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Kinetic, Thermodynamic and Adsorption Isotherms Studies on Removal of Copper(II) Ions from Aqueous Solutions Using Jumbo Grass (*Sorghum Bicolur Sorghum Sudanefe*)

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The removal of copper(II) ions from aqueous solutions using Jumbo grass (*Sorghum Bicolour Sorghum Sudanefe*) was studied and to investigate the utilization of this adsorbent. The newly prepared bio sorbent was characterized by FT-IR and scanning electron microscopy. The removal efficiency of copper(II) was carried out by batch mode methods. The adsorption capacity of the bio sorbent was influenced by changing the parameters such as bio sorbent dose, pH, contact time and initial ion concentrations. The maximum removal of copper(II) was 52 % at pH 7 and equilibrium reached at 180 min. From the experimental data the Langmuir, Freundlich and Temkin adsorption isotherm models were arrived and the pseudo first order, pseudo second order, Elovich and intra-particle diffusion kinetic models were also investigated. The monolayer maximum adsorption capacity (Q_m) of the biosorbent achived was 10.53 mg/g. Equilibrium data were well fitted to the Langmuir isotherm model and the pseudo second order kinetic model. Desorption of metal ions were also monitored by hydrochloric acid.

Keywords: Copper, Jumbo grass, Adsorption, Isotherm, Kinetic models.

INTRODUCTION

Copper is an essential element to human being and is required for various biological processes. Large intake of copper by man can have harmful, even fatal effects. Copper is the second toxic metal to aquatic organisms after mercury[1]. The accumulation of copper in human organisms like brain, liver, pancreases and skin leads to 'Wilson's disease due to absorption of copper by man[2]. The effect of copper on hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and necrotic changes in the liver and kidney was studied by Kalavathy *et al.*[3]. As per the safe drinking water act[4] the permissible limit of copper in drinking water is 1.3 mg/L. Hence, there is a necessary step need to treat industrial effluents containing such metals prior to discharge to protect human life. The biosorption is a newer technology developed which has been found to be superior to other techniques for removal of heavy metals from wastewater, because of its capability for adsorbing a broad range of different types of adsorbates efficiently and its simplicity of design[5]. Adsorbents are low cost if it is abundant in nature, requiring little processing and is a by-product of waste materials from industry. Plant waste is inexpensive as they have very low economic value. Natural plant waste is widely used for water treatment process. The aim of the present investigation is to use the jumbo grass (*Sorghum Bicolour Sorghum Sudanefe)* as bio adsorbent to evaluate the effectiveness for removal of copper(II) ions from waste water. A literature search reveals that no work has been studied on the removal of copper from aqueous solutions using jumbo grass as adsorbent.

EXPERIMENTAL

Preparation of adsorbent: Dry jumbo grass (*Sorghum Bicolour Sorghum Sudanefe*) powder used as an adsorbent which was collected from Palar river bed near Vellore District, Tamil Nadu. The plants were cleaned with running water to remove the impurities and other surface-adhered particles. The washed plant materials were sun dried for 7 days and cut into small pieces. The dried materials were ground well to fine powder and sieved, so obtained biomass was dried in over at 55 °C for 24 h and stored in desiccators. Here after Jumbo grass powder called as water washed jumbo grass (WJG) powder. The produced water washed jumbo grass adsorbent was characterized by FT-IR and SEM. The physical properties were analyzed.

Adsorption studies: All chemicals and reagents used were of analytical grades and double distilled deionized water was used in sample preparation. A stock solution of 1000 mg/L of copper(II) ions is prepared by dissolving 3.927 g of copper sulphate in doubly distilled water and the pH of the solution is adjusted using 0.1 N H_2SO_4 or 0.1 N NaOH. From the stock solutions, working solutions of 20 to 120 mg/L concentration of the adsorbates were obtained by serial dilutions. Concentration of the metal ions before and after adsorption was measured using a double UV-Visible spectrophotometer with 470 nm.

Batch equilibration method: All experiments were carried out at 30 °C in the batch mode. The batch mode was selected because of its simplicity and reliability. The batch experiments were done in different Erlenmeyer glass flasks of 250 mL capacity. A known amount of adsorbent (0.5 g) was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure better mixing. Each flask was filled with a known volume (100 mL) of sample before commencing stirring such as metal ion solution with an initial concentration of 20 to 120 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, separated and the equilibrium concentration of the metal ions was measured by UV-visible spectrophotometer. The adsorption capacity Q_e (mg/g) and percentage removal were calculated from eqns. 1 and 2, respectively.

$$Q_e = [C_o - C_e] \times V/M \quad (1)$$

$$\text{Removal (\%)} = [C_o\text{-}C_e] \times 100/C_o \quad (2)$$

where, C_o is the initial metal ion concentration in solution (mg/L), C_e is the final equilibrium concentration in solution (mg/L), V is the volume of the solution (L) and M is the mass of the adsorbent used (g). The effect of different parameters such as dosage of the adsorbent, initial concentration, contact time, pH and temperatures were studied on the removal of the copper(II) ions. All the experiments were conducted twice and the mean values are reported in this paper.

