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ADSORPTION THERMODYNAMICS OF Cu(II) IONS FROM WASTE WATER USING NEEM-LEAF BASED BIOSORBENTS

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ABSTRACT

Adsorption of Cu(II) ions onto a non-conventional plant biosorbent, Neem (*Azadirachta indica*) Leaf Powder (NLP), was investigated in batch adsorption experiments. Process parameters which include initial metal ion concentration and temperature of solution were varied in order to evaluate their influence on the adsorption process. The pH and NLP dosage were kept constant for the all experiments carried out. Results obtained indicate a spontaneous and endothermic adsorption which favours the adsorbate concentration of 500 mg/L at an optimum temperature of 333 K with a residence time of 60 to 90 min. At this optimal condition, the maximum adsorption capacity was found to be 446.5 mg Cu(II)/g NLP. The surface area of NLP is about 2.3102 m²/g, signifying an occurrence of chemisorption and ion exchange of Cu(II) ions on functional groups. Besides that, the adsorption of Cu(II) ions on NLP was found to fit Freundlich isotherm while following a pseudo-second order model. The study shows that NLP is a highly efficient biosorbent for adsorbing Cu(II) ions. The technology is promising and may be developed further for the removal of other heavy metals from wastewater.

Key Words : Neem leaves, Cu(II) ions, Wastewater treatment, Heavy metals, Biosorption

INTRODUCTION

Humanity has taken a great leap forward since its birth on this earth. The rise and fall of many human civilisations has brought forth the dawn of science and technology. This new modern age which is fuelled by rapid industrialisations 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. One main concern that requires much attention is the contamination of heavy metals into our earth's aquatic bodies. Contemporary industries such as the fertiliser

industries, pulp and paper mills, electroplating operations, mining operations and metal processing plants are the sources of heavy metal pollution¹⁻³. These heavy metals, for example copper, lead, zinc, chromium, nickel and aluminum are hazardous, as they remain toxic even at low concentrations and can accumulate through the food chain as they are non-biodegradable and cannot be metabolised by the body^{4,5}.

Heavy metals are divided into three groups, which include toxic metals (for example copper, lead,

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zinc, chromium, nickel, etc.), precious metals (for example palladium, silver, gold, etc.), and radionuclides (for example uranium, radium, etc.). Toxic metals are considered the most hazardous, both in ecological and health concerns. The heavy metal studied in this paper is copper (Cu), which is classified as a toxic metal and it is still extensively used and discharged from industrial processes⁵. Copper was identified as a pollutant by the United States Environmental Protection Agency (USEPA) since the 1980's and have since updated their criteria recently in 2007⁶. Copper generally exist in aqueous solutions like wastewater as free Cu(II) ions, which is easily absorbed into living organisms⁷. The concentration of Cu(II) ions of 1.3 mg/L is considered the minimum concentration before triggering a water quality control and monitoring system⁸.

Wastewater treatment is a necessity to achieve the future of complete sustainable development. Appropriate methods have to be identified beforehand to ensure its efficiency and capabilities. Heavy metal ions from aqueous solutions can be removed by physical, chemical and biological technologies³. Current conventional methods include chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon and others^{3,4,9,10}. However, these methods suffer drawbacks in terms of economic cost and feasibility. The recognition of biotechnological potential has urged researches to obtain alternative methods of heavy metal removal techniques which can benefit both the environment and the economy. These have lead to an up and coming technology called "biosorption".

