Available online at www.elixirpublishers.com (Elixir International Journal)

Pollution

Elixir Pollution 98 (2016) 42443-42446

ISSN: 2229-712X

Study of Adsorption of Copper Cu (II) Ions from Wastewater using Neem (Azadirachta Indica) Leaf Powder

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ARTICLE INFO

Article history:

Received: 27 July 2016;

Received in revised form: 23 August 2016;

Accepted: 2 September 2016;

Keywords

Biosorption,
Heavy metals,
Wastewater treatment,
Neem leaf powder,
Freundlich isotherm.

ABSTRACT

Heavy metal copper is the third most widely used metal in industries next to aluminium and iron. It finds its use in various industries like electroplating industries, battery manufacture, smelting, ship building, electrical transmission, construction of transportation vehicles, construction industry etc. The permissible limit of copper in water for human consumption as per World Health Organisation (WHO) is 0.05 to 1 mg/lit. Beyond this limit, the presence of Cu (II) ions is carcinogenic and toxic to human health. Therefore, there is a need to remove copper from waste effluents before allowing it to enter into any water body. The present study deals with the removal of copper by adsorption on neem leaves (Azadirachta indica) in batch experiment, by low-cost and high-capacity removal of Cu(II) ions from wastewaters. The influence of contact time, adsorbent dosage, effect of pH of solution and temperature effect were studied. Adsorption mechanism is found to follow the 'Freundlich' adsorption isotherm, indicating a multi layer adsorption process. Percentage removal of Cu (II) ions is found to be 88.516% at pH 3 for 0.1gm of Neem Leaf powder (NLP) dosage. The results obtained from this study shows that Neem leaf powder is an effective and economical adsorbent for copper removal from industrial wastewater.

Introduction

Industrial revolution marks a major turning point in history, almost every aspect of humanity was influenced in some way. It has taken a great leap forward since then in average income and population growth. This new modern age which is fuelled by rapid industrialisation has been very beneficial to mankind and has improved humanity's standards of living enormously. However, no revolution comes without a price, and the consequence mankind has to pay this time is the degradation of the environment, which if not looked into, could destroy mankind and all other life on earth. The industrial growth has caused water pollution which is one of the major concerns that requires much attention as heavy metals get contaminated into our earth's aquatic bodies.

Industries pollute the water to a maximum extent possible and this problem needs attention. Various industries like fertilizer, electroplating, pulp and paper mills, mining operations and metal processing plants are the major sources of heavy metal pollution. These heavy metals, for example copper, lead, zinc, chromium, nickel and aluminium are hazardous, and are toxic even at low concentrations and can accumulate through the food chain and cannot be metabolised by the body.

Heavy metals are divided into three groups, which include toxic metals (like copper, lead, zinc, chromium, nickel, etc.), precious metals (like palladium, silver, gold, etc.), and radionuclide's (like uranium, radium, etc.).

Copper (Cu) is classified as a toxic metal which is being extensively used and discharged from industrial processes. Copper being a major element needed for human health plays a vital role in the metabolism of lipids, carbohydrates and in proper functioning of the heart and blood vessels, but when it exceeds it becomes toxic. Excess amount of Cu(II) ions in the environment pose a substantial health hazard like liver and kidney failure, anaemia, gastrointestinal bleeding, nausea, dizziness, respiratory problems and even death. 1.5 mg/L is the maximum recommended quantity of Cu(II) ions that should be present in drinking water according to WHO (World Health Organisation). Strict environmental regulations have been imposed for the release or discharge of toxic heavy metals, by industrial activities in many countries[1]

Biosorption is an efficient and effective alternative to remove heavy metals from effluents. Various biomasses have been employed for the removal of these metals from waste effluents. [2 -9].Other materials that are found efficient and effective in the removal of pollutants from industrial effluents include orange bagasse [10], silica gel[11], Nanoparticles[12] , ionic liquid [13] and wheat straw [14]. The various advantages of biosorbents are their high versatility, high metal selectivity, minimal concentration dependence, high uptake, and cost-effectiveness. Moreover, these natural materials are abundantly available and can be disposed off without expensive regeneration due to their low cost. Some other examples of biosorbents include agricultural wastes, wood residues, sawdust, activated sludge, plant materials, bacteria, crustacean shells and natural minerals.

Neem (Azadirachta indica) is a plant that grows across the world and is used especially for medicinal purposes. However, the leaf, is found to contain abundant functional groups such as carbonyl, hydroxyl and amino groups which contain lone

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pairs of electrons needed for biosorption of cationic pollutants in solution. It has high potential in treating industrial effluents containing heavy metals. The present study deals with a biosorption of Cu(II)ions using neem leaves under various process parameters.

