from the waste water.

Color removal by neem leaves powder from methyl red and K2Cr2O7 solution was studied by [21]. 5gm/50ml and 5gm/40ml, the percentage removal was found to be 79.45% and 73.25% for Methyl Red Solution and K2Cr2O7 Solution. The maximum removal efficiency was observed up to 80% for prepared Neem leaves at optimum value of parameter. From the experimental finding it has been observed that the adsorbent material can be used successfully for removal of color.

3. CONCLUSION
This review clearly shows that Neem leaf serves as a potential alternative adsorbent to remove heavy/toxic metal ions from wastewater solution, this is due to the fact that the surface structures of neem leaf remains stable during long time agitation treatment and also can be obtained without excessive cost, highlighting its advantage as adsorbents. Also can be adopted and used widely in industries, and in addition to this, living organisms and surrounding environment will also benefit from the decrease or elimination of the potential toxicity created by the heavy metals.

4. REFERENCE