Adsorption isotherms: The adsorption isotherm is highly significant in the removal of metal ions by water washed jumbo grass powder were obtained using 20-120 mg/L of copper(II) concentrations. The equilibrium data were fitted to Langmuir[6], Freundlich[7] and Temkin isotherms[8]

Langmuir isotherm I:

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \quad (3)$$

Langmuir isotherm II:

$$1/Q_e = 1/bQ_mC_e + 1/Q_m \quad (4)$$

Freundlich isotherm:

$$\log Q_e = \log K_F + 1/n \log C_e \quad (5)$$

Temkin isotherm:

$$Q_e = B \ln A + B \ln C_e \quad (6)$$

The dimensionless separation constant R_L is an important characteristics for the Langmuir isotherm model which is defined as $R_L = 1/(1 + bC_o)$ where b is the Langmuir constant and C_o is the initial concentration of the metal ions. The values of R_L indicate the shape of the isotherm as follows[9]:

R_L value	Types of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Adsorption kinetics: The adsorption kinetic studies help to describe the rate of adsorbate uptake and rate controls at the solid-solution interface. The kinetics of adsorption on the adsorbent was analyzed using pseudo-first order model, pseudo-second-order model, Elovich model and intra-particle diffusion model.

Activation parameters: The Gibbs free energy change (ΔG°) was calculated from the equilibrium constant K (L/mol) related to the reciprocal of the Langmuir constant b[10]. The other thermodynamic parameters enthalpy and entropy were analyzed.

Desorption studies: Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. The desorption studies is carried out by using hydrochloric acid.

RESULTS AND DISCUSSION

Physico-chemical properties: The physical properties of the adsorbent water washed jumbo grass powder were given in Table-1. The data shows the presence of high percentage (11 %) ash content in adsorbent which inhabit surface development and reduces surface area of adsorbent[11,12] and hence lesser the adsorption capacity.

TABLE-1
CHARACTERISTICS OF THE ADSORBENT

Properties	Water washed jumbo grass
Density (g/cc)	0.3246
Moisture content (%)	9.9
Acid insoluble matter (%)	3.6
Water soluble matter (%)	7.13
Ash content (%)	11.00
pH	6.75

FT-IR analysis: The FT-IR spectra before and after adsorption of copper(II) ions on to water washed jumbo grass powder were shown in Fig. 1a and 1b. FT-IR spectra of water washed jumbo grass powder revealed that the presence of various organic functional groups[13]. Broad absorption bands appeared at 3418 cm^{-1} was due to stretching vibration of hydrogen bonded –OH and –NH bonds indicating the presence of hydroxyl and amide groups. The IR spectra metal loaded adsorbent showed a shift in the absorption frequency from 3420 to 3418 cm^{-1} indicating the possibility of binding of copper to the –OH and/or –NH group present in water washed jumbo grass by complex formation. The weak band observed at 2923 cm^{-1} was stretching vibration of C–H bond in methyl groups. The band at 1740 cm^{-1} was characteristic of carbonyl stretching of acids while 1250 cm^{-1} band associated with C–O stretching and OH bending mode[13]. After copper adsorption the 1740 cm^{-1} band shifted into 1738 cm^{-1} which is due to the corresponding carbonyl (ketone and carboxylic acid) stretching frequency, which represents the oxidation of substrate and binding of copper. There is shift in the frequencies of the absorption band of both C=O and C–O in carboxylic group (–COOH) due to metal binding. The C–O band shifts to high frequency 1257 cm^{-1} due to the high electron density induced by the adsorption of copper(II) on the adjacent carbonyl group. The spectra display a number of absorption peaks indicating the various chemical compounds of water washed jumbo grass powder. The bands shift indicates the involvement of these groups in biosorption of copper(II) by water washed jumbo grass powder.

