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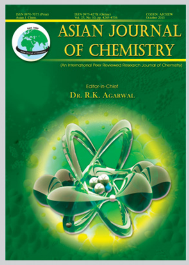

# Heavy Metal Removal from Aqueous Solution by Tamarind and Neem Leaves

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In this paper, biosorption of heavy metals by biosorbents such as tamarind leaves and neem leaves were studied for effluent treatment. The residual metallic ion concentrations were determined using an atomic absorption spectrophotometer. The results obtained after 150 min contact period showed that biosorbents such as tamarind leaves and neem leaves achieved the per cent removal of 64.8, 68.2, 64.5, 55.6 and 42.5 respectively for tamarind leaves and 61.2, 64.6, 61, 52.4 and 39.4 respectively for neem leaves for copper, zinc, nickel, chromium and lead ions respectively. The ability of biosorbents to adsorb metals ions as shown from the results can be used for the development of an efficient, clean and cheap technology for textile dyeing and bleaching effluent treatment along with solar evaporation.

**Key Words: Tamarind leaves, Neem leaves, Effluents treatment, Heavy metal, Wastewater treatment.**

## INTRODUCTION

The increase usage of heavy metals in industrial activities has caused the existence of them in wastewater. For example copper, zinc, nickel, chromium and lead which the wastewater of industries such as textile dyeing and bleaching industries, electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp contains them[1,2].

The inadequacy of the conventional methods of river dumping was further exposed by the death of fishes and even deforestation of nearby trees on shore, lake and pond 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 of their presence and accumulation have a toxic effect on living species[3]. Industrial wastewater containing metal ions such as copper, zinc, nickel, chromium and lead are common because their metals are used in a large number of industries such as textile dyeing and bleaching industries, electroplating, batteries, mine, metal finishing, brewery, pulp and paper industry, pharmaceutical and so on. Heavy metals are toxic to aquatic organisms even at very low concentration.

A conventional method for removing metals industrial effluents includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrance 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 wastewater. Biosorption is an effective and versatile method 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 fibres and coconut husk[5], water fern *Azlla 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 indigeneous biomaterials, tridax procumbents[12]. Apart from the plant based material chemical modification of various adsorbents, phenol formaldehyde cationic matrices[13], polyethyloamide modified wood[14], sulphur containing modified silica gels[12] and commercial activated charcoals also employed[15].

The tamarind tree and neem tree is noted for its drought resistance. Normally it thrives in areas with sub-arid to subhumid 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 groundwater levels. Tamarind and 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 ºC. It can tolerate high to very high temperatures and does not tolerate temperature below 4 ºC.

TABLE-1
EFFECT OF pH ON THE % REMOVAL OF HEAVY METALS

| pH | Copper | | Zinc | | Chromium | | Lead | | Nickel | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves |
| 5 | 55 | 46 | 56 | 54.2 | 58 | 55 | 48 | 46 | 56 | 48 |
| 6 | 58 | 56 | 61.2 | 57.6 | 61 | 58 | 54 | 52 | 60 | 50 |
| 7 | 64 | 61 | 64.8 | 61.2 | 62 | 60 | 56 | 53 | 64 | 54 |
| 8 | 57 | 56 | 58.2 | 58.1 | 55 | 52 | 50 | 49 | 58 | 52 |
| 9 | 50 | 48 | 56.4 | 56 | 52 | 50 | 50 | 48 | 52 | 48 |

The aim of the work is to study the removal of toxic heavy metal ions by tamarind leaves and neem leaves from synthetic wastewater and to offer this biosorbent as local replacement for existing commercial adsorbent materials[16].

## EXPERIMENTAL

**Preparation of biosorbents:** The tamarind leaves and neem leaves were dried for a period of 5 days. The leaves were cleaned with distilled water and dried at room temperature. The leaves were grounded with the grinding mill. The grounded leaf was sieved and was of particle size 0.25 to 0.5 mm. This was to allow for shorter diffusion path, thus allowing the adsorbate (tamarind and neem leaves) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption[17].

**Preparation of laboratory prepared solutions:** The initial concentration used was 5 ppm and the contact time was varied from 30 to 150 min.

A stock solution of copper, zinc, nickel, chromium and lead was prepared in distilled water with copper(II) sulphate, zinc(II) sulphate, nickel(II) sulphate, chromium(II) sulphate and lead(II) nitrate. 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[18].

**Adsorption experiment:** The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500 mL capacity were filled with 50 mL of the laboratory prepared solutions and 1 g of tamarind and neem leaves (grounded). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 150 min 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.

## RESULTS AND DISCUSSION

**Effect of pH:** Table-1 showed that tamarind leaves and neem leaves had a decrease in the adsorption rate for copper and zinc ions and an increase in the adsorption rate for chromium, lead and nickel ions when the pH of the laboratory prepared solutions was between the value of 5 and 7.

When alkalinity increased that is from pH value of 7 to 9 there was a further decrease in the rate of adsorption by tamarind and neem leaves for copper, zinc, chromium, lead and nickel ions in the synthetic wastewater. From the results obtained from the adsorption experiment it can be seen that the highest rate of adsorption by tamarind leaves and neem leaves was 64.8 and 61.2 removal for copper ion in the laboratory prepared solutions at pH value of 7. The reasons have been recommended to explain the decreased adsorption capacity at increasing adsorbent concentration such as availability of solute, electrostatic interactions and interference between binding sites[19].

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[20].

