CURRY TREE CARBON- A NOVEL ADSORBENT FOR THE REMOVAL OF ZN(II) IONS IN AQUEOUS MEDIUM

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ABSTRACT

The present study explored the ability of Curry Tree Carbon (CTC) for removal of Zn(II) ions from aqueous solution. Batch experiments were conducted. The sorbent, which was prepared by a simple and concise method, was able to bind heavy metal viz., Zn(II) ions with very high efficiencies. The adsorption study was confirmed through characterization tests such as Fourier transform infrared spectroscopy, X-ray diffraction analyses, scanning electron microscopy and elemental analysis. The CTC showed considerable capacity for the removal of Zn(II) ions from aqueous solution. The Langmuir isotherm model fitted well to experimental metal sorption. In this study, the sorption mechanism and ion exchange seem to be the most occurring phenomena.

KEYWORDS: CTC, Batch experiments, isotherm modeling, kinetic modeling.

1. INTRODUCTION

The presence of heavy metals in drinking water sources and in edible agricultural crops can be harmful to human. Heavy metals are highly toxic and they can damage nerves, liver, bones and also can block functional groups of vital enzymes. The major sources of heavy metals in water and soil are the effluents discharged from many industrial processes.[1] Removal of heavy metals from wastewater is a very important factor with respect to human health and environmental considerations.[2] The use of potentially low-cost sorbents to remove heavy metals from aqueous solutions has been intensely studied.[3] Adsorption has emerged out to be better alternative treatment methods. It is said to be effective and economical because of
its relatively low cost. Authors have claimed adsorption to be easiest, safest and most cost-effective methods for the treatment of waste effluents containing heavy metals.[4] In the present study, the effects of various parameters, viz. pH, adsorbent dose, initial metal ion concentration, and contact time on the biosorption capacity were investigated. Different isotherm models are applied to the experimental data. Kinetic and thermodynamic adsorptions are also investigated and reported.

2. MATERIALS AND METHODS
All the chemicals employed in the present study were purchased from Alfa Aesar Company and were used as received. Double distilled water was used throughout the work and the second distillation was made over alkaline permanganate. The glasswares used in the present study were of Borosil grade. The amount of Zn(II) ions in the solution were estimated following the standard procedure using Photocolorimeters.

2.1 Preparation of Curry tree Carbon (CTC)
The barks of curry leaf tree (Murraya koenigii) as a precursor material (a vegetable waste) were collected from a vegetable shop in Tiruchirappalli and cut into small pieces and dried (after removing the rinds) at 110°C for ~1 hour. [The barks are being thrown away as waste landfills, after removing the leaves (used as a flavoring agent) for cooking]. The dried pieces of curry leaf tree barks (~ 500g) were treated with concentrated sulphuric acid (1: 1 w/v). The mixing was done by adding small quantity of the material each time to acid taken in a one litre beaker with continuous stirring. Each time charring of the material occurred immediately, accompanied by evolution of heat and fumes. The residue was cooled to room temperature, washed with excess of water to remove free acid completely, filtered and dried at 110°C in an air oven for about an hour. Then, the material was heated for 90 min. in a muffle furnace at 170°C to complete carbonization and activation. The resulting carbon was filtered and washed with distilled water until a constant pH of the slurry was reached. Then it was dried for an hour at 110°C in a hot air oven. The dried material was ground well and sieved to desired particle size range. The carbon thus obtained from curry leaf tree was abbreviated as CTC (curry tree carbon).

2.2.1 Preparation of Zn(II) ions Solution
The metal ion chosen for the adsorption studies in the present work was Zinc(II). Stock solutions (1000 mg/l) of Zn(II) ions was prepared by dissolving required amount of Zinc Sulphate in one litre of distilled water.
2.2.2 Adsorption Experiments

Batch adsorption experiments were carried out at room temperature (30±1°C). Adsorption experiments were conducted at different conditions, viz. adsorbent size (75-425 µm), contact time (5–50min), pH (3–7), initial Zn (II) ion concentration (25–200mg/l), temperature (27°C – 47°C), agitation speed (50-200rpm) and CTC dose (0.25–2g/50ml). The mixtures were taken in a 125 ml conical flask and agitated on a mechanical shaker. The samples were filtered after analysis through Whatman 40 filter paper. The concentrations of metal ion were determined by using standard graph. Experimental analysis was repeated. The amount of metal ion adsorbed by the biosorbent at equilibrium ($q_e$, mg/g) was calculated as follows

$$q_e = \frac{(C_0 - C_e) V}{m}$$

where $V$ is the volume of solution treated in ml, $C_0$ is the initial concentration of metal ion in mg/l, $C_e$ is the equilibrium metal ion concentration in mg/l, and $m$ is the biomass in grams. The percent removal (%) of metal ion was calculated using the following equation.

$$Removal(\%) = \frac{(C_0 - C_e)}{C_0} \times 100$$

Characterization of CTC

The characterization of CTC before and after adsorption using FT-IR, XRD and SEM with EDX confirmed the adsorption of heavy metal ions onto the adsorbent.