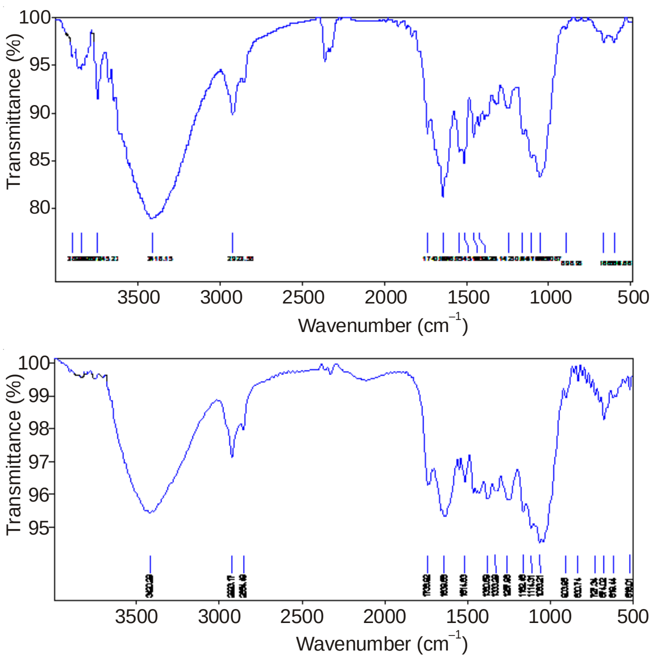

Fig. 1a & 1b FT-IR spectra before and after adsorption of copper(II) ions on to water washed jumbo grass powder

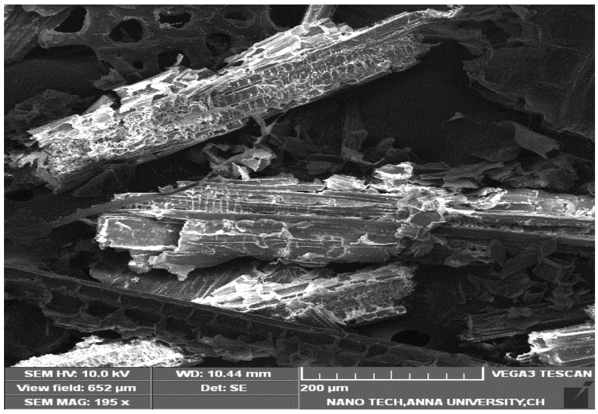

Fig. 2. SEM image of unloaded water washed jumbo grass adsorbent

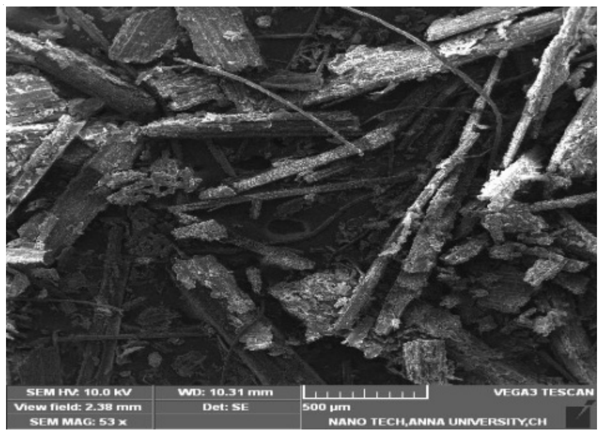

Fig. 3. SEM image of copper loaded water washed jumbo grass adsorbent

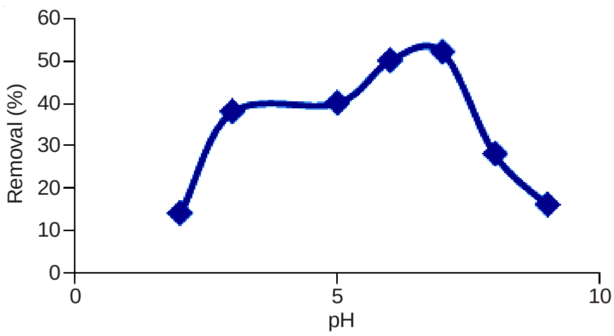

Fig. 4. Effect of pH on removal efficiency of efficiency copper ions by water washed jumbo grass at 30 °C

SEM analysis: The microstructure and surface morphology of the fresh water washed jumbo grass powder and copper loaded water washed jumbo grass powder were analyzed by scanning electron microscopy (SEM) and the images shown in Figs. 2 and 3. The SEM images of unloaded water washed jumbo grass powder revealing the nature of biomaterials which is fibrous and heterogeneous with lot of pores which are responsible for binding sites for metal ions. The uptake of copper(II) by water washed jumbo grass was demonstrated by the change in morphology of the adsorbent's surface. Based on the surface morphology result of water washed jumbo grass; it is suggested that produced water washed jumbo grass can be used as adsorbent for liquid-solid system due to the importance of fibrous materials.

