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EFFECT OF CHEMICAL TREATMENT OF NEEM LEAF ON BIOSORPTION OF COPPER (II) IONS FROM AQUEOUS SOLUTION

Sulaiman, M. S.
Department of Pure and Industrial Chemistry, Bayero University Kano, P.M.B 3011, Kano Nigeria
*E-mail of Corresponding author: sdanguguwa@gmail.com

ABSTRACT
The effect of chemical treatment of neem leaf on the biosorption of copper (II) ions from aqueous medium was investigated. Batch experiments were conducted using raw and chemically modified neem leaf biosorbent. The chemical modification was carried out using Sodium hydroxide, Manganese Oxide and EDTA solutions in order to enhance the capacity of the Cu(II) ions uptake.FTIR analysis confirms biosorption of the Cu (II) ions on the surface of the biosorbent. Results of the batch experiments revealed increase in biosorption capacity of the neem leaf powder when modified by NaOH. Maximum bisorption occurred in the first 15 minutes and the biosorption rate decreased thereafter. Neem leaf modified with 0.1 M NaOH gave the highest adsorption capacity of 79 mg/g.To study the extent of adsorption, the Langmuir and Freundlich models were used. The Langmuir isotherm model fits well with a high correlation coefficient (R^2) and demonstrates a monolayer biosorption.The Langmuir monolayer capacity and equilibrium coefficient of the modified neem leaf are56.8 mg/g and 0.162 L/mg respectively. This work shows that chemical modification of neem leaf powder using NaOH improves its biosorbent capacity.
Keywords: Biosorption, Chemical-treatment, Copper(II) ions, Neem leaf powder, Sodium hydroxide

INTRODUCTION

Water pollution has been known to be a cause of severe illness and sudden death in human beings around the world for many years. The risk is greater in many low and middle income countries where environmental pollution prevention and regulation measures have not been taken (Richard and Fuller, 2012). The pollutants include heavy metals like Copper which are extremely hazardous. The World Health Organization (WHO) recommends a safe amount of Cu (II) ions in drinking water as 2mg/l and 1.5 mg/l for industrial effluent discharge (Vafakhah *et al.*, 2014). The need therefore, arises for a way to reduce the amounts of these metals from water and industrial effluents.

Conventional methods like coagulation, filtration, ion exchange, precipitation and reverse osmosis have been applied for the removal of heavy metals from water. These methods however, have some disadvantages like high cost especially when the metals are present in low concentrations and dissolved in a large amount of water (De Souza *et al.*, 2012). This has ignited interest in cost effective and easily available products to treat water and industrial effluents.

Biosorbents prepared from agricultural waste and by-products have been widely studied. Some of the positive outcomes of such research include the utilization of plant residues as adsorbents for the removal of impurities from water, which is now gaining prominence in some parts of the world (Yongabi *et al.* 2011). Biosorption using renewable agricultural wastes offers a promising potential alternative to conventional technologies for treatment of industrial effluents. Many types of agricultural products have been investigated such as *moringa oleifera* seeds (Aminu *et al.*, 2014), rice bran (Montanher *et al.,* 2005), sawdust and pulp from cane (Albertini *et al.*, 2007), leaf,stem and root of holy oak (Prasad and Preitas, 2000), and so on. These biosorbents have been used in their native forms and they proved to be highly efficient, easy to handle and environment-friendly. However, adsorptive properties of biosorbents can be improved significantly by using chemical modification (Marshall *et al.,* 1999).Marshall and Jones, (1996) reported that soybean and cottonseed hulls treated with NaOH improved the adsorption capacity of Zn(II) as compared to the untreated soybean and cottonseed hulls.

This can be explained to be as a result of an increase of galactouronic acid groups that is generated during hydrolysis of *O*-methyl ester groups present in pectic substances (Low *et al*., 2000). Another work by De Souza *et al*. (2012) found that the chemical modification of orange peels with sodium hydroxide and citric acid promoted an adsorption that is energetically more spontaneous.