RESULTS AND DISCUSSION

3.1 Effect of Particle size

Particles with small size have large surface area and large adsorption capacity. Smaller sized particles reduce internal diffusion and mass transfer limitation for the penetration of the adsorbate inside the adsorbent as compared to larger size particles. It was observed that the maximum adsorption efficiency was achieved with particle size <75 µm for Zn$^{2+}$ by CTC. There was a decrease in adsorption efficiency when the particle size was increased. This may due to the lack of availability of the adsorption sites. Lower particle size showed maximum adsorption which may due to the availability of larger surface area.$^{[5]}$

3.2 Effect of pH

The pH of the solution significantly influences amount of metal ion adsorbed on to a sorbent, pH determines the behavior of the metal ions in aqueous solution. For CTC, the adsorption
capacity increases from pH 3.00 to 6.00 (due to the weak inhibitory effect of H$_3$O$^+$ ions). Above pH 7.00, metal hydroxides get precipitated. The maximum removal of Zn(II) ions onto CTC took place at pH 5.50.\cite{6}

### 3.3 Effect of contact time

The variation of percentage metal ions removal by CTC with contact time was determined. The percentage of metal ions removal approached equilibrium within 35 min. for the adsorption of Zn(II) ions by CTC. The fast adsorption may be due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the surface of the adsorbent at the beginning. The progressive increase in adsorption and consequently the attainment of equilibrium may be due to the limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbents.\cite{7}

### 3.4 Effect of metal ion concentration

The adsorption capacity increases as the metal ion concentration increases from 25 to 200 mg/l which must be due to the progressive increase in the electrostatic interaction between the metal ions and the absorbent active sites. Moreover, this can be by the fact that more adsorption sites are being covered as the metal ion concentration increases and higher initial concentrations lead to an increase in the affinity of the metal ions towards the active sites.\cite{8}

### 3.5 Effect of adsorbent dosage

The initial increment in adsorption capacity with increase in adsorbent dosage is expected, because, as the number of adsorbent particles also increases, the surface area available for metal ions attachment increases. The present study reveals that as the adsorbent dose increases from 0.25 g to 2.25 g, there is an increase in the adsorption of metal ions onto the surface of the adsorbents. It is plausible that with higher dosage of adsorbent, there would be greater availability of active/exchangeable sites\cite{9} for the Zn(II) ions.

### 3.6 Effect of agitation speed

The agitation speed less than 150 rpm favors the maximum removal of metal ions by CTC. Maximum removal of Zn(II) ions by CTC occurs at 50 rpm. The high agitation speed may shift the equilibrium process of adsorption and desorption towards the desorption.
3.7 Effect of temperature
The adsorption of Zn(II) ions from metal ion solution using the CTC was carried out in the temperature range of 27-47°C. Low temperatures favor the adsorption process for CTC. The decrease in adsorption with increasing temperature suggests weak adsorption interaction between biomass surface (CTC) and the metal ion[10], which supports physisorption.

3.8 Effect of other ions
The effects of other ions on the adsorptive removal of Zn(II) ions onto CTC is studied with various concentrations of sodium chloride solution and calcium chloride solution. The increase in the concentration of Cl⁻ ions (from NaCl) increases the adsorption of heavy metal ions onto CTC by pairing their charges. The Ca²⁺ ions (from CaCl₂) which have lesser density than the heavy metal ions decrease the adsorption of them by CTC.
Fig. 5 Effect of Agitation speed for the Removal of Zn(II) Ions.

Fig. 6 Effect of Contact Time for the Removal of Zn(II) Ions.

Fig. 7 Effect of Adsorbent Dose for the Removal of Zn(II) Ions.

Fig. 8 Effect of chloride ions- CTC.