Adsorption studies

Effect of pH: The effect of pH on the copper ions removal was analyzed over the range from 2 to 9 and the plot was given in Fig. 4. The percentage removal of copper ions was minimum at both low pH-(2) and high pH-(9) values because of H^+ ions competed effectively at low pH with copper(II) ions to occupy sorption sites on biosorbent surface and at higher pH, an increase of –OH ions causes decreases in adsorption of copper ions at adsorbent. The maximum removal of copper was found to be 52 % at pH 7. As the pH of the system increases from 3-7, the number of negatively charged sites on biomass surface increased and the number of positively charged sites decreases. This indicates that greater electrostatic attraction of the copper(II) ions by the water washed jumbo grass sorbent surface. Similar results were obtained for copper removal by marine green algae[14] and peat[15]. Other adsorption experiments were carried out with 7 pH.

Effect of dose: The adsorption of copper(II) ions on water washed jumbo grass powder was studied by varying the adsorbent dosage from 100-800 mg into series of 250 mL Erlenmeyer flasks which contain 100 mL of copper(II) ions solution of 20 mg/L concentration. A graph of % removal was plotted against the adsorbent dosage are shown in Fig. 5. It shows that the percentage adsorption increased with an increase in the water washed jumbo grass adsorbent dosage. The maximum removal was 42 % at 500 mg/100 mL adsorbent dose. This may be due to the increased water washed jumbo grass surface area and availability of more adsorption sites. However, % removal decreased after dose of 500 mg, may be due to decrease in adsorption surface area to copper resulting from overlapping of adsorption sites[16]. The optimal dose 500 mg/100 mL was fixed for other experiments.

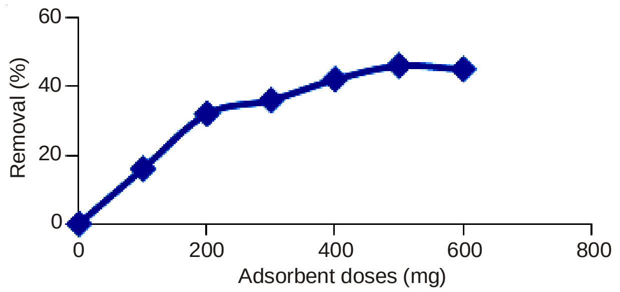

Fig. 5. Effect of adsorbent doses on removal efficiency of Copper ions by water washed jumbo grass at 30 °C

Effect of contact time: It reveals that the percentage of copper removal increases with increase with contact time till equilibrium has been reached. After the equilibrium time there is no significant adsorption taking place. The equilibrium time for copper adsorption on water washed jumbo grass powder was found to be 180 min and highest removal of copper from aqueous solution was 40 % which shown in Fig. 6. This equilibrium time is one of important parameters for an economical wastewater treatment system. Hence the optimal contact time 180 min used for the rest of parameters investigations.

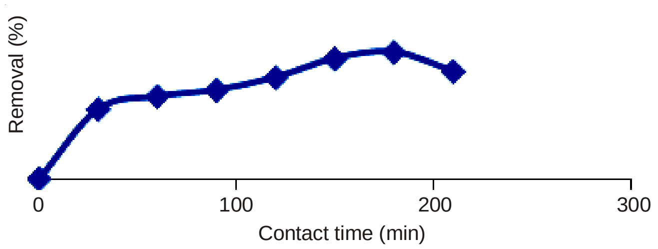

Fig. 6. Effect of contact time and initial concentration removal efficiency of copper ions by water washed jumbo grass at 30 °C

Effect of initial ion concentration: The effect of initial concentration on the percentage removal of heavy metal by water washed jumbo grass was shown in Fig. 7. It reveals that the percentage removal decreases gradually with the increase in initial ion concentration, the removal is highly effective on the 20 mg/L initial concentration after which removal decrease gradually from 35 to 26 %. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metal ion. However, at higher concentration the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. The maximum removal of copper was 35 %. All the parameters were evaluated with 20 mg/L concentration of copper ions. Similar report have been given by others[17,18].

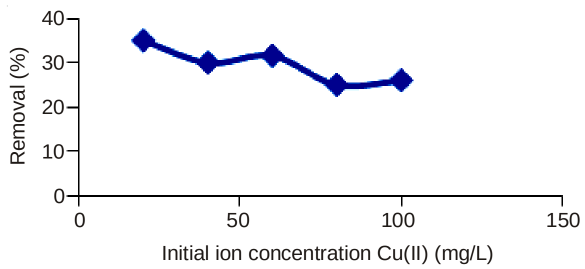

Fig. 7. Effect of initial concentration on removal of copper ions by water washed jumbo grass at 30 °C

Effect of temperature: The effect of temperature on the removal of copper by water washed jumbo grass powder was studied at 30, 40 and 50 ºC for concentration range 20-120 mg/L at pH 7. The results showed that the adsorption capacity was not affected significantly by temperature variations. Hence the adsorption of copper ions was favoured at low temperature thus the removal process was exothermic in nature.

