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RESEARCH ARTICLE

ADSORPTIVE REMOVAL OF ZINC FROM AQUEOUS SOLUTION BY BIOMASS CARBON PREPARED FROM NEEM (*AZADIRACHTA INDICA*) LEAF

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ABSTRACT

Potentially toxic trace elements, such as zinc, with high levels in water pose very serious problems around the world. Adsorption process is among the most effective techniques for removing of many heavy metal ions from different types of water. In this study, an attempt has been made to investigate the efficiency of economically cheaper, easily available and renewable biomass of Neem (*Azadirachta indica*) leaves for zinc adsorption from aqueous solutions. Biomass carbon samples were prepared from the zero-cost biomass waste of neem leaves. During the removal process, the effects of solution pH, adsorbent dose, contact time, temperature and initial metal ion concentration on adsorption efficiency by Neem Leaf Carbon (NLC) were studied. Experimental equilibrium data were analyzed by the Langmuir and Freundlich isotherm models. The optimum conditions obtained were 30 min contact time, 0.8g adsorbent dose, 45 ^{0}C, 0.12M Zn and pH 7 for zinc removal. The equilibrium data fitted well to the Langmuir and Fruendlich adsorption model with correlation coefficient (R^2) value of 0.992 and 0.961 respectively. The results revealed that zinc is considerably adsorbed on neem leaf derived carbon and it could be economic method for the removal of zinc from aqueous solutions.

INTRODUCTION

Global developments directed towards making human life more comfortable have greatly increased industrialization and urbanization. However, this trend has damaged the environment alarmingly, mainly due to the generation of a large amount of hazardous waste and the pollution of usable surface water. The major pollutants in wastewater are heavy metals such as lead, zinc, copper, cadmium, mercury, chromium and arsenic. These metals accumulate in living tissues/organs and can cause accumulative poisoning and serious health problems such as cancer and brain damage (M.S. Rahman and M.R. Islam, 2009). There are numerous methods which are currently employed to remove these metals from aqueous environment. Some of these methods are chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation. Adsorption using non-living biomass wastes has been found to be an economically feasible alternative for metal removal. This method offers the advantages of low cost, minimizing secondary pollution and high efficiency in wastes (B. Volesky and Z.R. Holan, 1995, T.A. Oyedepo, 2011). The use of nonliving biomass in biosorption is more practical and advantageous because living biomass cells often require the addition of fermentation media which increases the biological oxygen demand or chemical oxygen demand in the effluent. In addition, non-living biomass is not affected by the toxicity of the metal ions, and they can be subjected to different chemical and physical treatment techniques to enhance their performance. There are so many adsorbents have been used, still new adsorbents are the need of the hour due to the increasing demand for treatment of industrial wastewater. Many low cost adsorbents have been developed and tested for heavy metal ion removal so far, which reflect varying adsorption efficiencies depending upon the type of adsorbents used. Irish Peat moss (B. Sen Gupta et al, 2009), pine cone powder (A.E. Ofomaja et al 2010), kenaffiber (C.M. Hasfalina et al, 2012), sugar beet pulp (Z. Aksu, and I.A. Isoglu, 2005), tea (B.M.W.P.K. Amarasinghe, and R.A. Williams 2007) and many others have been tested for Zn^{2+} removal. Neem (*Azadirachta indica*) leaves is one of the world's most important medicinal tree that is widely cultivated in tropical countries for its valuable applications in pharmacy and cosmetics. Neem leaf is a low cost adsorbent which is biodegradable and agro-waste which may act as a significant material for zinc adsorption. Neem leaf, an agro waste is discarded all over the world as useless material. It is causing waste management problems though it has some compost, cosmetics and adsorbent potentiality. It is an abundant, readily

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available, low cost and cheap, environment friendly bio-material. Considering the above criteria, neem leaf was selected to prepare the biomass carbon. A step was taken to prepare biomass carbon from neem leaf and used for removal of zinc from water. The main aim of this research was to determine the potentiality and adsorption capacity of neem leaf derived carbon as adsorbent for removal of zinc. Thus the purpose of the present work was to investigate the possibility of carbon derived from neem leaf which is locally available, free of cost all over India as an adsorbent for the removal of Zn from aqueous solution and the results have been presented in a simplified and systematic way. The work also stresses Green Environment from Waste concept, which is the want of the hour. The effects of various operating parameters on adsorption such as pH, initial concentration of Zn ions, adsorbent dosage, temperature and contact time were studied.