**Effect of contact time:** In the adsorption system, contact time plays a vital role irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the kinetics and dynamics of adsorption of copper, zinc, chromium, lead and nickel ions in the synthetic wastewater by tamarind leaves and neem leaves (ground), the adsorption experiments were carried out at different contact time (range: 15 to 150 min) at constant initial concentration. For all the metal ions present in the laboratory prepared solutions, there was a progression in the percentage removal of metal ions present in the wastewater with time. From the result of the adsorption experiment, copper ion had the highest per cent removal of 64.8 at the end of 90 min, followed by nickel, zinc, chromium and lead ions respectively by tamarind leaves and 61.2 % removal of nickel ion at the end of 90 min followed by copper, zinc, chromium and lead. For tamarind and neem leaves, there was a progression in the rate of adsorption but it was not linear at any time.

Table-2 showed that with increase in contact time, the adsorption rate of the tamarind and neem leaves increased. It was also observed that the rate of adsorption increased significantly for some of the metal ions present in the laboratory prepared solutions between 90 to 120 min of contact time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

**Effect of dose of adsorbent:** It is observed that the larger the surface area, the larger the amount of metal ion adsorbed

TABLE-2
EFFECT OF CONTACT TIME ON THE % REMOVAL OF HEAVY METALS

| Contact time (min) | Copper | | Zinc | | Chromium | | Lead | | Nickel | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves |
| 15 | 56 | 56.4 | 54.6 | 55.4 | 50.1 | 44.5 | 46.2 | 46.8 | 56.2 | 56.2 |
| 30 | 58 | 58.6 | 58.7 | 57.2 | 50.1 | 48.2 | 48.4 | 46.8 | 58.4 | 58.4 |
| 45 | 62 | 60.1 | 60.1 | 57.2 | 54.8 | 50.4 | 48.4 | 48.6 | 58.4 | 58.4 |
| 60 | 64 | 60.1 | 60.1 | 58.1 | 54.8 | 50.4 | 51.4 | 50.2 | 61 | 60.2 |
| 90 | 64.8 | 60.1 | 68.2 | 58 | 58.4 | 52.1 | 51.4 | 50.2 | 62.6 | 61.2 |
| 120 | 63 | 58.4 | 58.4 | 57.6 | 55.3 | 50.4 | 50.2 | 48.6 | 61.4 | 60.2 |
| 150 | 61 | 55.4 | 57.1 | 55 | 55.3 | 50.4 | 50.2 | 46.8 | 58.4 | 58.4 |

TABLE-3
EFFECT OF DOSE OF ADSORBENT ON THE % REMOVAL OF HEAVY METALS

| Dose of adsorbent ($g/L^{-1}$) | Copper | | Zinc | | Chromium | | Lead | | Nickel | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves | Tamarind leaves | Neem leaves |
| 10 | 46.4 | 52.6 | 42.6 | 46.2 | 48.4 | 51 | 38 | 40.2 | 44.6 | 32.5 |
| 20 | 64.8 | 61.2 | 64.6 | 60.2 | 60.2 | 58 | 54.3 | 52 | 60.2 | 46.8 |
| 30 | 64.8 | 61.2 | 64.6 | 61.8 | 60.2 | 60.2 | 58.2 | 55.2 | 62 | 60.1 |
| 40 | 64.8 | 61.2 | 64.6 | 61.8 | 60.2 | 60.2 | 58.2 | 55.2 | 62 | 60.1 |
| 50 | 65 | 61.2 | 64.6 | 61.8 | 64 | 60.2 | 60 | 57 | 62 | 60.1 |

(Table-3). The removal of copper, zinc, chromium, lead and nickel ions in the laboratory prepared solutions by adsorption on tamarind and neem leaves was studied at various dose of adsorbents (range: 10 to 50 g/L) with a constant initial concentration and at the optimum contact time (for tamarind leaves: 120 min and neem leaves: 150 min).

The percentage removal of copper, zinc, chromium, lead and nickel ions in the laboratory prepared solutions is noted to be exponentially increasing with increase in dose of adsorbent. This may be due to the increase in availability of the active sites due to the increase in the effective surface area resulting from the conglomeration of the adsorbent, especially at higher adsorbent concentration[21]. The relative percentage removal of copper, zinc, chromium, lead and nickel ions is found to be insignificant after a dose of 10 g/L of tamarind leaves, which is fixed as the optimum dose. The optimum dose of neem leaves 15 g/L. The amount of copper, zinc, chromium, lead and nickel ions adsorbed was observed to vary exponentially in accordance with a fractional power term of the dose of adsorbent, that is $(dose)^n$, where n = fraction. This suggests that the adsorbed copper, zinc, chromium, lead and nickel ions either blocked the access to the internal pores or caused particles to aggregate and thereby inducing the availability of active sites for adsorption[21,22].

## Conclusion

The relative adsorptive capacity (%) of various adsorbents namely tamarind leaves and neem leaves for the adsorption of copper, zinc, chromium, lead and nickel ions under optimum and identical experimental conditions by using biosorption technology was studied. The ground tamarind and neem leaves was very effective in the removal of heavy metals from the laboratory prepared solutions. Both the biosorbents are efficient biomaterial for the removal some heavy metals from industrial wastewater. The percent removal is around 64.8 and 61.2 with an effective dose of 20 and 25 $g/L^{-1}$ of bioadsorbent (tamarind and neem leaves). The process can be effectively used in the heavy metals removal in industrial wastewater since it is available as free of cost. From the studies, it is clearly observed that there may be of natural cleaning of pond and lake water, which is surrounded by tamarind tree and neem tree.

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