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Biosorption of Cu(II) from Aqueous Solution by Gokarna Leaves Powder as a Low Cost Adsorbent

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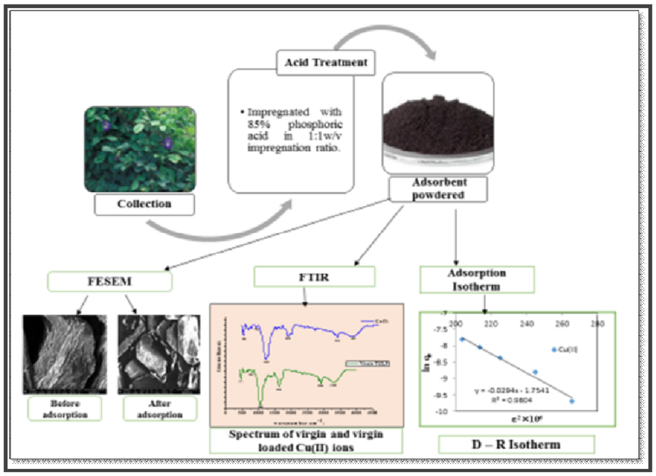
ABSTRACT

Adsorption capacity of Cu(II) ions onto acid treated gokarna leaves powder was investigated using batch adsorption method by optimizing various parameters like pH, contact time, adsorbent dosage, particle size, concentration and temperature. The biosorbent was characterized before and after adsorption by SEM, EDX, FTIR, DLS, CHNS and BET. Thermodynamic studies revealed that the adsorption process has been found to be exothermic in nature. The Langmuir, Freundlich, Temkin, D-R and Jovanoic isotherms were used to describe the adsorption equilibrium studies of acid treated gokarna leaves powder at different concentrations. D-R isotherm shows better fit than Langmuir, Freundlich, Temkin and Jovanoic isotherm in the concentration range studied. Experimental data were analyzed in terms of three kinetic models such as pseudo 1st order, pseudo 2nd order and intraparticle diffusion model and the result showed that the biosorption process of Cu (II) followed well pseudo 2nd order kinetics. Desorption studies show Treated gokarna leaves powder (TGLP) possesses an excellent reusability.

Graphical Abstract



Highlights:

- Maximum removal (95.52%) of copper ions (0.01M) was observed at pH 5, contact time 90 min, adsorbent dosage 0.5g and particle size 105 µm.

- SEM, EDX and FTIR studies clearly indicated adsorption on cu(II) ions on ATGLP
- Adsorption kinetics followed pseudo 2nd order rate equation.
- Adsorption of Cu(II) ions follows D – R and Freundlich isotherm
- Adsorption process was found to be spontaneous and thermodynamically favorable
- The acid treated gokarna leaves powder have been easily recovered

Keywords: Adsorption, Desorption, Gokarna leaves, Isotherms, Kinetics, Thermodynamics.

INTRODUCTION

Disposal of industrial waste water is one of the most pressing problems in the world, because such effluents usually contain considerable amount of heavy metal ions such as Cu(II), Ni(II), Co(II), Cd(II), Cr(VI), Pb(II) and Hg(II) [1-3]. These heavy metals are highly toxic and can damage the aquatic environment and human beings. Hence the removal and recovery of these metals from waste water streams is important. Copper is one of the most widely used heavy metals. It is mainly employed in electrical, smelting, mining, metal plating, electroplating, pigment and metallurgical industries in large amount, Cu is toxic to living organisms. Water polluted with Cu (II) ions affect the human health and leads to anaemia, it also affects liver, kidney, pancreas, stomach, myocardium, dizziness, diarrhea and causes intestinal irritation, neurotoxicity and Wilson's disease [4]. Therefore, there is a growing need for the development of new innovative and cost effective methods for removal of heavy metal ions. A number of techniques are being used for the removal of metal ions from aqueous solutions such as chemical precipitation, evaporation, ion exchange, solvent extraction, electrolysis, reverse osmosis and membrane filtration which are expensive and non-environmental friendly as compared to adsorption [5]. Adsorption is considered to be one of the most suitable, easy handling, cost effective with availability of different adsorbents. Recently, many researchers have used low cost adsorbents from agricultural waste materials for removing heavy metal ions. Plant leaves and agriculture by-products are among the adsorbents that have been widely applied for removing heavy metal ions and other pollutants; these include leaves of maize leaf [6], neem leaves [7], *solanum tuberosum* [8], *imperata cylindrica* leaf [9], mango leaf [10], soyabean hulls [11], Chitosan [12], chestnut shell [13], spent mushroom [14], opuntia biomass [15], *Spirodela polyrhiza* [16], mixed waste activated carbon [17], *Couroupita guianensis*[18], *Hibiscus cannabinnus* kenaf [19], sugaecane baggase [20], *eucalyptus* seeds [21], *Neurospora crass* [22], *Sacchromyces cerevisiae* [23], dried cactus [24], Biochar herb residue [25] and *C. Camphora* [26]. In the present investigation, we have used acid treated gokarna powder for the removal of Cu(II) ions from its aqueous solution. The biosorbent was characterized by Fourier transform infrared (FTIR), SEM with Energy dispersive X-ray (EDX), Brunauer- Emmett- Teller (BET), Carbon, Hydrogen and Nitrogen (CHN) and Dynamic light scattering (DLS) analysis. The influence of operating parameter such as pH, adsorbent dose, contact time, particle size, concentration and temperature on the biosorption of Cu(II) onto TGLP was investigated.