Biosorption is defined as a process employing a suitable dead biomass to adsorb heavy metals from aqueous solutions¹¹. The high affinities between the adsorbate, in this case the heavy metal ions, and the biosorbents, attracts and binds them in different mechanisms¹². These mechanisms include physiochemical mechanisms, ion exchange combinations, complexation, coordination, adsorption, electrostatic interaction, chelation and micro-precipitation^{3,13,14}. Though newly discovered, biosorption provides many advantages over the current conventional methods available. Firstly, the use of biosorbents is cheap as it utilises material which is abundant or in some

cases waste materials^{9,15}. In addition, there is a wide array of available biosorbents, some of which can bind and collect heavy metals with no specification, while there are also others which are specific for certain types of metals^{15,16}. Biosorbents also have regenerative abilities, where it can be reused once the heavy metals adsorbed is recovered and recycled¹⁵. Besides that, biosorption is also highly effective in adsorbing metallic ions in low concentrations, thus allowing the collection of heavy metals from dilute solutions¹⁷. Currently the biosorbents that are being considered are rice husk¹⁸, barks¹⁹, leaf powders²⁰, tree ferns²¹, groundnut shells²², macadamia nutshell²³, holly oak²⁴, paper mill sludge²⁵ and others. Though biosorption provides an edge over other conventional methods, it still requires further studies to obtain its optimum pH, dosage, particle size, agitation, and temperature²⁶.

Plant leaves are considered the cheapest, most abundant and renewable natural source of biosorbents. However, not all plant leaves can be efficient at adsorbing heavy metals into its structure. They have to have the right active group that can adsorb heavy metal ions. One such plant that is being currently researched is the leaves of the neem tree. Research of heavy metal removal with neem leaves are very limited²⁷⁻³⁰. Thus, the aim of this study is to conduct some research on the capability of NLP to adsorb Cu(II) ions from aqueous solutions. The findings may be helpful for future researches using NLP.

MATERIAL AND METHODS

Fresh neem leaves were first gathered from a local tree. The leaves were then washed and cut into sizes of 1 cm x 1 cm and sun dried for about a day in a clean tray. Once the leaves were dried to a brownish colour, they were placed into a Memmert Oven at 60°C for about 24 hours for crisp drying. After that, the leaves were ground in the Retsch SM100 cutting mill and sieved in the Retsch ZM200 ultra centrifugal mill to a constant particle size range of 80-100 µm. The prepared NLP was then stored in an inert plastic bottle with silica-gel desiccant to hinder moisture absorbance from the air.

The metal ion solution used in this study was from copper (II) chloride. During the temperature

variation experiments, 1000 mL of stock copper (II) chloride solution with a concentration of 100 mg/L was prepared. The preparation was done by diluting 1000 mL of deionised water with 0.1 g of hydrated copper (II) chloride salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (purchased from HmbG Chemicals) in a volumetric flask. Standard solutions of 10 mg/L, 20 mg/L and 30 mg/L were prepared later by appropriate dilutions for the spectroscopic calibration with the Perkin Elmer, Analyst 400, Atomic Absorption Spectrometer (AAS).

The concentration variation experiments required 1000 mL of a stock copper(II) chloride solution of 500 mg/L. Similarly, the solution was prepared by diluting 0.5 g of hydrated copper (II) chloride salts with 1000 mL of deionised water in a volumetric flask. The 500 mg/L solution was then diluted to obtain the 100 mg/L, 200 mg/L, 300 mg/L, and 400 mg/L Cu (II) solutions. Likewise standard solutions were also prepared in the same manner.

The adsorption was done in a batch process. Firstly, a conical flask was filled with 100 mL of copper (II) chloride solution at 100 mg/L concentration. Then, the water bath shaker was set at 30°C with its agitation rate at 125 rpm. When the temperature had stabilised, 0.1 g of NLP was added into the conical flask and the stopwatch started immediately. For the first half an hour, in every 10 minute intervals, 1 mL of solution was extracted for metal ion testing with the AAS. Once the time reached 30 minutes, the interval was then extended to 30 minutes for the subsequent 4 hours. Once the experiment was over, the solids in the conical flask were filtered out and dried. They were then brought for analysis with the Scanning Electron Microscope-Energy Dispersive X-Ray spectrometer (SEM-EDX).

Experiments were repeated five times with different temperature settings of the water bath, which include 40°C, 50°C, 60°C, 70°C and 80°C. From the results, the optimal temperature was obtained and the concentration variation experiments were carried out with Cu (II) solutions of 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500mg/L.