Fig. 9 Effect of Calcium ion.
3.9 Instrumental analysis
The characterization of CTC before and after adsorption using FT-IR\textsuperscript{[11]}, XRD\textsuperscript{[12]} and SEM\textsuperscript{[13]} with EDX confirmed the adsorption of Zn(II) ions onto the adsorbent. The change in surface morphology in SEM image after the sorption process indicates the presence of heavy metal ions. The same is confirmed by the EDX analysis.

3.9.1 FTIR spectra
The FT-IR spectra obtained for CTC is measured. Surface functional groups in CTC are detected by Fourier-transform infrared spectroscopy. It can be observed that the spectrum displays a number of bands corresponding to several functional groups on the activated carbon surface that may facilitate the adsorption process only relevant peaks was considered for discussion. The spectrum of CTC showed a broad band at 3425.11 cm\textsuperscript{-1}, characteristic of the OH stretching vibrations mode of hydroxyl functional groups including hydrogen bonding of chemisorbed water or may be due to binding of OH group with polymeric structure. The band at 2919.45 cm\textsuperscript{-1} could be attributed to C-H stretching of aliphatic carbon or it can be due to CH\textsubscript{2} or CH\textsubscript{3} deformation. The peak at 1592.58 cm\textsuperscript{-1} is related to C=C stretching for unsaturated aliphatic structures. The presence of transmittance peaks at 868.91 cm\textsuperscript{-1} and 757.30 cm\textsuperscript{-1} in CTC are due to out-of-plane aromatic C-H deformation vibration containing isolated hydrogen atoms. Bands between 1538-1650 cm\textsuperscript{-1} and 1360-1470 cm\textsuperscript{-1} are assigned to asymmetric and symmetric stretching vibrations of carboxylate ion.

3.9.2 XRD study
The XRD patterns for CTC before and after adsorption of Zn(II) ions are shown respectively. The sharp peaks present in the Figures indicate the crystalline nature of the material. In addition, several other low intensity peaks corresponding to various crystalline phases of carbons have also been observed. The porous nature of CTC has been decreased after the adsorption process.

After the adsorption of metal ions, the intensity of the highly organized peaks are slightly diminished, indicating the physisorption process.

3.9.3 SEM with EDX study
Energy Dispersive X-ray Spectroscopy (EDX) were conducted inside the SEM on different samples before and after the adsorption of Zn(II) ions onto CTC. So the difference in cell wall thickness cell diameters, analyzed EDX spectra and the morphological changes on the
surface, in synergy provide the evidences for the adsorption of metal ions onto CTC. The surface morphological changes in the CTC cells after the adsorption of Zn(II) ions are shown. Zn(II) ions adsorption preserves the smooth nature of the CTC cell walls.

Fig. 10 FTIR spectrum of CTC before adsorption.

Fig. 11 FTIR spectrum of CTC after adsorption of Zinc.

Fig. 12 XRD of CTC before adsorption.
Fig. 13 XRD of CTC after adsorption of Zn.

Fig. 14 SEM before and after adsorption.

Fig. 15 EDX before and after adsorption.
3. Adsorption isotherm

Analysis of adsorption equilibrium data is important for optimizing the design of an adsorption system. Adsorption isotherm expresses the relationship between metal ions adsorbed onto the adsorbents and metal ions in the solution and provides important design parameters for adsorption system. Several isotherm models have been widely used to model the equilibrium of adsorption system. Langmuir and Freundlich models are the most widely used models in the case of the adsorption of Zn (II) onto CTC nano particles adsorbent.

The formation of a monolayer adsorbate on the adsorbent is represented by the Langmuir isotherm model.\[^{[14]}\]

Thereby, the Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is applicable for monolayer sorption onto a surface containing a finite range of indistinguishable sites. The model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate within the plane of the surface. Based on these assumptions, Langmuir has drawn the subsequent equation

\[
q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}
\]

Langmuir sorption parameters are determined by remodeling the equation into linear type.

\[
\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e}
\]

Where,

\[C_e = \text{equilibrium concentration of adsorbate (mg/l)}\]
\[q_e = \text{amount of Zn(II) ions (CTC ) at equilibrium (mg/g)}\]
\[Q_0 = \text{maximum monolayer coverage capacity (mg/g)}\]
\[K_L = \text{Langmuir isotherm constant (l/g)}\]

The values of $Q_0$ and $K_L$ are computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ as given in Fig. 16. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter $R_L$, which is a dimensionless constant mentioned as separation factor or equilibrium parameter.