MATERIALS AND METHODS

Preparation and activation of the adsorbent: The leaves of gokarna were collected from home garden. These waste materials were washed with double distilled water to remove dusts and impurities. Initially leaves are kept for drying at room temperature for 6h and then in an oven at 80°C till they turn dark grey. Then they were pulverized and passed through mesh screens. The dried material was subjected for acid treatment (ratio 1:1) and kept at room temperature overnight. The treated leaves were washed with double distilled water to remove free acid. Finally, the adsorbent was dried at 100°C for 5h. The dried TGLP was then stored in a desiccator for further studies.

Chemicals: All the chemicals like copper sulphate, Sulphuric acid, orthophosphoric acid and sodium hydroxide were of analytical grade. The aqueous solutions were prepared in distilled water.

Characterization of adsorbent: TGLP was characterized before and after adsorption using different techniques. Surface morphology of the adsorbent was studied using scanning electron microscopy (FET Nova nano SEM-450) EDX was used for quantitative determination of the elements present in the sample**.** The Fourier transforms IR (FTIR) spectra of the samples were recorded using a spectrophotometer (Shimadzu 8400) in the range of 4000-400 cm^{-1} using KBr disk for reference. Determination of surface area, average pore size and pore volume was performed using a BET surface analyzer model Auto IQ-2 (Quantachrome instruments), while carbon, hydrogen and nitrogen content was determined using a CHN analyser (Thermofinnigan instrument). Determinations of particle size, polydispersity and diffusion coefficient were performed using a DLS (Brookhaven).

Adsorption Experiment: In order to get effective removal of metal ions, various parameters viz; pH, contact time, adsorbent dosage, particle size and concentration were optimized. For each experiment, 25mL of metal ions solution of known concentration was introduced in a 100 mL round bottom flask. The pH of the solution was adjusted using 0.01M NaOH and 0.01M H_2SO_4. Solution was continuously stirred on magnetic stirrer, and after specific time it was centrifuged and supernatant solution was filtered and analyzed.

The concentration of copper ions in aqueous solutions was determined by UV-Visible spectrophotometer. The percentage adsorption was determined using the following equation:

$$\%\,Adsorption = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

The adsorption capacity of the adsorbent was evaluated by using the following equation:

$$q_e = \frac{C_o - C_e}{m} \times V \qquad (2)$$

Where, q_e is the amount of metal ions adsorbed by TGLP (g g^{-1}); C_o is the initial metal ions concentration in contact with TGLP (g L^{-1}); C_e is the final metal ions concentration in aqueous solution (g L^{-1}) after adsorption; m is the mass of the adsorbent (g) and V is the volume of metal ions solutions (L).

Desorption of metal ions: TGLP loaded with copper ions at optimized conditions were treated with various volumes (4-20 mL) of 0.1M HNO_3 with contact time 60 min. Concentration of desorbed metal ions was measured by UV- Visible spectrophotometer. % Recovery of metal ions calculated using the following equation:

$$\%\,Recovery = \left(\frac{C_d}{C_a}\right) \times 100 \qquad (3)$$

Where, C_d is amount of metal desorbed (g L^{-1}) and C_a is amount of metal adsorbed (g L^{-1}).

RESULTS AND DISCUSSION

The proximate analysis of the raw materials and the physicochemical properties of the prepared TGLP were determined by standard methods (Table 1).

Adsorption studies:

Effect of pH: pH of the solution was varied between 3 to 7 and the results are shown in figure 1. The % removal of Cu(II) increases with pH and then decreases as observed from figure 1 . This is attributed to the competition of hydrogen ions with Cu(II) ions for active sites on the adsorbent surface. Increase in deprotonation results in the increase of negatively charged sites which enhanced attractive force between surface of adsorbent and copper ions resulting into higher adsorption capacity. Further decrease in adsorption capacity was due to the formation of precipitate of copper ions at higher pH.

Table 1. Characterization of adsorbents

S. No.	Properties	Values
	Proximate analysis	
1	Density (g cm^3)	0.4406
2	pH	4.58
3	Moisture content (%)	6.95
4	Ash content (%)	3.92
5	Volatile matter (%)	68.72
6	Fixed carbon (%)	20.41
	Physico-chemical properties	
1	BET Surface area (m^2 g^{-1})	4.13
2	Total pore volume (cm^3 g^{-1})	1.32×10^{-2}
3	Average pore Diameter (A°)	5.84×10^{2}
	CHN Analysis	
1	Carbon (%)	75.48
2	Hydrogen (%)	2.35
3	Nitrogen (%)	4.40

Effect of Contact time: The effect of contact time for adsorption of copper ions was studied by varying the time between 10 to 120 min (Figure 2). As contact time increased, efficiency of removal also increased (Figure2). The adsorption rate was rapid at the beginning of the adsorption process, and then the rate became constant after the equilibrium time. The saturation point is nearly reached at 90 min, at this point the metal ions amount being adsorbed onto the materials is in a state of dynamic equilibrium with the metal ions amount desorbed from the adsorbent.