In this work, the effect of chemical modification of Neem leaf powder on the biosorption of Copper (II) ions from aqueous solution was studied.Characterization of the modified and unmodified biosorbent was done using FTIR and the adsorption phenomenon such as surface coverage and sorption equilibrium was investigated using Langmuir and Freundlich models.

MATERIALS AND METHODS

Materials

The aqueous solution of the heavy metal used in the experiment was prepared by dissolving $CuCl_2$ in distilled water. The Neem leaf used was collected freshly from a local tree in Kano, Nigeria, and all impurities that might be present were washed with plenty of water, and then rinsed with distilled water. The neem leaves were thengrounded to smaller particle size,then sieved to obtain a particle size of about 32-45μm and 45 – 62 μm size.

Surface modification of Biomass

"Pre-treatment of biosorbents using different types of modifying agent such as base solutions (calcium hydroxide, sodium hydroxide, sodium carbonate), mineral and organic acid solutions (Hydrochloric acid, nitric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, methanol), oxidizing agent (Hydrogen peroxide), dye (reactive orange) can extract soluble organic compounds and enhance chelating efficiency" (Ngah and Hanafiah, 2007).

Samples of the powdered neem leaf were treated with0.1M NaOH (Sodium hydroxide), 0.1M MnO_2(Manganese Oxide) and 0.1M EDTAsolutions in order to enhance the capacity of the Cu(II) ions uptake. And later with 0.1, 0.2 and 0.5 M NaOH.

The raw neem leaf powder and the modified Neem leaf powder were labelled NLP and MNLP respectively.

Characterisation of Neem Leaf

To understand the binding mechanism of copper ions on the adsorbent surface, spectroscopic analysis was carried out using a Fourier Transform Infrared spectrophotometer (FTIR) to determine the functional groups available in the neem leaf(Febriana, 2010).

Batch Biosorption Experiment

Batch biosorption experiments were conducted and the effect of modification or pre-treatment on adsorption of copper was studied. The batch adsorption experiment was carried out using both the raw neem leaf powder (NLP) and also the modified neem leaf powder (MNLP).

After all the adsorption experiments, the amount of Cu(II) ions in the solution was analysed for residual metal ion concentration by Elmer AA-400Atomic Absorption Spectrometer (AAS) instrument. Metal uptake is then evaluated from the equation:

$$q_e = \frac{C_o - C_e}{M} V \quad \ldots\ldots\ldots\ldots \quad (1)$$

Where Co and Ce are initial and final copper concentration, $V$is the volume of the biosorbate and M is the weight of the biosorbent.

RESULTS AND DISCUSSION

Surface Functional Groups

Different adsorption peaks displayed by FTIR indicates the presence of various functional groups on the surface of both the NLP and MNLP before and after adsorption. Based on the attribution of peaks, it can be seen that NLP contains different types of functional groups and different biosorption processes such as ion exchange, electrostatic attraction and complexation might be involved in the adsorption mechanism. By comparing the fresh NLP, MNLP and Cu(II) loaded NLP and MNLP; it can be observed that there are shifts in some certain cases in wave number indicating metal binding process on the NLP and MNLP surfaces. This clearly indicates that the neem Leaves biomass was chemically modified and with possibility of pore size development for metal uptake (Yazici *et al*., 2007).

Table.1 Summarised FTIR spectra of NLP and MNLP.