2. Methodology

2.1 Biomass Preparation

The Neem leaves were collected from Chintalavalsa village, Vizianagaram district, Andhra Pradesh, India. The leaves were rinsed with distilled water to remove dirt and impurities and then sun dried for 24 hours in a clean tray. Once the leaves were dried to brownish color, they were placed into a heating oven at $60^{\circ}C$ for about 18 hours for crisp drying. After that, the leaves were ground in electrical mixer and sieved in British Standard Sieve (BSS) from 150 to 200 mesh size to obtain particle size of 75 to 80 micron. The prepared neem leaves were stored in an inert plastic zip lock bag to hinder moisture absorbance from air.

2.2 Preparation of Solution

$CuSO_4.5H_2O$ was used as the source for copper stock solution. 0.5gm of $CuSO_4.5H_2O$ was dissolved in 1Litre of distilled water to obtain 1000 (mg/lit) of copper stock solution. The prepared solution was stored in volumetric flasks for further experimental use.100ml of this solution was used each time for adsorption experiment to study at various pH, adsorbent dosage, contact time and adsorption study.

2.3 Batch Biosorption Study

Batch adsorption experiments were carried out at various NLP dosages and contact time. NLP dosages used were 0.05, 0.1, 0.15, 0.2 g/lit. The NLP was mixed with 100ml of Cu (II) ion solution and agitated on magnetic stirrer equipment at a speed of 200 rpm for 80 minutes. Temperature was kept constant at 25°C by adjusting the dial on stirrer. For each adsorbent dosage, the pH was varied between 2 to 5. After every 20 minutes, solutions were withdrawn out for metal analysis for titration with EDTA. Metal analysis enabled the calculation of the total amount of Cu (II) ions adsorbed on the NLP.

2.4 Titration Analysis Procedure

For Metal analysis titration was carried out with EDTA. 0.01M. EDTA stock solutions were prepared and filled in burette. Conical flak of 100 ml was taken and 10ml of filtrate which was obtained after adsorption experiment was added into it followed by 20 ml distilled water, 3ml of pH-10 Buffer solution and a drop of FSBS indicator. The end point of titration was from purple to green color. The composition of metal left in filtrate was determined by the formula:

$M_1V_1/n1=M_2V_2/n2$ ------------------- (1)

M_1= Molarity of EDTA Solution

M_2=Molarity of Cu (II) ions to be obtained

V_1= Volume of EDTA run down

V_2= Volume of filtrate sample (10 ml)

Amount of Cu (II) adsorbed is determined by Adsorption Capacity which is given by:

$q= (C_o-C_e)/m_a$ --------------------------- (2)

Where,

- q – Adsorption capacity (mg/g)
- Co – initial concentration of metal in the solution (mg/L)
- Ce – equilibrium concentration of metal in the solution (mg/L)
- ma – adsorbent dosage (g/L)

2.5 Adsorpsion Isotherms

Adsorption isotherms are the most important tools used in describing the stability of adsorbate at a fixed temperature and pH. Adsorption units can be designed and operated using the isotherm model, which describes the various behaviour of adsorption [21]. Even, the application of biosorption technique in the commercial scale requires proper quantification of the biosorption equilibrium. Equilibrium of an adsorption is reached whenever there is an equal amount of ion adsorbed and desorbed. In this study, the Langmuir and Freundlich isotherms were used to describe the equilibrium characteristics of Cu(II) adsorption onto NLP.

The Langmuir isotherm [15] is given in equation (3) as below:

$q_e= q_m*(b*Ce)/(1+bC_e)$ -----------------------------(3)

Where:

q_e – equilibrium adsorption capacity (mg/g)

q_m – maximum adsorption capacity (mg/g)

b – Langmuir constant

Ce – equilibrium concentration (mg/L)

Its linearized form is given in equation (4). By plotting Ce/qe versus Ce, the Langmuir constants can be obtained. The constants give an indication of the adsorption capacity and efficiency.

$C_e/q_e = (1/q_m*b) + (C_e/q_m)$ ------------------------------------ (4)

There is also another constant for the Langmuir isotherm called the equilibrium or separation parameter, RL, which is defined as in equation (5). R_L is a dimensionless constant.