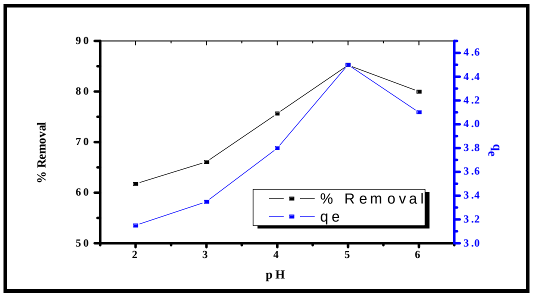


Figure 1. Effect of pH on copper adsorption onto TGLP.

Experimental conditions: Contact time: 60 min, adsorbent dosage: 0.5 g, particle size: 250 µm, concentration: 0.01 M.

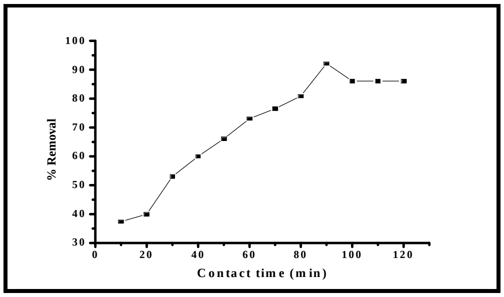


Figure 2. Effect of contact time on copper adsorption onto TGLP.

Experimental conditions: pH: 5, adsorbent dosage: 0.5 g, particle size: 250 µm, concentration: 0.01 M.

Effect of Adsorbent dosage: Adsorbent dose has a large influence in adsorption process and it determines the potential of biosorbent during the number of binding sites accessible to remove metal ions at a specified initial concentration. Adsorbent dosage varied in to range of 0.1-0.6 g. As can be seen from this figure, the percent removal of Cu(II) increased with an increasing adsorbent dosage (Figure 3). It can be explained as on increasing the adsorbent dose, the active sites available for sorption of Cu(II) ions also increase and as a result more sorption take place. However, the adsorption capacity showed an opposite trend. As the adsorbent dosage was increased from 0.1 to 0.6 g, the adsorption capacity reduced to 4.9 to 3.8 (g g^{-1}) respectively. The decrease in adsorption capacity is basically due to sites remaining unsaturated during the adsorption process.

Effect of Particle size: Surface area of the adsorbent is an important parameter for adsorption. The effect of particle size on the percentage removal of metal ions is shown in figure 4. This figure indicates that the percentage removal of metal ions decreased with the increase in particle size. As the particle size is smaller, the surface area per unit weight of adsorbent is larger and consequently the higher percentage of metal ions removal is noted.

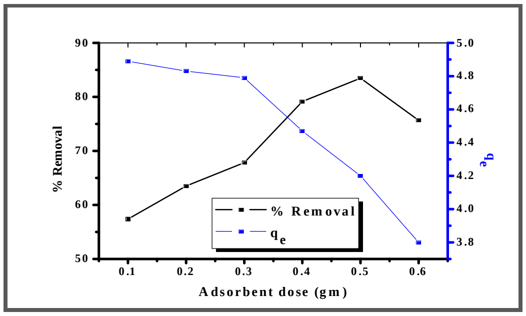


Figure 3. Effect of adsorbent dosage on copper adsorption onto TGLP.
Experimental conditions: pH: 5, contact time: 90 min, particle size: 250 µm, concentration: 0.01 M.

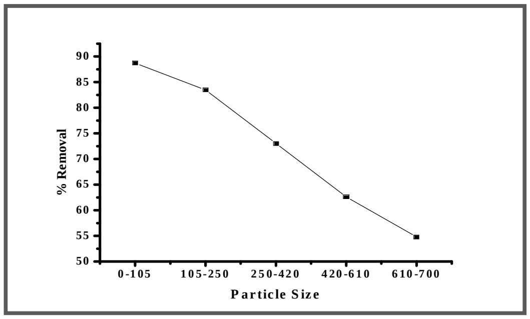


Figure 4. Effect of particle size (µm) on copper adsorption onto TGLP.
Experimental conditions: pH: 5, contact time: 90 min, adsorbent dosage: 0.5 g, concentration: 0.01 M

Effect of Concentration: The concentration of metal ions plays an important role in the adsorption capacity. The effect of concentration on the adsorption of copper ions has been studied over the range of 0.002 to 0.01M at 25°C and the results are shown in figure 5. It was observed that the % removal of metal ions decreased with increasing concentration. The metal ions concentration provides the necessary driving force to overcome the resistance of mass transfer from the aqueous phase to the solid phase. The increase in concentration also enhances the interaction between copper ions and treated gokarna leaf powder. The adsorption capacity increased from 9.2 to 8.1 g g^{-1} by increasing the metal ion concentration from 0.002 to 0.01M. This could be because of the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration on the surface of the adsorbent.

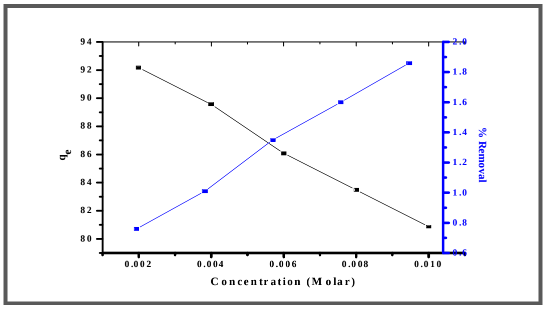


Figure 5. Effect of concentration on copper adsorption onto TGLP
Experimental conditions: pH: 5, contact time: 90 min, adsorbent dosage: 0.5 g, particle size: 105 µm.