NLP	***Cu(II) Loaded NLP***	***NaOH MNLP***	***Cu(II) Loaded NaOH MNLP***	***MnO2 MNLP***	***Cu(II) Loaded MnO2 MNLP***	***EDTA MNLP***	***Cu(II) Loaded EDTA MNLP***	***Assignment***
3862.04	3905.83-3763.96	3943.09-3816.06	3988.17-3841.83	3947.30-3660.04	3866.20	-	3977.86	N-H
	3664.22	3648.10-3616.86	3578.14	3581.93				O-H
3363.34	3275.97	3436.70	3487.72	3336.45	3452.20	3446.23-3446.23	3468.11	N-H streching
	2931.12			2916.08-2899.97	2885.60		2930.15-2874.25	O-H streching
2624.25	2568.10	2367.62	2564.99	2557.89	2637.05		2724.58	C-H
1637.57	1637.58	1640.24	1639.33	1638.57	1640.11	1639.49	1639.87	C=O Streching
1070.59								C-O-C
595.09	582.36	581.56	582.26	608.70	606.09	585.78	593.80	C-X

3.2 Effect of Chemical Treatment on Adsorption.

The chemical treatment or modification of NLP was done to find out whether adsorbents with improved metal-binding capacity can be produced. The effect of treatment of NLP on biosorption of Cu(II) ions using different modifying agents is shown in Table 2. The modification of biomass removes mineral matter and also introduces oxygen to the surface. This changes the surface chemistry of original sample (Bhatti *et al.*, 2009). The table shows that chemical treatment using NaOH enhanced adsorption capacity greatly while treatment using EDTA reduces the adsorption capacity of the neem leaf.

Table 2.Effect of treatment on NLP using different modifying agents at a fixed initial concentration of 100 mg/L.

Time (min)	**NLP**	**MNLP (NaOH)**	**MNLP(MnO_2)**	**MNLP(EDTA)**
		% Removal		
15	9.8	27.0	14.3	5.3
30	11.2	40.6	19.4	7.4
45	33.6	43.7	19.5	14.3
60	33.9	45.7	21.7	16.6
90	38.0	45.8	23.4	18.7
120	39.0	47.4	28.2	19.7

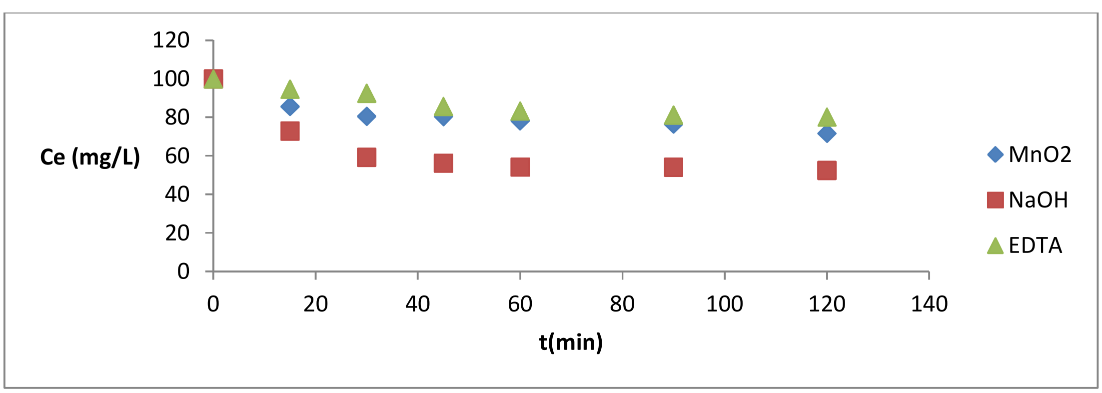

Fig: 1Effect of Treatment on Various Chemically Modified NLP.

The effect of modification using different concentrations of NaOH was studied and the results shown in Figure 2. As observed from the graph, NLP treated with 0.1M of NaOH has an adsorption capacity of 79 mg/g, when treated with 0.25 and 0.5M of NaOH, it has an adsorption capacity of 69 mg/g and 60 mg/g respectively. This indicates that neem leaf powder modified using 0.1M of NaOH has the highest removal capacity.