RESULTS AND DISCUSSION

All data and results obtained from the studies were tabulated and the appropriate graphs and isotherms were plotted. The effects of temperature and concentration variation on the Cu (II) adsorption capacity of NLP is discussed in this section.

Effect of temperature

Referring to **Fig. 1**, equilibrium adsorption capacity increases from 20 to 80 mg/g as temperature rises from 303 to 333 K. This is because of the occurrence of greater mass transfer by collisions at high temperature. While the frequency of collision increases, the probability of successive collision leading to adsorption gets higher. As a result, more ions are adsorbed to give higher adsorption capacity at equilibrium. The extent of adsorption increases with respect to temperature suggests that adsorption is endothermic instead of exothermic. Chemisorption occurs when the extent of adsorption is enhanced at elevated temperature. It is a short and strong interaction involving orbital overlapping and electrons exchange. An increase of temperature causes an activation of active sites for adsorption and high temperature reduces mass transfer resistance for ions to diffuse to binding sites^{30,31}. After 333 K, equilibrium adsorption capacity decreases to 23 mg/g. The reduction might be the reason of lignin and hemicelluloses breakdown at high temperature, causing a change in the chemical state of bonds available for binding. Most potential sorption sites are situated on cellulose, hemicelluloses and pectins on the cell wall. Their sorption characteristic is due to the presence of active functional groups such as hydroxyl, carboxylic, carbonyl, amino and nitro groups³². From the graph, optimum temperature was found to be 333 K (60°C), which has the highest equilibrium adsorption capacity of 80 mg/g.

Effect of Cu (II) ion concentration

For the concentration variation experiments, the equilibrium adsorption capacity increased linearly from 66 to 446 mg/g as shown in **Fig. 2**.

The solution contains more ions at high concentration, inducing a steep concentration gradient from the bulk of liquid to the surface of adsorbent. Thus, more ions diffuse to fixed available binding sites, causing more ions adsorbed per mass of adsorbent. With an adsorbent dosage of 1 g/L and ion concentration

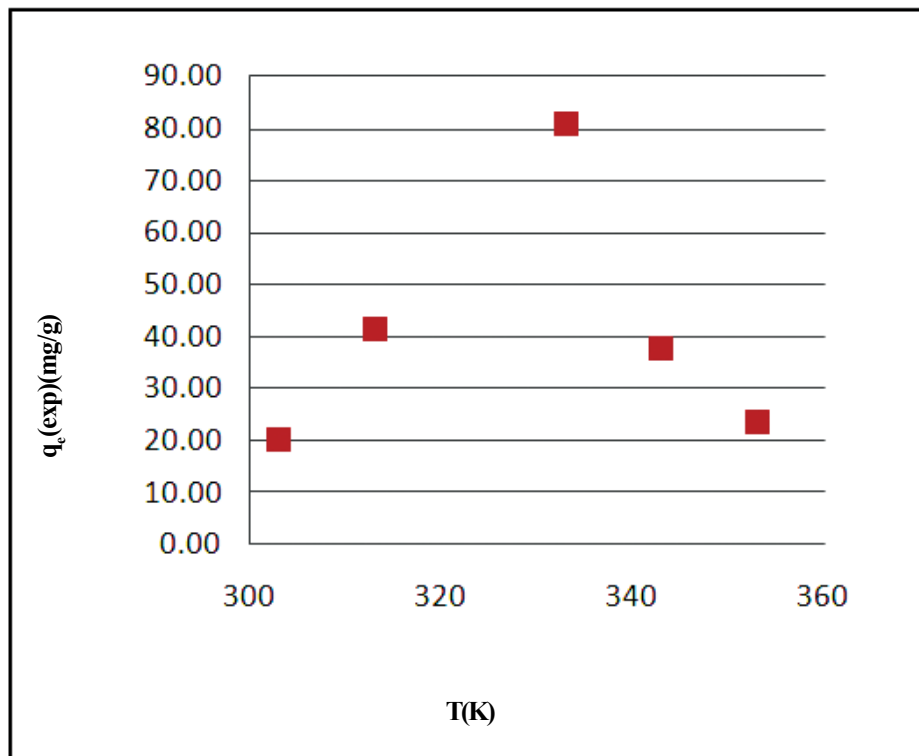


Fig. 1 : Variation of the extent of Cu (II) ions adsorption on NLP for metal ion concentration of 100 mg/L and adsorbent dosage of 1 g/L