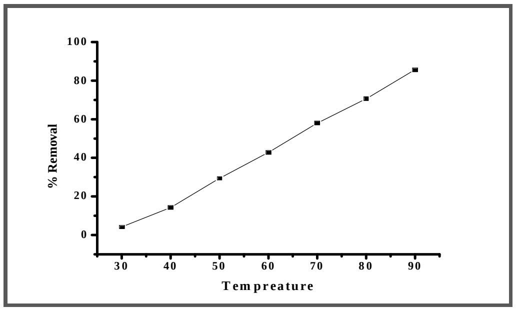


Figure 6. Effect of Temperature (°C) on copper adsorption onto TGLP
Experimental conditions: Under optimized parameters

Effect of Temperature: The adsorption of Cu (II) ions was studied at different temperatures (30-90°C) under optimized conditions. The adsorption efficiency was found to increase with increase in temperature as shown in figure 6. This may be due to the generation of new adsorption sites on the surface of the adsorbent and also increased rate of diffusion of the adsorbent which leads to the increased adsorption

Fe-SEM studies: The morphological and structural characteristics of TGLP were studied using field emission scanning electron microscope. The micrographs of the virgin and metal ions loaded chitosan are shown in figure 7.

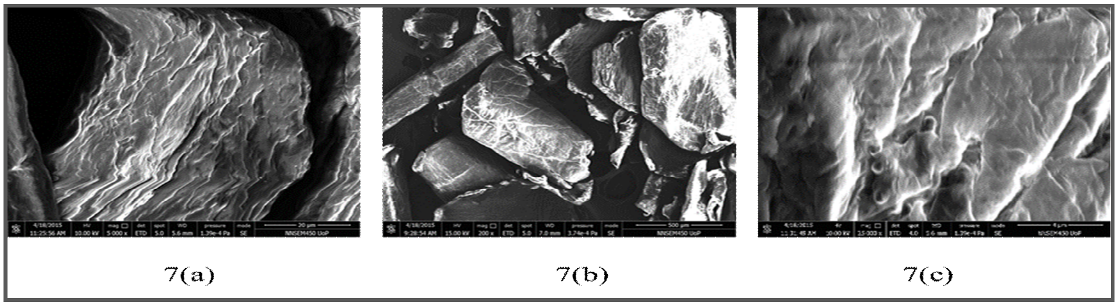

7(a) 7(b) 7(c)

Figure 7. Scanning electron microscope image of (a) Virgin TGLP, (b) TGLP loaded with Cu(II) ions and (c) after desorption of 0.01M Cu(II).

It can be seen that the porosity and surface structure of the virgin TGLP changes after loading with metal ions. The number of available sites decreased after adsorption.

EDX studies: The EDX spectra of the TGLP and TGLP loaded with metal ions are shown in figure 8. The EDX spectrum of TGLP clearly shows presence of Cu (II) ions after adsorption.

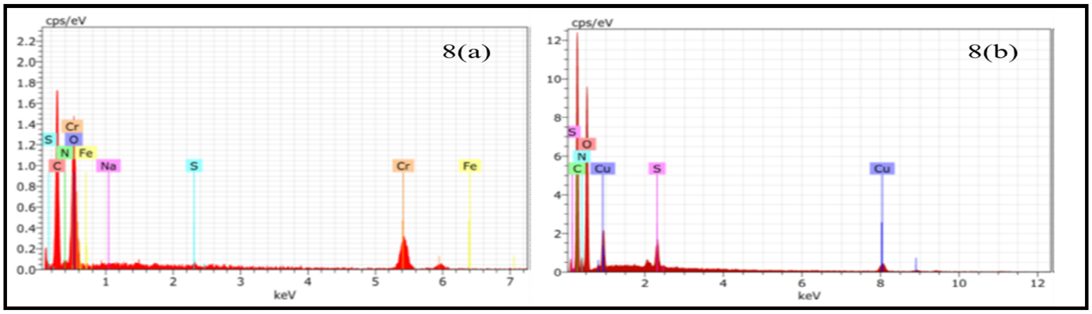


Figure 8. Energy dispersive spectrum of (a) Virgin TGLP, (b) TGLP loaded with Cu(II) ions.