Adsorption isotherm

Langmuir Isotherm model: Langmuir isotherm is based on the adsorption takes place at specific homogeneous sites within the adsorbent. Once a metal or dye molecule occupied a site, no further adsorption can take place at the sites. Homogeneous adsorption occurs with each molecule having same enthalpies and same activation energy. Saturation value is reached with monolayer adsorption. The linear eqn. 7 of Langmuir isotherm was used in this study.

$$1/Q_e = 1/bQ_mC_e + 1/Q_m \quad (7)$$

where, C_e is the equilibrium concentration of the sorbate (mg/L), Q_e is the amount of copper(II) ions adsorbed at equilibrium (mg/g), b is the adsorption energy of the sorbent surface, Q_m is the maximum sorption capacity (mg/g). The Langmuir constant b and Q_m are calculated from the slope and intercept of the linear plot of $1/Q_e$ against $1/C_e$ which are given in Table-2. The Langmuir isotherm plot of copper(II) ions sorption onto water washed jumbo grass was shown in Fig. 8. The maximum adsorption capacity (Q_m) of copper(II) on water washed jumbo grass powder calculated from Langmuir graph was 10.53 mg/g at 30 °C. The Q_m value for copper on water washed jumbo grass is higher than chromium(III) on water washed sorghum straw (9.35 mg/g)[19]. Table-3 shows that the previous studies reveals the copper adsorption on various adsorbents. The recorded value of the present study of copper(II) on Jumbo grass have a reasonable adsorption capacity which suggests that this biosorbent (water washed jumbo grass) could be used for the removal of metals from waste water. From the Langmuir constants it was possible to conclude that copper(II) adsorption on water washed jumbo grass powder follow the Langmuir model. The correlation coefficient value [R^2 = 0.986] was close to unity prove the best fits for the Langmuir isotherm model. The parameter R_L values between 0 and 1 indicate the favourable adsorption for all initial concentration (C_o) at various temperatures 30, 40 and 50 °C. The calculated R_L values are given in Table-4.

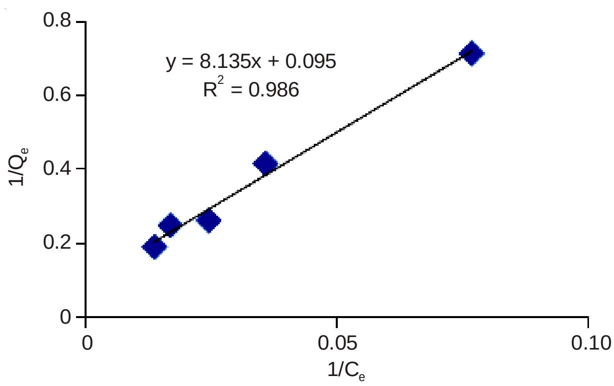

Fig. 8. Langmuir isotherm model of copper(II) ions sorption onto water washed jumbo grass biomass at 30 °C

TABLE-2
LANGMUIR, FREUNDLICH AND TEMKIN ISOTHERM PARAMETERS WITH TEMPERATURE

Isotherm model	Parameters	Temperature (°C)		
		30	40	50
Langmuir	Q_m (mg/g)	10.53	9.260	4.390
	b (L/mg)	0.011	0.010	0.005
	K_L (L/mg)	0.014	0.017	0.023
	R^2	0.986	0.978	0.979
Freundlich	n	1.351	1.721	1.369
	KF (L/g)	4.721	2.275	3.373
	R^2	0.972	0.960	0.910
Temkin	A (L/g)	1.453	1.452	1.473
	B	0.228	0.218	0.189
	R^2	0.939	0.989	0.907

TABLE-3
COMPARISON OF ADSORPTION CAPACITY OF COPPER(II) WITH VARIOUS ADSORBENTS

Name of the adsorbent	Q_m (mg/g)	Reference
Saw dust	1.74	20
Palm fibre	2.00	21
Bagasse fly ash	2.26	22
Activated rubber wood saw dust	5.73	23
Lignite carbon	5.90	24
Chitosan	7.55	25
Water washed Jumbo grass	10.53	Present study
Wheat shell	10.84	26
Tree fern	11.70	27
Banana peel	13.23	28
Marine green algae	24.50	14