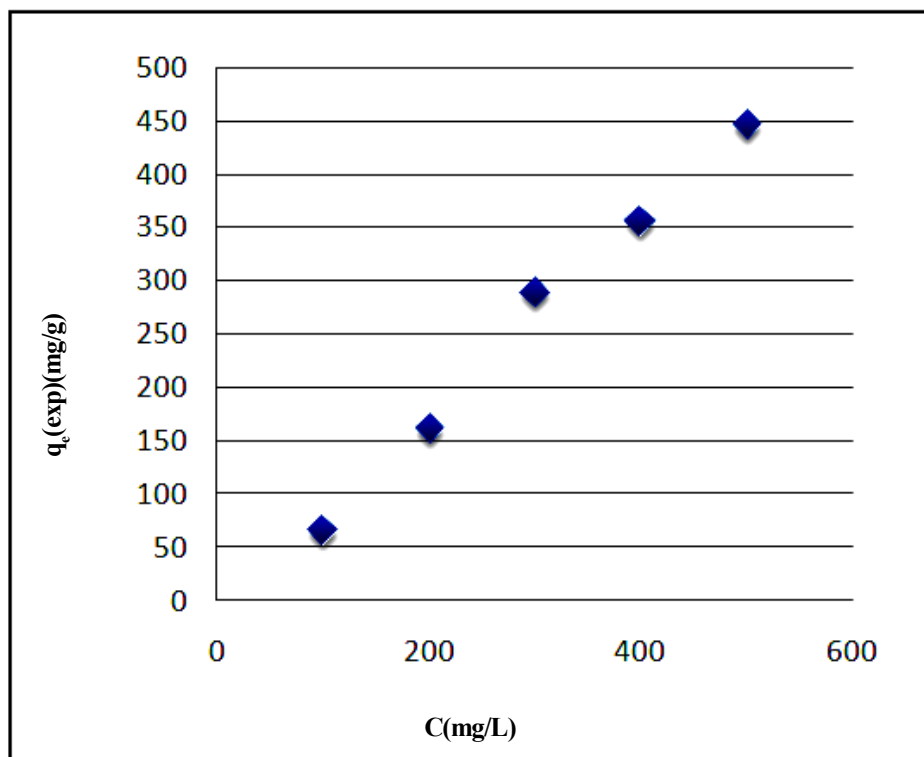


Fig. 2 : Variation of the extent of Cu (II) ion adsorption on NLP at 333 K at an NLP dosage of 1 g/L

of 500 mg/L, the adsorbent has still not reached its saturation point. This suggests that 1 g/L of NLP has the capability to treat an effluent with Cu (II) ion concentration of more than 500 mg/L before its saturation is reached. However, care should be taken while designing because the phenomenon could alter when the system is employed to adsorb Cu (II) ions from a multi-component system. Intensive competition with other species will reduce its capacity greatly. A similar trend was observed when pretreated red rose distillation sludge was employed to adsorb Cu (II) and Zn (II) ions at 303 K at an adsorbent dosage of 1 g/L²⁶.

Thermodynamic studies

Thermodynamic study is carried out to verify on the feasibility and mechanism of Cu (II) ion biosorption on NLP. Three parameters employed for the analysis are enthalpy change, ΔH , entropy change, ΔS and the change of Gibbs free energy, ΔG . These parameters are determined in Eq. 1.

$$\log \frac{q_{e(\text{exp})}}{C_e} = \frac{\Delta S}{2.303R} - \left(\frac{\Delta H}{2.303RT} \right) \quad (1)$$

A plot of $\log \frac{q_{e(\text{exp})}}{C_e}$ over $\frac{1}{T}$ is produced to determine ΔH and ΔS from the intercept and slope of plot, where $q_{e(\text{exp})}$ is the equilibrium adsorption capacity in mg/g; C_e the equilibrium ion concentration in mg/L; ΔS the entropy change in kJ/mol.K; R the universal gas constant at 8.314 J/mol.K; ΔH the enthalpy change in kJ/mol and T the temperature in K.