Experimental

Preparation of Neem Leaf Carbon (NLC)

Neem leaf used as raw material in this work was procured from a local garden. The midrib, which divides the blade into two lamina halves is removed with little hand pressure. The precursor was washed exhaustively with distilled water to remove adhering impurities from the surface, air-dried, cut to 1-2 cm size. The dried mass was finally heat treated in a furnace at 350 ^{o}C for 2 hours. The heat treated sample was washed several times with dilute HCl followed by de-ionized water until the washings are neutral to pH and its conductivity is minimal. The final mass of carbon lump was dried, ground and sieved to 250 mesh size. The powder prepared in this way is called Neem Leaf Carbon (NLC).

Preparation of adsorbate solution

All chemicals used were of analytical grade. Stock standard solution of Zn^{2+} has been prepared by dissolving the appropriate amount of $ZnSO_4$. $7H_2O$ in deionized water. This stock solution was then diluted to specified concentrations.The pH of the system was adjusted using reagent grade NaOH and HCl respectively. All plastic sample bottles and glassware were cleaned, then rinsed with deionized water and dried at 60˚C in a temperature controlled oven. All biosorption experiments in this study were carried out in 250 ml Erlenmeyer flasks with a working volume of 100 ml Zn (II) solution. The flasks were agitated on a rotary shaker set at 120 rpm speed and at 35 ^{o}C temperature. The biomass free supernatant obtained was analyzed for residual Zn(II) concentration was found out volumetrically using EDTA as titrant and EBT indicator.

The amount of metal ion adsorbed per gram of the biomass and was calculated using the equation below:

$q_e = (Ci - Ce)V/M$

where q_e is the amount of metal ion biosorbed per gram of the biomass in mg/g, Ci is the initial concentration of the metal ion in mg/L, Ce is the equilibrium concentration of the metal ion in mg/L, M is the mass of the biomass in grams and V is the volume of the metal ion in litres. The experiment was performed in triplicate and the mean value taken for each parameter.

RESULTS AND DISCUSSION

Effect of contact time on Zn (II) adsorption

The effect of contact time on the adsorption of Zn ions using NLAC was studied and the results are shown in Figure 1.

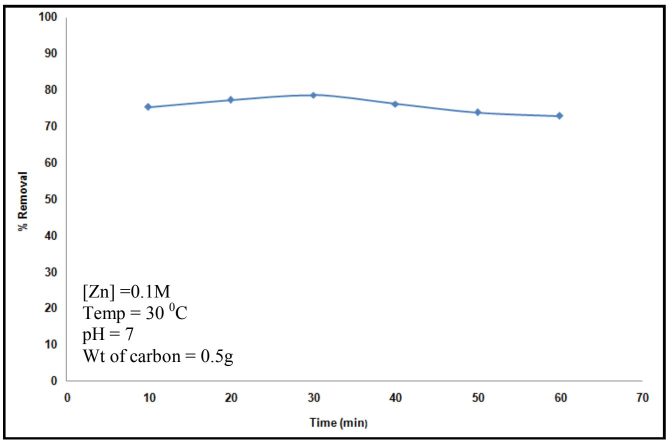

Figure 1. Effect of contact time on adsorption of Zn

From the results, it was observed that there is a rapid initial adsorption in the first 10 min, followed by a longer period of much slower sorption until about 30 minutes when equilibrium was reached, after which there was no significance increase in Zn (II) ion uptake. Initially Zn(II) ion uptake was rapid because there are plenty of readily available sites for adsorption to occur. Subsequently, biosorption increased in the second phase but with a much slower rate until 30 minutes when equilibrium was reached. From figure 1, it is noted that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent, temperature, initial metal ion concentration and pH of solution were kept constant. The results indicated that on increasing the contact time from 10 to 30 minutes Zn (II) removal was increased from 75% to 78% on using NLC as adsorbent. From 30 to 60 minutes, the percentage removal of Zn (II) using NLC starts decreasing which showed that equilibrium was reached at 30 minutes itself. Thus the results illustrated that after 30 minutes desorption predominates over the adsorption which infers that the optimum contact time for maximum removal of Zn (II) ions using NLC was 30minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment. Recent researches have shown that adsorption equilibrium is dependent on the type of biomass and not on the method of preparation of biomass carbon. S.Rengaraj et al (2002) and Nwachukwu and M.A. I.J. Alinnor (2012) reported equilibrium time of 2 hours for the adsorption of phenol onto palm seed coat activated carbon and sorption analysis of nitrophenol onto fly ash.