$R_L=1/ (1+bC_o)$ - -- (5)

Where:

Co – initial concentration (mg/L)

The R_L value indicates the nature of the Langmuir adsorption

Where,

Unfavourable adsorption gives a value of $R_L> 1$

Linear adsorption a value of $R_L = 1$

Favourable adsorption a value of $0 < R_L< 1$ and

Irreversible adsorption a value of $R_L = 0$

The Langmuir isotherm fulfils a monolayer adsorption process.

For multilayer adsorption, the Freundlich isotherm is used. It is given in equation (6) as below. Its linearized form is given in equation (7).

$q_e = k_f\, Ce^{1/n}$ ---(6)

Where:

- kf – Freundlich constant that indicates adsorption capacity
- n – Freundlich constant that indicates adsorption intensity

$lnq_e = lnk_f + (1/n)*lnC_e$ -------------------------------------(7)

For favourable adsorption, the fulfilling condition is $0 < n < 1$.

3. Results and Discussions

3.1 Effect of pH on biosorption

pH being a key controlling parameter in the biosorption process of metal ions from aqueous solutions, affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during the reaction.

Figure 1 shows the effect of pH on the removal of Cu (II) ions from aqueous solution using neem leaf powder. The results showed that the biosorption was low at strong acidic medium and adsorption capacity increases with increasing pH values, until a certain value was reached. Bisorption increases between 2 to 5 pH. The optimum pH value was chosen to be 5 to avoid the precipitation of Cu (II) ions. The reason being Cu(II) ions precipitates above pH 5 in the form of $Cu(OH)_2$ and bisorption cannot occur.

3.2 Effect of contact time on biosorption

Contact time is a fundamental parameter in all transfer phenomena of biosorption. To establish the equilibration time for maximum uptake of copper, the percentage removal of copper ions on the adsorbent were studied as a function of contact time. The results are shown in figure 2. It shows that the rate of adsorption of copper was rapid at the beginning. The removal of copper rapidly occurs up to 87.01% initially and then increases to 88.516% then remains constant further for 0.1gm of NLP Dosage. For 0.05g NLP dosage the removal % of copper ions was from 66.04% to 72.53%. It proves that removal % efficiency decreases after 40 minutes. So the optimum Contact time is 40 minutes. There is no significant change in the uptake of copper by the adsorbents after about 40 min although all the experiments were carried out up to 80 min. This can be attributed to saturation of the adsorbents by the copper.

3.3 Effect of concentration on biosorption

As shown in figure 3, there is slight and gradual increase in percentage removal with increasing dose for different pH values. It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent. But there is slight decrease in percentage removal at pH 3 on increase of adsorption dosage. For pH 3 the optimum adsorption dosage is 0.1gm NLP.

3.4 Effect of temperature

The adsorption increases with increase in temperature up to 60°C and then decreases. This is because of the occurrence of greater mass transfer by collisions at higher temperature. The percent removal of ions increases with increase in temperature and this suggests that the process is an endothermic process. After 60°C, decrease in percent removal may be due to inactivation of hydroxyl, carboxylic, carbonyl, amino and nitro groups at higher temperature. So, the optimum temperature for higher % removal of Cu (II) ions on Neem Leaf Powder is 60°C, as shown in figure 4.

3.5 Langmuir Isotherm

The Langmuir Isotherm is given in figure 5, (Ce versus Ce/qe). The equation obtained from the plot is y=0.526x-19.28 with regression value of 50.5% and Langmuir constants are given below.

qm(mg/g)	1.9011 mg/g
b(L/g)	-0.02782
R^2	0.505
R_L	-0.096061 (not favourable)

3.6 Freundlich Isotherm

The Freundlich Isotherm plot is shown in figure 6,(lnCe versus lnqe). The equation obtained from the plot is lnqe =1.619lnCe+2.739 with regression value of 69.1% and Freundlich values are given below.

Kf(mg/g)	16.3299
n	0.617<1 (favourable)
R^2	0.691

As a conclusion, NLP was found to be a reliable biosorbent for the removal of Cu (II) ions from solutions. Adsorption using lower NLP dosage was found to give larger adsorption capacity values.

In this study, the optimal dosage of NLP was found to be 0.1g/L, which was able to absorb 88.516 % of the Cu (II) ions from the solution at temperature 60°C and pH 3.

This is relatively high compared to many other biosorbents. The adsorption capacity may be improved by altering the experimental conditions such as the concentration, pH and temperature. The adsorption favourably fit a Freundlich isotherm, indicating a multilayer adsorption process of Cu (II) ions on NLP.