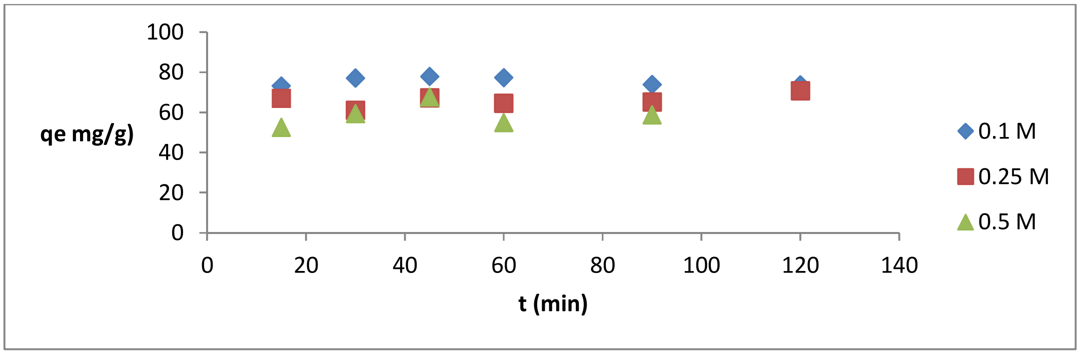

Fig: 2 Effect of pre-treatment on NLP at 333K and NLP dosage of 1.0 g/L using NaOH

Adsorption Isotherms

The equilibrium state of adsorbent, adsorbate and solute concentration is described by an adsorption isotherm. It specifies the concentration of the adsorbate surface equilibrium on the adsorbent as a function of bulk concentration of adsorbate in the solution. Several isotherms were proposed by various studies in past years based on different assumptions. But the Langmuir adsorption isotherm and Freundlich adsorption isotherm are the common popular isotherms used to explain adsorption mechanism. A general formula used for equilibrium isotherm is given as follows:

$$q_s = \frac{KC_s}{(A + BC_sD)} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

q_s(mg g^{-1}) and C_s(mg dm^{-3}) are the solid phase and fluid phase solute equilibrium concentration. K, A, B, and D are the constants of isotherm (Mckay, 1996).

The Langmuir linear plot of C/q Vs C for NLP and MNLP is shown in Fig 3 and Fig 5 while that of Freundlich of Log q Vs Log C is shown in Fig. 4 and Fig. 6.The Langmuir coefficient shows a wide range of values. The Langmuir monolayer capacity q_{max} has a value of 7.97 mg/g for the NLP and 56.8 mg/g for MNLP. The Langmuir equilibrium coefficient *b*had value of 0.0195 L/mg for NLP and 0.162 L/mg for MNLP. It is likely that the sites in the MNLP holding the Cu(II) ions are energetically non-uniform and nonspecific; therefore the adsorption coefficients have wide range of variation (Sharma and Bhattacharyya, 2005).

The value of Freundlich coefficient n was found to be 0.37 for NLP, while it is 2.94 for MNLP. K_f is 0.024 for NLP and 0.924 for MNLP. The values match to the favourable adsorption process.

Biosorption of Cu(II) ions based on the values of the correlation coefficient (R^2) was found to fit better with the Langmuir isotherm.This indicates a monolayer coverage of the adsorbate on the surface of adsorbent and that adsorption occurs at specific sites on the adsorbent (Vafakhah *et al.,* 2014).