Effect of pH on Zn (II) adsorption

The effect of pH on the adsorption of Zn ions using NLC was studied and the results are represented in Figure 2. pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution. The pH range of 2 -7 was chosen, as the precipitation of Zn(II) is found to occur at pH ≥ 7 (G.A. Waychunas et al, 2002). Variation of adsorption capacity of NLC for Zn(II) ions with pH is shown in Figure 4. The removal of metal ions from solution by adsorption is highly dependent on the pH of the solution.

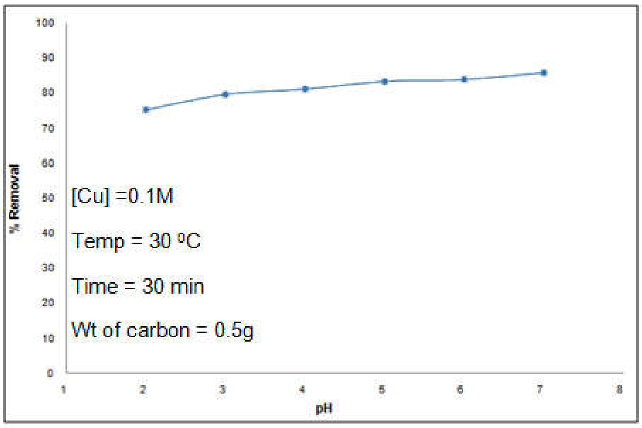

Figure 2. Effect of pH on adsorption of Zn

The biosorption of Zn(II) ions increases steadily with increase in intial pH and the maximum equilibrium adsorption capacity of 85.9% is observed at pH 7. Increases in metal removal with increase in pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (> pH 7) is due to formation of soluble hydroxy complexes (R. Ramya et al 2011, G. Wang, 1995). The adsorption of Zn (II) ion was found mainly to be influenced by solution pH.

Effect of adsorbent dose on Zn (II) adsorption

The effect of adsorbent dose on the adsorption of Zn ions using NLC was studied and the results are shown in Figure 3.

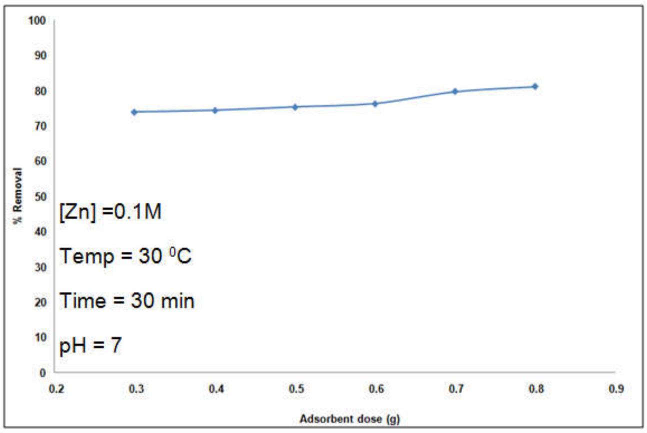

Figure 3. Effect of adsorbent dose on adsorption of Zn

Adsorption efficiency of Zn (II) adsorption was studied by varying the amount of adsorbent from 0.3 to 0.8g keeping other parameters (pH, metal ion concentration, temperature and contact time) constant. This shows that removal efficiency of the zinc usually improved on increasing adsorbent doses. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure it is clear that only slight increase in adsorption after a certain amount of adsorbent was added (0.5g). The maximum % removal of Zn (II) was about 81.1% for NLC at dosage of 0.8g. This result also suggests that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent. Our findings are in good support with M. Hussein et al (2007).