FTIR Studies: The FTIR spectrum of acid treated gokarna leaves powder display a number of absorption peaks indicating the presence of different types of functional groups in the adsorbent (Figure 9) the broad and strong peak ranging from 3000-3600 cm^{-1} represents overlapping hydroxyl and amine stretching vibrations, which is consistent with the peaks at 1059 cm^{-1} assigned to C–O and C-N stretching vibration. The peaks at 2936 cm^{-1} are assigned to asymmetric and symmetric CH_2 groups. The peak at 1626 cm^{-1} could be assigned to carboxylate and imine groups. The peaks in the region 1400-1600 cm^{-1} could be assigned to aromatic skeleton vibration and the peaks around 1150-1250 cm^{-1} correspond to phenolic hydroxyl groups in lignin. The peaks observed in the region of 1049 are assigned to acetal groups. Peaks with wave numbers less than 1000 cm^{-1} indicate the presence of phosphate and sulphate groups. Some distinct changes in the spectrum can be noted after copper adsorption. The peak at 3368 cm^{-1} shifted to 3342 cm^{-1}, which suggests chemical interaction between copper ions and –OH and –NH groups. The carboxylate group was also involved in copper adsorption as the wavenumber shifted from 1618 cm^{-1}. The peak of acetal group shifted from 1049 cm^{-1} for copper loaded adsorbent. The peak for phosphate group represented by the wavenumber at 963 cm^{-1} disappeared after copper adsorption. Therefore, the FTIR study reveals that different types of functional groups were involved in the binding of copper ions, including hydroxyl, carboxyl, amino, ether, phenolic and phosphate.

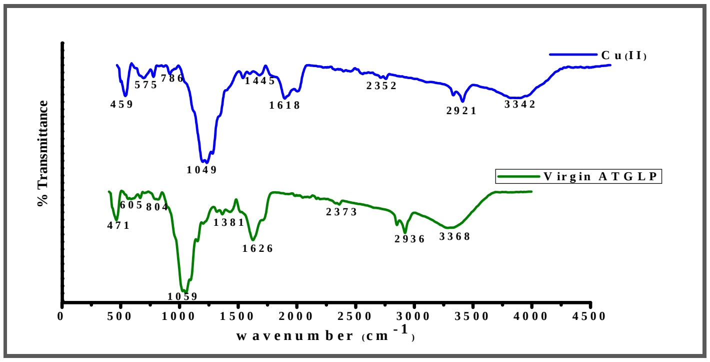


Figure 9. Spectrum of virgin TGLP and TGLP loaded with Cu(II) ions.

DLS Studies: Dynamic light scattering method is widely used for the determination of particle size. The TGLP particle size was found to be 20603.57 nm (polydispersity 0.410 and Diffusion coefficient 20382X10^{-9} cm^2 s^{-1}) in methanol solvent while TGLP loaded with copper ion particle size was found to be 1363.36 nm (polydispersity 0.286 and Diffusion coefficient 3.592X10^{-9} cm^2 s^{-1}). The change in particle size may be due to the presence of acetal and imine group and to strong interaction between the anionic group of hydroxyl, carboxyl, amino, phenolic and phosphate group of TGLP and cationic group of copper ions.

Thermodynamic study for adsorption: The values of thermodynamic parameters like free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) of the adsorption process were calculated by following equation:

$$\ln K = \frac{-\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \qquad (4)$$

$$\Delta G^\circ = \Delta H^\circ + T\Delta S^\circ \qquad (5)$$

Where K, R and T are the equilibrium constant.

The Van't Hoff plot is presented in figure 10. The plot of ln K versus 1/T was found to be linear ΔH° and ΔS° are calculated from slope and intercept, respectively.

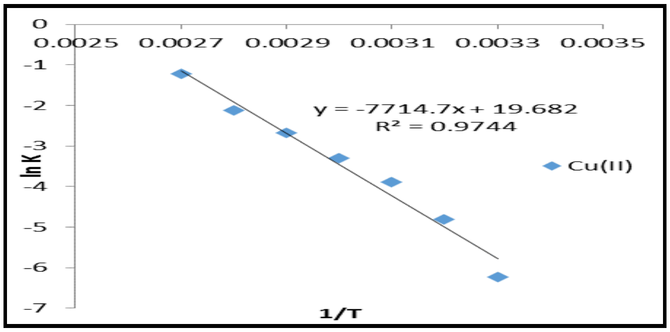


Figure 10. Thermodynamics study for adsorption of Cu(II) ions onto TGLP.

The thermodynamic parameters studied at different temperature are listed in table 2. As seen from this table, the positive values of ΔG° confirming the non- spontaneous nature of the adsorption. The positive values of ΔH° imply that the interaction between the metal ions and adsorbent is endothermic in nature; while the positive values of ΔS° specify the amplified randomness throughout the sorption process.

Table 2. Estimated values of ΔG°, ΔH° and ΔS° for adsorption of Cu(II) on acid treated gokarna leaves powder at different temperature.

Element	ΔG° (kJ (mol K)$^{-1}$							ΔH°(kJ mol^{-1})	ΔS° (kJ (mol K)$^{-1}$
	303 K	313 K	323 K	333 K	343 K	353 K	363 K		
Cu(II)	14.56	12.92	11.28	9.648	8.012	6.376	4.739	64.134	163.62

Adsorption Kinetics: To inspect the mechanism of adsorption process, characteristic constant of adsorption such as mass transfer and chemical reaction, were determined by using a pseudo 1st order, pseudo 2nd order and intraparticle diffusion model.

Pseudo 1st order kinetics: A linear form of pseudo 1st order model is:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (6)$$

Where q_e is the amount of metal ions adsorbed at equilibrium (g g^{-1}); q_t is the amount of metal ions adsorbed at time t (g g^{-1}); k_1 is the rate constant of pseudo first order kinetics (min^{-1}). The equation is known as the Lagergren equation. The rate constant k_1 was calculated from the linear plot of log (q_e-q_t) versus time (Figure 11). The R^2 values are very less suggesting that the biosorption of Cu (II) ions does not follow pseudo 1st order kinetic model.