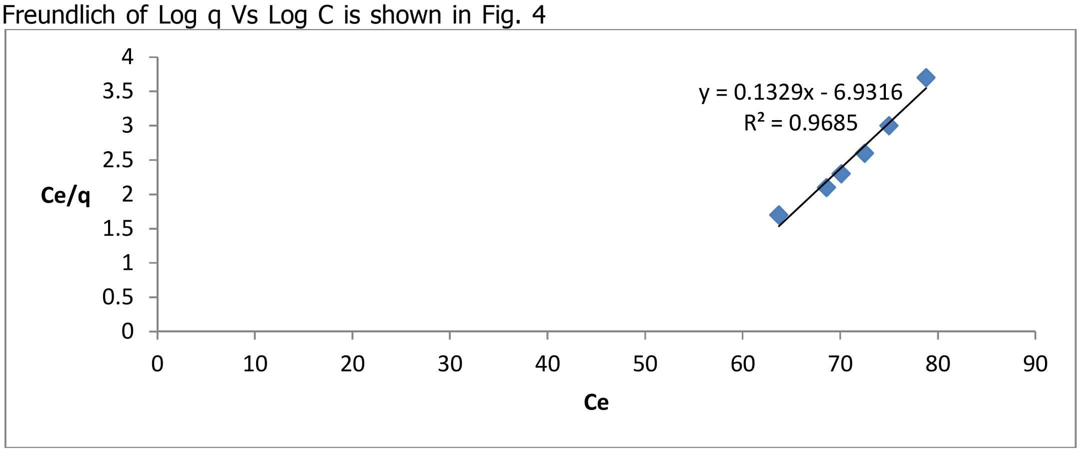

Fig: 3 Langmuir plot of Cu (II) ion adsorption on NLP at 333K and adsorbent dosage of 1.0 g/L.

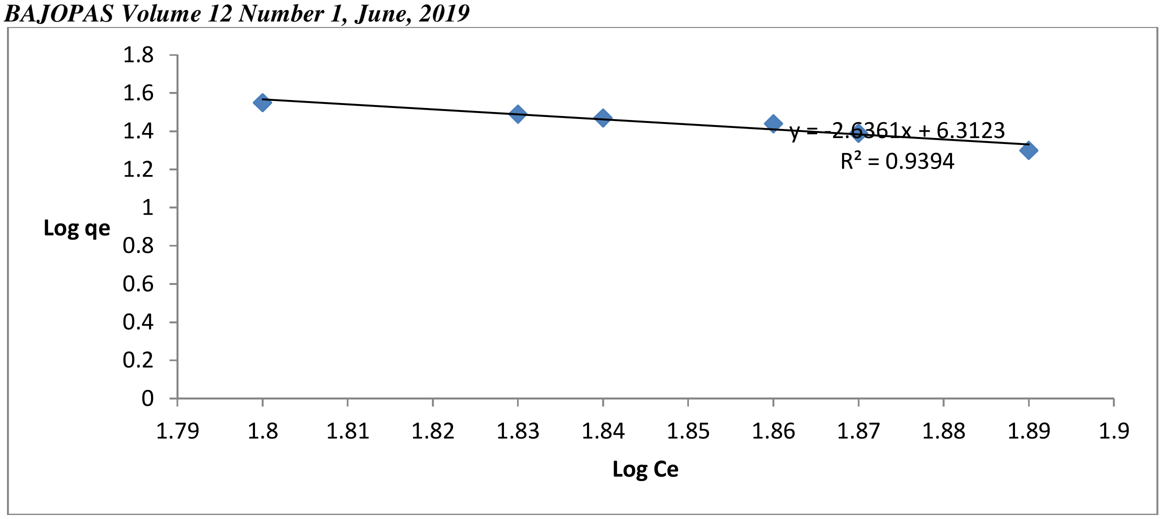

Fig: 4 Freudlich plot of Cu (II) ion adsorption on NLP at 333K and adsorbent dosage of 1.0 g/L.