TABLE-4
DIMENSIONLESS SEPARATION FACTOR (R_L) FOR COPPER ON WATER WASHED JUMBO GRASS WITH VARIOUS TEMPERATURES

Initial concentration of copper (mg/L)	R_L values: Temperature (°C)		
	30	40	50
20	0.8143	0.8334	0.9044
40	0.6868	0.7144	0.8254
60	0.5932	0.6262	0.7592
80	0.5223	0.5558	0.7023
100	0.4666	0.5002	0.6542

Freunlich Isotherm model: The Freundlich isotherm is derived by assuming a heterogeneous surface, with non-ideal and reversible multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over surface of the adsorbent. It is assumed that an increase in the adsorbate concentration also increases the amount adsorbed on the surface of the adsorbent. The Freundlich equation expressed as

$$q_e = K_F C_e^{1/n} \quad (8)$$

The linear form of the isotherm can be represented as follows:

$$\log Q_e = \log K_F + 1/n \log C_e \quad (9)$$

Freundlich isotherm constants 1/n and K_F of the adsorbent are calculated from the slope and intercept of the linear plot obtained log Q_e aginst log C_e as shown in Fig. 9. The adsorption intensity or surface heterogeneity was measured from the slope of of the plot and its value (1/n = 0.740) was close to one indicates that the surface is less heterogeneous. The 1/n value less than 1, also indicates favourable adsorption. However, the

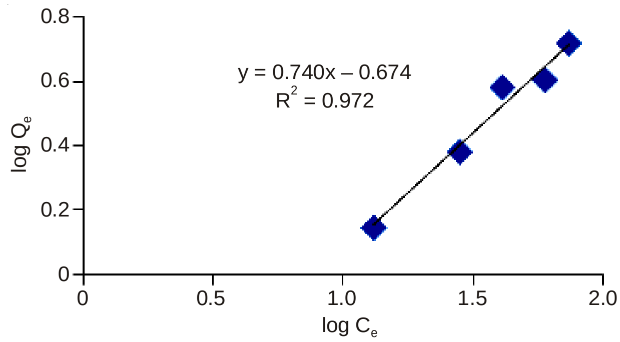

Fig. 9. Freundlich isotherm model of copper(II) ions sorption onto water washed jumbo grass biomass at 30 °C

higher correlation coefficient value obtained from Langmuir (R^2 = 0.986) compared to Freundlich plot (R^2 = 0.972) suggest that adsorption was taken place on monolayer adsorption on adsorbent than the heterogeneous surface of multilayer adsorption.

Temkin isotherm model: Temkin[29] isotherm model provides the effect of indirect adsorbate-adsorbent interaction isotherm which explained the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage due to the above interactions. The linear form of isotherm can be expressed as follows:

$$q_e = B \ln A + B \ln C_e \quad (10)$$

where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the equilibrium binding constant (L/g), R is the gas constant (8.314 J/mol/L) and T is the absolute temperature (K), C_e is the concentration of adsorbate in solution at equilibrium (mg/L). A linear plot of q_e *versus* ln C_e enables the determination of the isotherm constants A and b from the slope and the intercept. The data were listed in Table-2. If the values of A decreased with increase in temperature the adsorption considers chemisorptions of an adsorbate onto adsorbent[30]. The Temkin isotherm was fairly fitted well as compared to the Langmuir, Freundlich isotherm due to the low correlation coefficient (R^2 = 0.939) value for the adsorption of copper(II) ion on water washed jumbo grass powder.

Adsorption kinetic studies: The adsorption kinetic studies help to identify the adsorption mechanism and evaluate the efficiency of various adsorbents for metal removal which depends on the physical and/or chemical properties as well as governed by surface adsorption on the pore wall of adsorbent. For determining the kinetics of adsorption of copper onto water washed jumbo grass powder was studied by four kinetic models such as the pseudo-first order model, the pseudo-second order model, the Elovich model and intra particle diffusion model.

Pseudo-first order model: The pseudo-first order model was analyzed by Lagergren[31] whose linear form is represented as:

$$\log (q_e - q_t) = \text{Log } q_e - k_1 t/2.303 \quad (11)$$

where, q_e (mg/g) and q_t (mg/g) are the amount of metal adsorbed at equilibrium and at a given time t (min) and k_1 is the pseudo-first order rate constant (L/min). The linear plot of log (q_e- q_t) *versus* t shows that the Lagergren equation which is shown in Fig. 10. The slope and intercept of the straight line of the plot gives the values q_e and k_1 are summarized in Table-5.