Pseudo 2nd order kinetics: A linear form of pseudo 2nd order model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2\, {q_e}^2} + \frac{1}{q_e} t \qquad (7)$$

Where k_2 is the rate constant of pseudo second order kinetics (g. mg^{-1}.min^{-1}); q_e is the amount of metal ions adsorbed at equilibrium (g g^{-1}) q_t is the amount of metal ions adsorbed at time t (g g^{-1}) k_2 and q_e can be determined from the slope and intercept of the plot t/qt versus time (Figure 12) respectively.

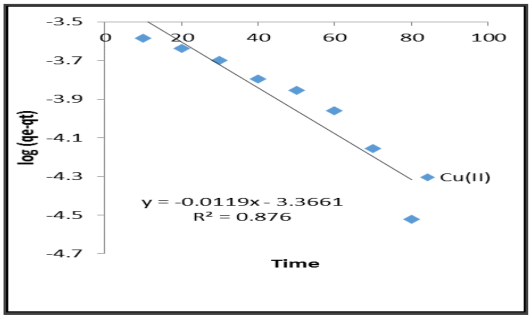


Figure 11. Lagergren plot for removal of copper ions onto TGLP.

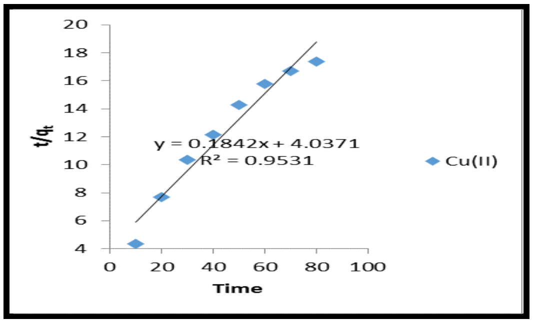


Figure 12. Pseudo 2nd order plot for removal of copper ions onto TGLP.

Intraparticle diffusion model: This model describes about the diffusion of the adsorbate from the outer surface into the pores of TGLP. The Intraparticle diffusion equation is given by

$$q_t = k_{id} t^{0.5} + C \qquad (8)$$

Where k_{id} is the particle diffusion rate constant in g.mg^{-1}.min^{-1}; and c is the intercept. A plot of q_t versus $t^{0.5}$ (Figure 13) gives the value of k_{id}.

Table 3. The parameters of the kinetic constants obtained for Cu(II) ions onto TGLP.

Metal	Kinetic Models							
	Pseudo 1st order			Pseudo 2nd order			Intraparticle Diffusion	
	K_1 (min^{-1})	q_e ($g\ g^{-1}$)	R^2	K_2 ($g\ mg^{-1}.\ min^{-1}$)	q_e ($g\ g^{-1}$)	R^2	k_{id} ($g\ mg^{-1}\ min^{-1}$)	R^2
Cu(II)	0.025	0.00043	0.876	8.389	0.00054	0.953	0.517	0.859

The values of R^2 for the pseudo 2nd order model were higher than those of the pseudo 1st order and intraparticle diffusion model. The pseudo 2nd order kinetic model suggests that the rate limiting step of the biosorption is probably controlled by chemisorption (Table 3).

Adsorption Isotherm: The adsorption isotherms of copper ions were fitted using different isotherm models; Langmuir isotherm, Freundlich isotherm, temkin isotherm, Javaonic Isotherm and D-R isotherm.

Langmuir Isotherm: Langmuir Isotherm represents the equilibrium distribution of metal ions between solid and liquid phase. The linear Langmuir isotherm allows the calculation of adsorption capacity and Langmuir constant by the following equation

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{b q_{max}}\right)\frac{1}{C_e} \qquad (9)$$

Where q_e the amount of adsorbate adsorbed per unit mass of TGLP ($g\ g^{-1}$), b the constant related to the affinity of the binding sites ($L\ g^{-1}$), q_{max} the maximum amount of metal ion per unit of TGLP ($g\ g^{-1}$), and C_e the adsorbed metal concentration at equilibrium. Therefore, the plot of 1/qe against 1/Ce (Figure 14) gives a straight line with a slope of $1/ab$ and an intercept of 1/b.

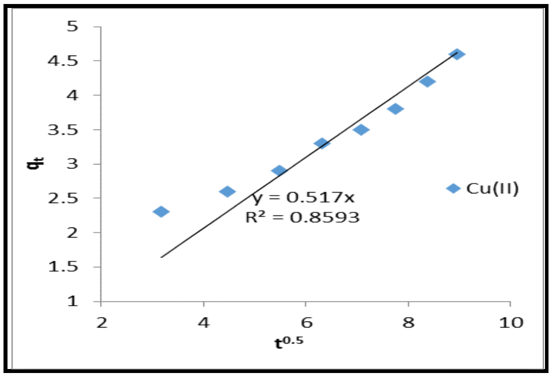


Figure 13. Intraparticle diffusion plot for removal of copper ions onto TGLP.