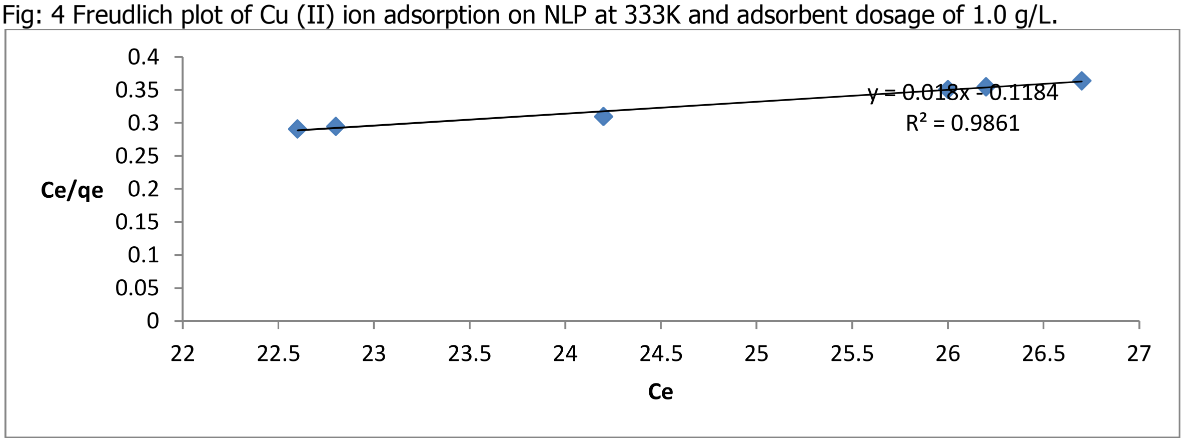

Fig: 5 Langmuir plot of Cu (II) ion adsorption on MNLP at 333K and adsorbent dosage of 1.0 g/L.

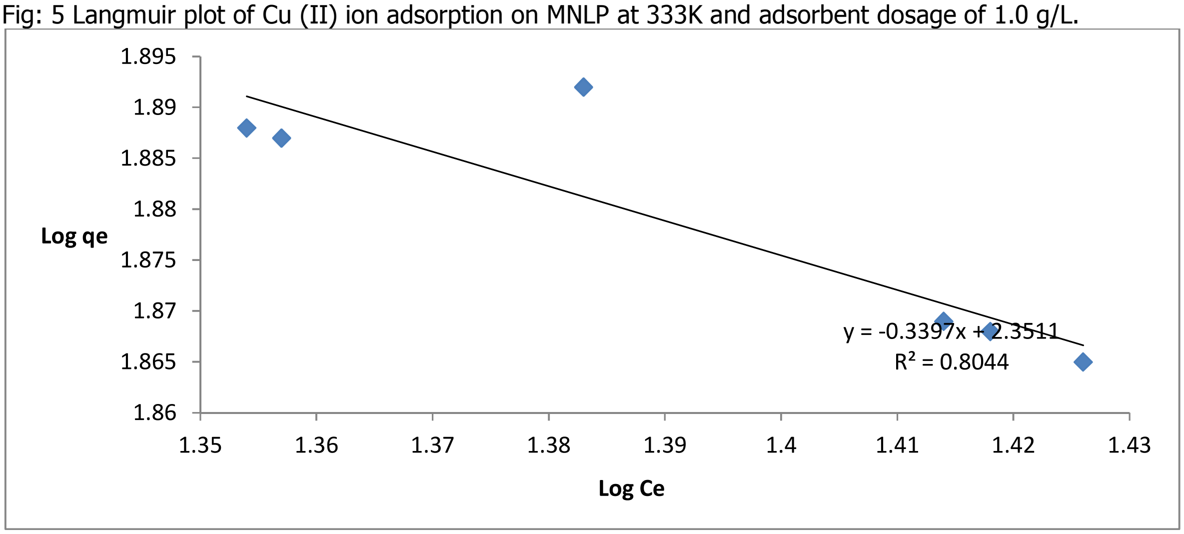

Fig: 6 Freundlich plot of Cu (II) ion adsorption on NLP at 333K and adsorbent dosage of 1.0 g/L

CONCLUSION

To investigate the effect of chemical modification of neem leaf on biosorption of copper (II) ions from aqueous solution, sodium hydroxide, magnesium oxide and EDTA solutions were used for the modification. Adsorptive capacity of the NLP was improved by modification using NaOH, but poor when modified using $MnO_2$and EDTA. The resu lts also showed that concentration of the NaOH and the contact time are important parameters that affect the sorption. The Langmuir isotherm showed a better fit than the Freundlich isotherm. The results from this study showedthat NaOH modified neem leaf powder could be suitable and cost effective biosorbent for copper (II) ions from aqueous solutions.