Acknowledgement

The authors are thankful to the Principal, Dr. K.V.L. Raju and the management of MVGR College of Engineering, Vizianagaram, (A.P.) for their constant support and encouragement.

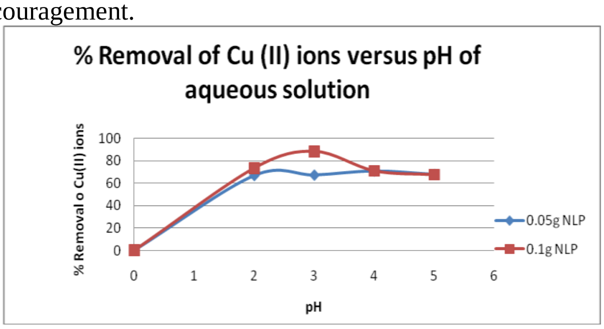

Figure 1

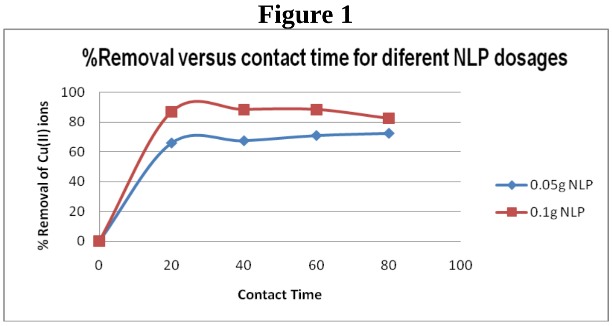

Figure 2

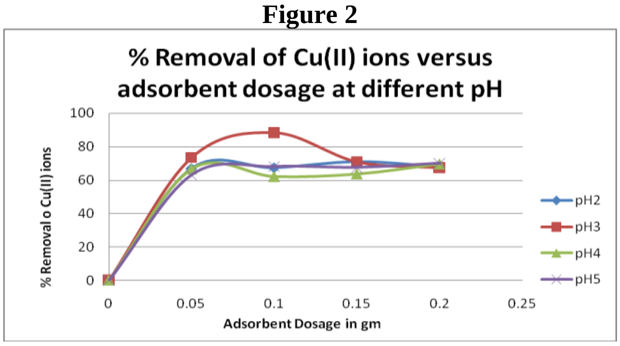

Figure 3

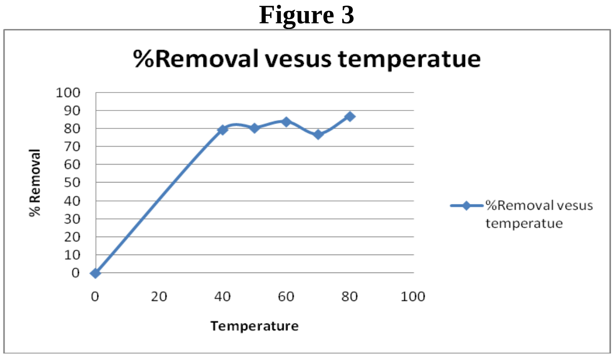

Figure 4

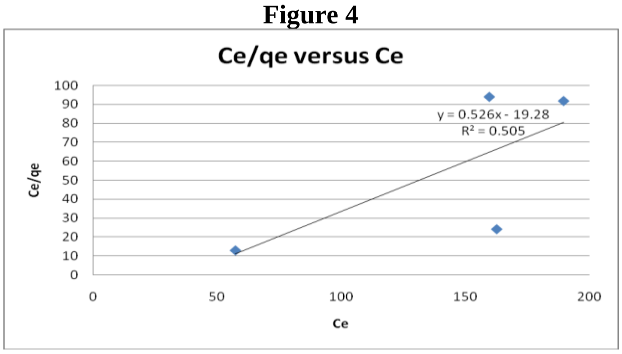

Figure 5

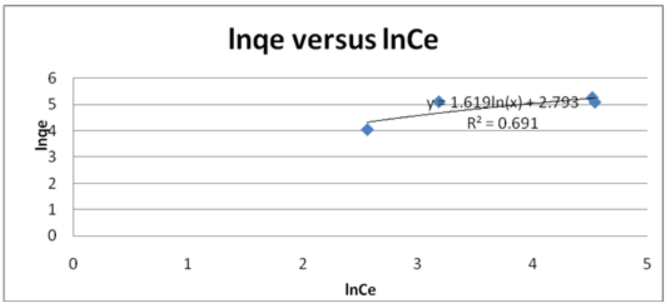

Figure 6

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