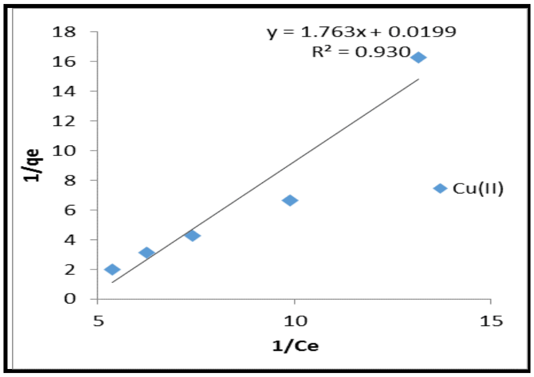


Figure 14. Langmuir Isotherms for removal of Cu(II) ions onto TGLP.

Freundlich Isotherm: The Freundlich isotherm equation is used for the depiction of multilayer with the contact stuck between adsorbed molecules. The linear form of Freundlich isotherm model is given by the equation

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log K \qquad (10)$$

Where q_e the amount of adsorbed per unit weight ($g\ g^{-1}$); K the Freundlich constant; n the Freundlich constant related to adsorption intensity. Freundlich constants, n and K can determined from linear plot of log q_e versus log C_e (Figure15). The values of n were found to be below unity (Table 4) implies chemisorption process.

Table 4. Equilibrium parameters for adsorption of Cu(II) ions onto TGLP

Adsorption isotherms	**Constants**	**Value**
Langmuir Isotherm	α (g g-1)	0.113
	q(max) (L g^{-1})	50.25
	R^2	0.923
Freundlich Isotherm	K	158.49
	N	0.4912
	R^2	0.975
Temkin Isotherm	B	6.078
	A	1.497
	R^2	0.975
D – R Isotherm	Q_{DR} (mol g^{-1})	0.173
	β	0.029
	E (kJ mol^{-1})	4.153
	R^2	0.980
Jovanoic isotherm	q_m (g g^{-1})	-7.952
	K_J	1.619
	R^2	0.930

D–R Isotherm: The D-R isotherm equation, distinguish between physical and chemical adsorption. The linearized form of D-R isotherm model is given by the following equation

$$\ln q_e = \ln Q_{DR} - \beta\epsilon^2 \qquad (11)$$

Where q_e the amount of adsorbed per unit weight (g g^{-1}), C_e the equilibrium metal ion concentration (g L^{-1}), QDR the maximum adsorption capacity (mol g^{-1}), β the activity coefficient of mean free energy, ϵ the Polanyi potential. The value of ϵ was calculated from the equation

$$\epsilon = RT\ln(1 + \frac{1}{Ce}) \qquad (12)$$

A linearized plot of ln q_e versus ε^2 enable to determine the values of β and Q_{DR} from the slope and intercept (Figure 16). From the value of activity β coefficient, biosorption mean free energy E (kJ mol^{-1}) is determined as follows

$$E = 1/\sqrt{(-2\beta)} \qquad (13)$$

Where E is the mean adsorption energy (kJ mol^{-1}) and β is the Dubinin-Radushkevich constant. The calculated D-R constants and mean free energy for adsorption are shown in table 4. The value of mean free energy E calculated from D-R isotherm model was 4.513 kJ mol^{-1}. If the value of E lies between 8-16 kJ mol^{-1} the process is said to follow chemical ion exchange while E< 8kJ mol^{-1} then the process follows physical adsorption. In the current study the biosorption process of Cu(II) ions onto acid treated gokarna leaves powder follows physical adsorption.

Temkin Isotherm: Temkin isotherm based on the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and characterized by a uniform distribution of binding energies up to some maximum binding energy can be represented in a linear form as follows:

$$q_e = BlnA + BlnC_e \qquad (14)$$

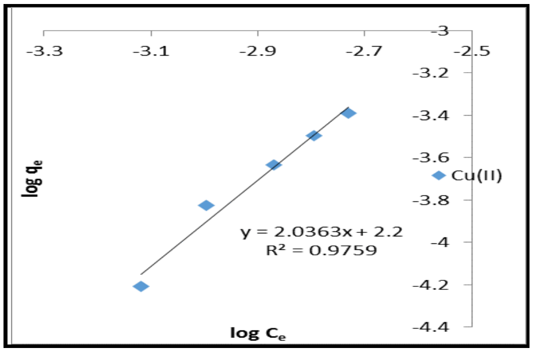


Figure 15. Freundlich isotherms for removal of Cu(II) ions onto TGLP.

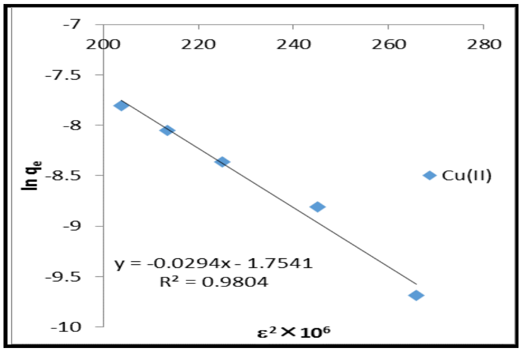


Figure 16. Dubinin-Radushkevich isotherms for removal of Cu(II) ions onto TGLP.

$$B = RT/b \qquad (15)$$

Where q_e the amount of adsorbed per unit weight (g g^{-1}); C_e the equilibrium metal ion concentration (g L^{-1}); A the Temkin isotherm constant and b the constant related to heat of sorption. The A and B can be calculated from the intercept and slope of the linear plot of q_e against ln C_e (Figure 17).