REFERENCES

Albertini, S., Carmo, L.F., Prado-Filho, L.G. (2007).Use of sawdust and pulp from cane as adsorbents of Cadmium.*Cienc. Technol. Aliment.* 27: 113-118.

Aminu, I., Garba, M.D. and Abba, Z.Y. (2014). Biosorption Potentials of Moringa Oleifera seed in textile effluent treatment.*International Journal of Scientific and Engineering Research.*5(8): 1286-1292.

Bhatti, H.N., Khalid, R. And Hanif, M. A. (2009). Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge. *Chemical Engineering Journal*, 148 pp. 434-443.

De Souza, J.V.T., Diniz, K.M., Massocato, C.L., Tarley, C.R.T., Caetano, J. and Dragunski, D.C. (2012). Removal of Pb (II) ions from aqueous solution with orange sub-products chemically modified as biosorbent. *Bioresources*. 7(2): 2300-2318.

Febriana, N., Lesmana, S. O., Soetaredjo, F.E., Sunarso, J. and Ismadji, S. (2010) Neem leaf utilization for copper ions removal from aqueous solution.*Journal of the Taiwan Institute of Chemical Engineers, 41, pp. 111–114.*

Low, K.S., Lee, C.K. and Liew, S.C. (2000). Sorption of cadmium and lead from aqueous solutions by spent grain. *Process Biochemistry*, 36 pp 59–64.

Marshall, W.E. andJohns, M.M. (1996) Agricultural by-products as metal adsorbents: sorption properties and resistance to mechanical abrasion. J. Chem. Technol. 66: 192-198

Marshall, W.E., Wartelle, L.H., Boler, D.E., Johns, M.M. and Toles, C.A. (1999). Enhanced metal adsorption by soybean hulls modified with citric acid. *BioresourcesTechnol.* 69: 263-268.

Mckay, G. (1996). Use of adsorbents for the removal of pollutants from wastewaters. CRC Press, USA.

Montanher, S.F., Oliveira, E.A and Rollemberg N.C. (2005) Removal of metal ions from aqueous solutions by sorptions onto rice bran. *Journal of hazard material,* 117, pp. 207-211

Ngah, W.S.N. and Hanafiah, M.A.K.M. (2008)Surface modification of rubber (*Hevea brasiliensis*) leaves for the adsorption of copperions: kinetic, thermodynamic and bindingmechanisms. *Journal of Chem. Technol. Biotechnology*, 84, pp. 192–201

Prasad, M.N.V. and Freitas, H. (2000). Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* L. (holly oak). *Environ. Technol.* 110: 277-283.

Richard, M.C. and Fuller, S.E. (2012). Impacts of sewage irrigation on heavy metals distribution and contamination. Journal of Environmental Science. 31:805-812.

Sharma, A., Bhattacharya, K. G. (2005) *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium. *Journal of Hazardous Materials* 125, pp.102–112

Vafakhah, S., Bahrololoom, M.E., Bazarganlari, R. and Saeedikhani, M. Removal of copper ions from electroplating effluent solutions with native corn cob and corn stalk and chemically modified corn stalk. *Journal of Environmental Chemical Engineering.*2(1): 356-361

Yazici, H., Kilic, M. and Solak, M. (2008). Biosorption of copper (II) by Marrubium globosum subsp. Globosum leaves powder: Effect of chemical pre-treatment. *Journal of Hazard Mater*, 151, pp. 669 – 675.

Yongabi, K.A., Lewis, D.M. and Harris, P.L. (2011). Application of Phytodisinfectants in water purification in rural Cameroon.*African Journal of Microbiology Research*. 5(8): 628-635.