Effect of temperature on Zn(II) adsorption

The effect of temperature on removal of zinc ion using NLC was studied within the range of 35 to 60 ^{0}C and the results are represented in Figure 4. Other parameters such as dose of adsorbent, pH, metal ion concentration, contact time and pH of solution were kept constant. The temperature dependence of the adsorption process is related with several thermodynamic parameters.

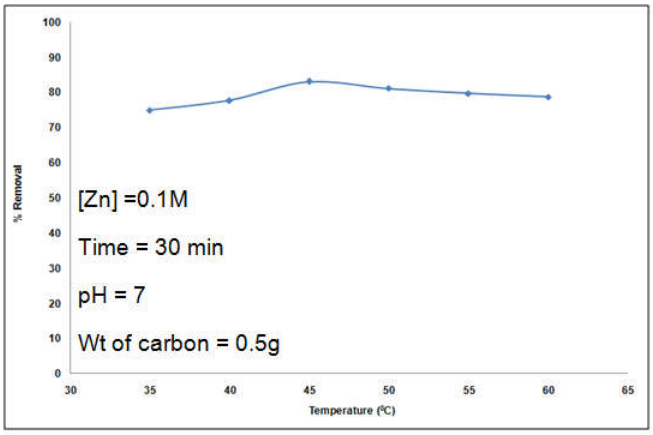

Figure 4. Effect of temperature on adsorption of Zn

The temperature showed the negative effect on adsorption of Zinc using NLC. With increase in temperature from 45 to 60 ^{0}C the removal of copper ions was decreased from 83.0 to 78.7% for NLC. From the figure 4 it is clear that the low temperatures are in favour of zinc ion removal. This may be due to a tendency for the zinc ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of zinc is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature. Similar findings are also reported by other researchers (M. C. Ncibi et al, 2007, S. Chakraborty et al, 2005).

Effect of initial metal ion concentration on Zn (II) adsorption

The effect of initial zinc concentration on the zinc adsorption rate was studied in the range 0f 0.06-0.16M (variation of 0.02M) at pH 7, temperature 30 ºC, 0.5g of adsorbent and 0.1M metal ion concentration and 30 min contact time. The results obtained are represented in Figure 5. From the figure 5 it was observed that the percentage of removal decreased with increase in initial zinc concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial zinc concentration. Therefore it was evident from the results that zinc adsorption was dependent on the initial metal concentration. Similar results have been also reported by several researchers (G.Mekay et al, 1982, R.S. Shelke et al, 2010, J. A. Stephen, et al, 1989).