Jovanoic Isotherm: The Jovanoic isotherm which is based on the same assumptions of the Langmuir isotherm also considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules on the homogeneous surface and can be represented in a linear form as follows:

$$ln q_e = ln q_m + K_J C_e \qquad (16)$$

Where q_e the amount of adsorbed per unit weight (g g^{-1}); C_e the equilibrium metal ion concentration (g L^{-1}); q_m is the maximum amount adsorbed (g g^{-1}); K_J is the constant related to the energy of adsorption. The q_m and K_J can be calculated from the intercept and slope of the linear plot of lnq_e against C_e (Figure 18).

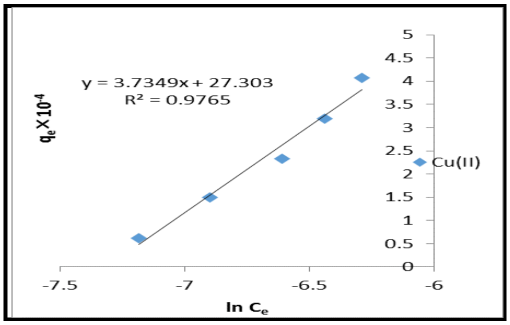


Figure 17. Temkin isotherms for removal of Cu(II) ions onto TGLP

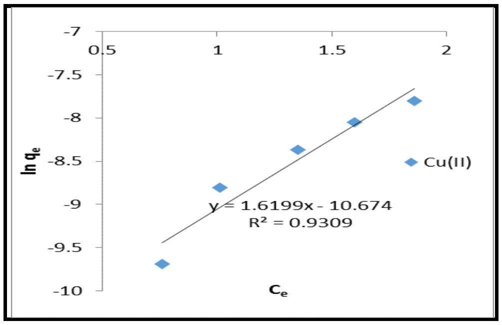


Figure 18. Jovanoic isotherms for removal of Cu(II) ions onto TGLP.

The theoretical parameters of isotherms along with regression coefficient are listed in table 4. According to R^2 values in this table, copper biosorption follows the five isotherm models in the order D-R isotherm > Jovanoic isotherm > Freundlich = Temkin > Langmuir isotherm for acid treated gokarna leaves powder at the experimental circumstances investigated.

Desorption: Desorption of metal ions (0.01M) loaded on TGLP under optimized conditions was carried out with 0.1M HNO_3 as an eluent. As can be seen from figure 19, the maximum desorption (85.32%) was observed by using 20 mL of HNO_3. The result shows that the disbursed copper ions can be effectively recovered.

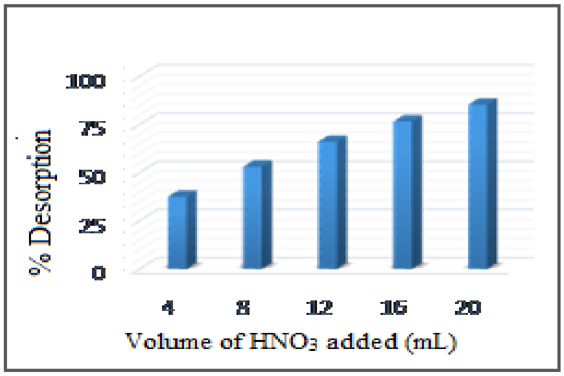


Figure 19. Desorption of Cu(II) ions loaded on TGLP using 0.1M HNO_3.

Comparison of various adsorbents: The obtained results are compared with the literature reports where in removal of Cu(II) ions was studied using various adsorbents. A comparative data is shown in table 5.

Table 5. Comparison of adsorption capacity of Cu(II) with various adsorbent.

Adsorbent	q_{max} (mg g^{-1})	Reference
Neurospora crassa	12.30	[22]
Saccharomyces cerevisiae	10.72	[23]
Rubber leaves	14.97	[27]
Neem leaf powder	18.29	[28]
C. camphora leaves powder	17.87	[26]
S. tuberosum leaves powder	42.74	[8]
***Gokarna* leaves powder**	**50.25**	**Current study**

An examination of above table reveals that the adsorption capacity of adsorbents used in the present work for removal of Cu(II) ions is greater than the other adsorbents used by different researchers. Thus adsorbent used in the present study are promising adsorbents for industrial waste water treatment.

APPLICATION

Acid treated gokarna leaves powder can be effectively used for the removal of Cu(II) ions from aqueous solution. The developed method is cost effective, efficient and can be applied to other metals also.

CONCLUSIONS

Gokarna leaves modified with acid solution demonstrated a satisfactory ability to adsorb copper ions from aqueous solutions. The optimum conditions for Cu(II) adsorption were: pH 5, contact time 90min, adsorbent dose 0.5g, particle size 105µm concentration 0.002M and temperature 90°C The thermodynamic study showed that adsorption of copper ions on TGLP was non-spontaneous and exothermic in nature. The kinetic study revealed that the pseudo 2nd order equation provided the best correlation, suggesting a chemisorption process. The results obtained from the equilibrium isotherms adsorption studies of copper ions indicated to be well fitted to the D-R isotherm equation under the concentration range studied. The results from the present study showed that gokarna leaves powder may be used as an economical, environmentally friendly and effective adsorbent to remove copper ions from industrial waste water.

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