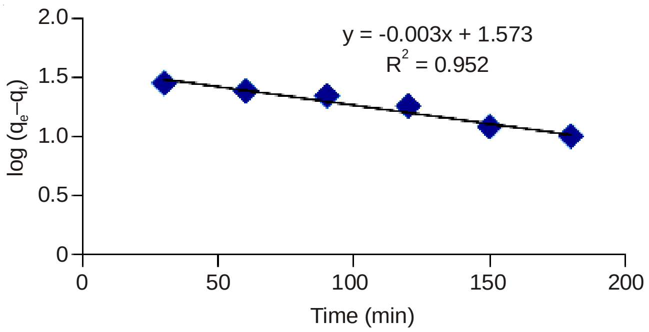

Fig. 10. Pseudo first order kinetics of copper(II) sorption onto water washed jumbo grass biomass at 30 °C

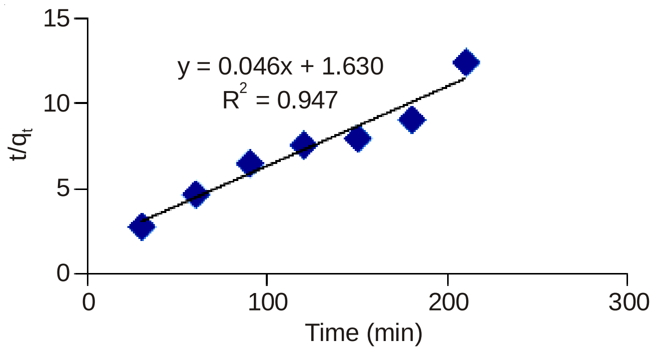

Fig. 11. Pseudo second order kinetics of copper(ll) sorption onto water washed jumbo grass biomass at 30 °C

The low correlation coefficient ($R^2 = 0.952$) and abnormal q_e values for the pseudo-first order kinetic fit, suggesting that the adsorption process does not follow the pseudo-first order model.

Pseudo-second-order model: For the analysis of adsorption mechanism Ho and Mckay[32] proposed a pseudo-second order kinetic model and its linear form as follows:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (12)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate adsorbed on the surface of the adsorbent at equilibrium and at a given time t (min) and k_2 (g/mg/min) is the pseudo-second order rate constant. The parameters k_2 and q_e can be calculated from linear plot of t/q_t *versus* t which shown in Fig. 11. The initial adsorption rate (h) can be calculated from k_2 and q_e values using eqn. 13:

$$h = k_2 q_e^2 \quad (13)$$

h (mg/g/min) represents the amount of metal adsorbed per unit mass of adsorbent and unit time. This value (h) can be used to compare the initial sorption rate of metals on various adsorbents at similar conditions. The data are given in Table-5. The calculated q_e (333.33 mg/g) value of pseudo-first order differed a lot; whereas second order value (25.00 mg/g) was closer to the experimental value. The correlation coefficient value was found very high ($R^2 = 0.947$). The results reveals that the adsorption process follows the pseudo-second order kinetic model and also suggests that the rate controlling step in adsorption of copper is chemisorptions involving valance forces through the exchange of electrons between sorbent and sorbate[33].

Elovich model: The Elovich equation was developed to explain the kinetics of chemisorptions of gas onto solids[34] and its differential form is represented in eqn. 14. The parameters α is the rate initial concentration (mg/g.min) which also represents the rate of chemisorptions at zero coverage and parameter β is the desorption constant (g/mg) and is related to the extent of surface coverage and the activation energy of chemisorptions[15]:

$$dq_t/d_t = \alpha \exp(-\beta q_t) \quad (14)$$

where q_t is the amount sorbed at time t and α and β are constants during any one experiment. To simplify the Elovich eqn. 15 becomes:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad (15)$$

The α and β can be obtained from the slope and intercept of the linear plot of q_t against ln (t). Eqn. 15 used to best the applicability of the Elovich equation to the kinetics of copper(II) sorption on water washed jumbo grass. The Elovich equation considers the rate-controlling step in the diffusion of the adsorbate molecules and describes chemisorptions on adsorbents and has been applied for the adsorption of solute from liquid solution. Correlation coefficient (R^2) of Elovich model for adsorption of copper onto water washed jumbo grass was found to be fairly good and the adsorption is may be controlled by diffusion and chemisorptions. The Elovich model parameters α, β and R^2 are summarized in Table-5.