\[
R_L = \frac{1}{1+(1+K_L C_0)}
\]
This isotherm is used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich.[15]

\[ Q_e = K_f C_e^n \]

Where \( K_f \) = Freundlich isotherm constant
\( n \) = adsorption intensity
\( C_e \) = equilibrium concentration of adsorbate
\( Q_e \) = amount of Zn(II) ions adsorbed per gram of the adsorbent at equilibrium

By linearizing the above equation,

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]

The constant \( K_f \) is an approximate indicator of adsorption capacity, while \( 1/n \) is a function of the strength of adsorption in the adsorption process. If \( n = 1 \) then the partition between the two phases are independent of the concentration. If the value of \( 1/n \) is below one, it indicates a normal adsorption. On the other hand, \( 1/n \) being above one indicates cooperative adsorption.

**Fig. 16** Langmuir isotherm for Zn(II) ions removal by CTC.

**Fig. 17** R.L for Zn(II) ions removal by CTC.

**Fig. 18** Freundlich isotherm for Zn(II) ions removal by CTC.
From the Langmuir study, the separation parameter for CTC is calculated to confirm the favorable ion exchange/adsorption. The $R^2$ value proves the fitness of Langmuir isotherm model for the adsorption process. The Freundlich isotherm results for the various initial metal ion concentrations reveal the conditions that are favourable for the sorption process.

5.1 Kinetic studies

The Lagergren pseudo-first order\[^{[16]}\] rate expression is given as

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t$$

where $q_e$ and $q_t$ are the amounts of Zn(II) ions adsorbed (mg/g) on CTC at equilibrium and at time $t$ respectively and $k_1$ is the rate constant of pseudo first order adsorption (min$^{-1}$). The slope and intercept values of the straight line obtained by plotting $\log (q_e - q_t)$ against $t$, are used to determine the pseudo first order rate constant ($k_1$) and the theoretical amount of adsorbed calcium ion per unit mass of adsorbent $q_e$, respectively.

Pseudo first order plot shows reasonably good linearity till equilibrium time. This indicates that the adsorption follows first order kinetics and weak vanderwaal forces (physisorption).

6 Thermodynamic Parameters

The effect of temperature on the adsorption of Zn(II) ions on CTC in 27, 32, 37 and 42°C. The results show that the adsorption capacity of Zn(II) ions onto CTC decreased with increase in temperature, indicating that the adsorption process is exothermic in nature. The pseudo-second order rate equation of Zn(II) ions adsorption on CTC is expressed as a function of temperature by Arrhenius equation as shown below:

$$\ln K = \ln A - \frac{E_a}{RT}$$
where $E_a$ is the Arrhenius activation energy (kJ/mol); $A$, the Arrhenius factor; $R$, the gas constant; and $T$, the solution temperature. Positive activation energy is the energy that overcomes the adsorption to occur. However, the negative activation energy indicates the absence of energy barrier to cause the adsorption to occur. The $\ln k$ vs $1/T$ gives a straight line with slope $-E_a/R$ and intercept $\ln A$. The negative value of the activation energy indicates that the energy barriers are absent in the reaction process and that the reaction is exothermic. On increasing the temperature, there is a reduction in the probability of the colliding molecules capturing one another, and this results in a negative activation energy.

### Table 1 Thermodynamic parameters of adsorption of Zn(II) ions on CTC.

<table>
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<th>S. No.</th>
<th>Thermodynamic Parameters</th>
<th>Temperature (K)</th>
<th>Thermodynamic Values</th>
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<td>$E_a$</td>
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### 7 CONCLUSION

An attempt was made for the removal of the Zn(II) ions from aqueous solution using CTC. CTC is an adsorbent obtained from the curry tree barks (a vegetable waste), which is found to have $>90\%$ efficiency for the removal of Zn(II) ions. Hence, the present adsorption study can be considered as a green technique for the removal of Zn(II) ions. The testing of CTC as an adsorbent for removing of Zn (II) from aqueous solution is done. The batch study parameters, pH of the solution, adsorbent dose, adsorbent concentration and contact time are found to be effective on the adsorption efficiency of Zn (II). The experimental data obtained from kinetic and isotherm studies well fits the kinetic model and Freundlich isotherm model. The thermodynamic study indicates that the adsorption of Zn (II) is endothermic in nature. The results revealed that the preparing of CTC as an adsorbent is a simple and economic method. In addition, due to its biodegradability, it is considered as friendly environmental adsorbent.
REFERENCES


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