The change of Gibbs free energy is calculated as given in Eq. 2²⁷.

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

The change of Gibbs free energy is a measure of spontaneity of reaction. Negative value implies that the reaction is feasible, occurs spontaneously to forward reaction and is thermodynamically favourable. Enthalpy change is an energy interaction with the environment while the reaction takes place. An exothermic reaction emits heat and therefore final energy state is lower than initial energy state to give a negative enthalpy change and vice versa. Entropy is an indication for the system's degree of freedom and on the reversibility of the system. For a system communicating to an

external heat sink or source, entropy must increase or remain the same. As the entropy increases, uniformity of system is improved. Hence, the process occurs spontaneously. Entropy change is a measure for a reversible and irreversible heat flow through a boundary. For a small temperature difference, the entropy change is zero denoting reversible heat flow. As final entropy is greater to give positive entropy change, there is an irreversible heat flow through the system.

From the Van't Hoff plot, the change of enthalpy, ΔH is calculated to be 568.9 kJ/mol and the change of entropy, ΔS is 5.03 kJ/mol.K. The enthalpy change of adsorption is commonly known to be negative because adsorption is exothermic in nature. This is logical because energy evolved as bonds are formed between ions and the active functional groups on the adsorbent. A positive enthalpy change obtained implies that the adsorption on Cu (II) ions on NLP is endothermic. An input of energy is required to bring about the bond formation. This is because the bonding is short and as a result, energy is needed to overcome the repulsive force of attraction as ions bind in a short distance from adsorbent. This agrees with the optimum temperature of 333 K obtained in the study, as external source of heat energy is needed for the endothermic reaction to occur. High temperature favours an endothermic reaction and it is deduced that chemisorption occurs due to the formation of stronger bonds which remain bonded at high temperature.

The entropy change is positive as mentioned earlier. For the biosorption system of Cu (II) ions on NLP, the heat flow is irreversible due to an increase of entropy³³. The system occurs spontaneously due to a rise of entropy as the system shifts to a state which is more uniform and stable. All the change of Gibbs free energy is negative as shown in **Table 1** revealing again that biosorption system is spontaneous in nature for adsorption to occur. The system emits free energy to surrounding and transits to a thermodynamically stable energy state. The change of Gibbs free energy increases according to temperature suggests that the reaction is energetically favourable at high temperatures.

Isotherm and kinetic studies

Table 1 : The change of Gibbs free energy calculated at varied temperature for Cu (II) ion adsorption on NLP at solution concentration of 100 mg/L and NLP dosage of 1 g/L

T [K]	ΔG [kJ/mol]
303	-955.176
313	-1005.48
323	-1055.78
333	-1106.07
343	-1156.37
353	-1206.67

For this study, isotherms were plotted and kinetic studies were also carried out. As for the isotherm, it was found that the system fit a Freundlich relationship, indicating a multi-layered adsorption of Cu(II) ions on NLP. And for kinetics, it was found that the system followed a pseudo-second order model with chemisorption as the rate-determining step. This part of the study is reported in literature elsewhere.

CONCLUSION

Following are the conclusion drawn from the discussed results obtained in this study :

1. The optimum adsorption temperature for was found to be 333 K.
2. Maximum adsorption capacity for NLP was at a solution concentration of 500 mg/L and temperature 333 K, with the value of 446.5 mg/g.
3. Thermodynamically, the adsorption process is endothermic and occurs spontaneously.
4. NLP is a favourable biosorbent for the removal of Cu(II) from aqueous solutions.

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