Intra-particle diffusion model: Generally, the adsorbate migrates from the liquid phase to the surface of the adsorbent particles occurs in three consecutive steps: (1) film diffusion step, (2) transport of adsorbate within the pores of the adsorbent and (3) intra-particle diffusion process. The intra-particle diffusion theory[35] was developed and assumes that intra-particle diffusion is the only rate controlling step of the adsorption process when the negligible diffusion of the liquid film surrounding the adsorbent. The intra-particle diffusion is investigated by it's mathematical expression as follows:

$$Q_t = K_{id} t^{½} + C \quad (16)$$

where q_t is the amount of metal ions adsorbed at time t, C is the intercept and K_{id} is the intra-particle diffusion rate constant (mg $min^{0.5}$ g^{-1}). If intra-particle diffusion was involved in the adsorption then a plot of q_t against $t^{1/2}$ would gives linear relationship. The slope was used to identify the intra-particle diffusion rate constant, K_{id} and the intercept C value give an idea of the boundary layer thickness; the larger the intercept,

TABLE-5
KINETIC PARAMETERS FOR ADSORPTION OF COPPER(II) IONS ON WATER WASHED JUMBO GRASS AT 30 °C

Kinetic model	Linear equation	Reaction constants	q_e (mg/g)	R^2
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$K_1 = 0.00691\ min^{-1}$	333.33	0.952
Pseudo-second order	$t/q_t = 1/k_2 q_e^2 + (1/q_e)_t$	K_2 = 0.00075 g/mg.min	25.0	0.950
Elovich model	$q_t = 1/B \ln(ab) + 1/B \ln(t)$	A = 21.40 mg/g.min; B = 0.0866 g/mg	–	0.897
Intra-particle diffusion	$q_t = K_{id} t^{1/2} + C$	$K_{id} = 1.164\ mg/g.min^{0.5}$; C = 3.989	–	0.955

TABLE-6
THERMODYNAMIC PARAMETERS FOR COPPER(II) ADSORPTION BY WATER WASHED JUMBO GRASS POWDER

Temperature (K)	Langmuir constant (b)	K = 1/b	-ΔG° (KJ/mol)	-ΔH° (KJ/mol)	-ΔS° (KJ/mol)
303	0.01143	87.489	11.27		
313	0.00999	100.100	12.01	30.73	0.0642
323	0.00528	189.140	14.08		

the greater the effect of the boundary layer. The values of K_{id} and C are shown in Table-5. The deviation of straight lines from the origin indicates that the pore diffusion is not the sole-rate determining step[36]. It can also be concluded on the basis of C value. If intercept value (C = 3.989) is not equal zero, then the intra- particle diffusion is not the rate-controlling step.

Thermodynamic parameters: Thermodynamic parameters associated with the adsorption, the thermodynamic parameters were calculated using the following eqns. 17-19. The calculated values are given in Table-6.

$$k = 1/b \quad (17)$$

$$\Delta G^\circ = -RT \ln k \quad (18)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19)$$

where, ΔG° is the Gibbs free energy change (KJ/mol), T is the temperature (K), R is the gas constant (8.314 J mol/K) and k is the equilibrium constant related to Langmuir constant equal to 1/b[10]. The ΔH° and ΔS° values obtained from the slope and intercept when plotting ln k against 1/T. The negative values of ΔG° show that the adsorption is highly and spontaneous. The negative value of ΔH° indicates the reaction is exothermic in nature. The negative value of ΔS° also indicated randomness of adsorption of copper on adsorbent water washed jumbo grass powder[37].

Desorption studies: Desorption studies help to elucidate the nature of adsorption and reuse of the adsorbent and the metal ions. The studies were carried out by using 0.1 M hydrochloric acid desorption was more than 70 % removal of adsorbed copper(II) ions. Desorption of the copper(II) ions by dilute mineral acids/alkalis indicates that the copper(II) ions are adsorbed onto the water washed jumbo grass powder through physisorption[38].

Conclusion

The equilibrium and kinetic studies for the removal of copper from aqueous solution by water washed Jumbo grass was analyzed. The prepared water washed Jumbo grass adsorbent would be quite useful for removing heavy metals from waste water solutions. The effect of copper adsorption on water washed jumbo grass by various factor such as pH, contact time, dosage, initial ion concentration and temperatures were investigated. The equilibrium parameters have been evaluated with respect to Langmuir, Freundlich and Temkin isotherm and the equilibrium data fitted well to Langmuir isotherm than other isotherms. Kinetic studies reveal that the adsorption of copper on water washed jumbo grass obeyed very much for pseudo-second order than pseudo-first order, Elovich and intra-particle diffusion models. The thermodynamic parameters were calculated which reveals that adsorption was spontaneous and exothermic in nature.

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