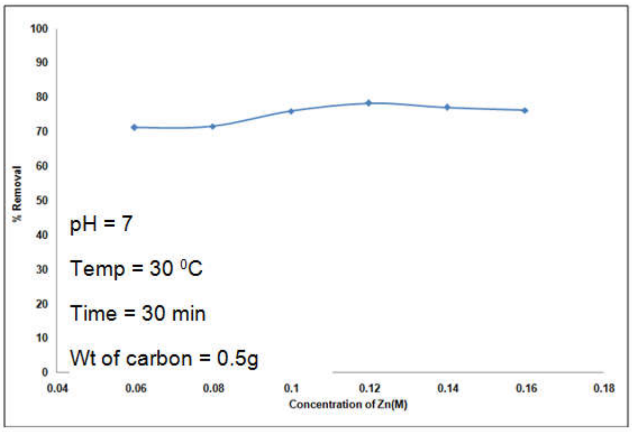

Figure 5. Effect of initial metal ion concentration on adsorption of Zn

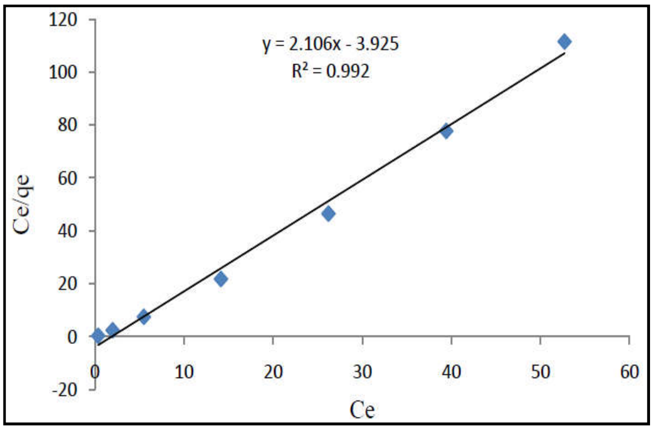

Figure 6. Langmuir adsorption isotherm for Zn adsorption

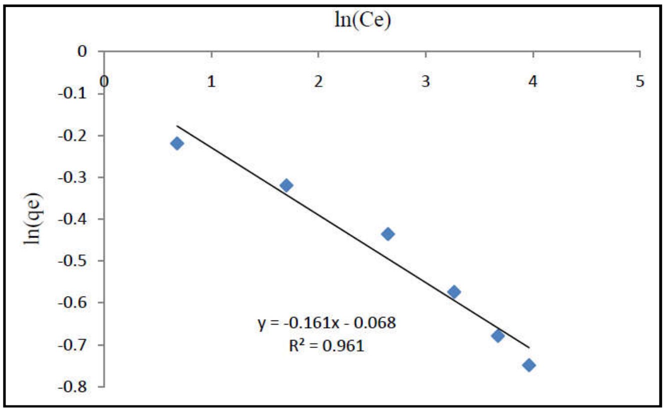

Figure 7: Freundlich adsorption isotherm for Zn adsorption

Adsorption Isotherms

The relationship between the amount of Zn (II) ion and its equilibrium concentrations are described using the Freundlich and Langmuir models and the plots are represented in Figures 6 and 7. Langmuir isotherm constants were determined from a plot of Ce/qe against Ce while that of Freundlich isotherm constants were determined from the plot of ln qe against ln Ce as shown in Table 1.

Table 1. Langmuir and Freundlich parameters for Zn(II) ion removal at 298 K

Adsorption Models	K_L	K_F	q_m(mg/g)	R^2	N
Langmuir	0.5366		0.4748	0.992	
Freundlich		6.211		0.961	1.07

The isotherm correlation coefficient (R^2) of Langmuir and Freundlich model equations for the adsorption of Zn (II) ion NLC was 0.992 and 0.961 respectively. The results obtained showed that Langmuir biosorption model was the best fit for the biosorption of Zn (II) ion using NLC indicating a physical biosorption. To summarize, we have described how biomass carbon powder from GREEN biomass waste namely NEEM LEAF can be produced and attempted to evaluate its potential as an adsorbent for removal of zinc from waste water.

Research Highlights

- The work is based on Waste-to-Energy concept.
- The work focuses on preparing low-cost biomass carbon for zinc removal from waste water using GREEN BIOMASS namely NEEM LEAF!

Conclusion

The present investigation is carried out to study the suitability of a novel indigenous adsorbent, neem leaf derived carbon (NLC) for the removal of heavy metal such as zinc from the wastewater.

- Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the Zn were concerned.
- The optimum pH of solution for Zn removal was found to be 7.
- Within the scope of the experimental investigation the optimum temperature was found to be 45 ^{0}C.
- The optimum time for adsorption of zinc was found to be 30 minutes.
- Initial metal ion concentration showed the negative effect on adsorption efficiency i.e. at lower levels the adsorption was higher.
- Adsorbent dosage showed the positive effect on adsorption efficiency i.e. at higher adsorbent dose the adsorption was higher.
- Our research work is designed in such a way of take waste, make products, and turns them to resources which is the reverse of the global scenario of take resources, make products, and turn them to waste.

The present research concludes that there is no need of complex activation procedure for the preparation of biomass carbon with superior adsorption behaviour. Thus the usage of biomass waste materials/residues as precursors of carbons as adsorbent offers significant potentials for reducing the cost and environmental damage resulting from uncontrolled disposal of these residues. This approach is thus interesting as it deals simultaneously with the water treatment and recycling of environmental waste. *Thus the study provides an effective way to value-added utilization of discarded biomass in the area of GREEN ENVIRONMENT.* However, further research should attempt to improve the adsorption capacity of adsorbents and apply this method to the removal of metals in large scale.

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