



A Novel Agricultural Waste Adsorbent, Watermelon Shell for the Removal of Copper from Aqueous Solutions

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Abstract: The present study deals with the application of Watermelon Shell, an agricultural waste, for the adsorptive removal of Cu(II) from its aqueous solutions. This paper incorporates the effects of time, dose, temperature, concentration, particle size, agitation speed and pH. Analytical techniques have been employed to find pore properties and characteristics of adsorbent materials. Batch kinetic and isotherm studies have also been performed to understand the ability of the adsorbents. The adsorption behavior of the Cu(II) has been studied using Freundlich, Langmuir and Tempkin adsorption isotherm models. The monolayer adsorption capacity determined from the Langmuir adsorption equation has been found as 111.1 mg/g. Kinetic measurements suggest the involvement of pseudo-second-order kinetics in adsorptions and is controlled by a particle diffusion process. Adsorption of Cu(II) on adsorbents was found to increase on decreasing initial concentration, increasing pH up to 8, increasing temperature, increasing agitation speed and decreasing particle size. Overall, the present findings suggest that watermelon outer shell is environmentally friendly, efficient and low-cost biosorbent which is useful for the removal of Cu(II) from aqueous media.

Key words: Watermelon shell; Adsorption; Copper; Kinetics models; Isotherms models

INTRODUCTION

Heavy metals released to environment have continuously increasing trends as a result of industrial activities and technological developments, which is a significant threat to the environment and public health due to their toxicity, accumulation in food chain and persistence in nature [1]. Toxic heavy metal ions introduced to the aquatic streams by means of various industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. [2, 3]. Several episodes due to heavy metal contamination in aquatic environment have increased the awareness about the heavy metal toxicity [4]. Moreover, high intakes of these metals can cause liver, kidney and pancreas damage [5].

Removal of copper (Cu(II)) from waste water is crucial and its toxicity for human beings is at levels of 100-500 mg per day [6, 7]. Cu(II), is one of the major contaminants emanating from electrical, electroplating and metal

finishing industries. It is often found in high concentrations near mines, landfills and waste disposal sites [8]. The World Health Organization in 2006 recommended 2.0 mg/L as the maximum acceptable concentration of copper in drinking water [9]. In human copper toxicity causes itching and dermatization, keratinization of the hands and soles of feet [10, 11]. Severe gastro-intestinal irritation and possible changes in the liver and kidney occur due to intake of excessively large doses of copper [12]. Inhalation of copper spray increases the risk of lung cancer among exposed workers [13]. Hence the removal of copper from wastewater before its discharge into the aquatic system is extremely important and deserves immediate attention.

The selection of a particular treatment procedure depends on the nature of the effluent, waste type and concentration, presence of other constituents, level of removal required and economics [14]. Conventional physico-chemical methods for removing heavy metals from waste streams include chemical reduction,

electrochemical treatment, ion exchange, precipitation and evaporative recovery [15]. These processes have significant disadvantages, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products and are generally very expensive when the contaminant concentrations are in the range of 10-100 mg/l [16]. Similarly, activated carbon, the most widely used adsorbent in the treatment of waste water, is expensive and may also require complexing agents to improve its ability to remove inorganic matter [17].

Of late biosorption has proven to be an effective technology for the removal of heavy metals. Many low-cost adsorbents have been used for this purpose such as carrot residues [11], *Sargassum wighiti* [20], lentil, wheat, rice [13], rice husk [21], nanoparticles [22] and tea industry wastes [23] but there is still a need for adsorbents which are cheap, easily available and efficient. In recent years, versatile methods for cleaning of wastewater by employing cost-effective and efficient adsorbents have been developed [20].

Furthermore, besides a strong metallic affinity, the search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural origin as potential metal adsorbents [24-26]. These low cost materials have not been studied as extensively as other biosorbents, owing to their local, rather than global availability [17] and therefore, in this investigation, the biosorption capacity of a typical lignocellulosic plant biomass and a waste product from the food industry, namely Watermelon outer shell, is considered.

The main objective of this work was to evaluate the adsorption performance of locally derived Watermelon Shell (WS), namely *Citrullus lanatus* for the removal of Cu(II) from single aqueous solutions [27]. The Cu(II) adsorption equilibrium and kinetics were determined. Langmuir, Freundlich and Temkin isotherm equations were employed to quantify the adsorption equilibrium. The effects of solution pH, adsorbent concentration, temperature and ionic strength on Cu(II) adsorption were examined. An intraparticle diffusion model was used to investigate the adsorption mechanisms.

MATERIALS AND METHODS

Adsorbent: Watermelon Shells (WS) were collected from Tiruchirapally, were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at sun light in a shade for 48 hours. The shells were then kept in an air oven at 333–343 K for 24 hours. The dried shells were then converted into fine powder by

grinding in a mechanical grinder. The powder was sieved to get the adsorbent with size ranged 150 to 300 μm . The powder was sieved. After drying for several hours at room temperature, the WS powder was preserved in air tight glass bottles for use as adsorbents.

Conventional chemical as well as analytical techniques were employed to ascertain different characteristics of adsorbents. Specific gravity of WS was determined using a mercury porosimeter. Size of material selected was 150 to 300 μm . The loss on ignition (LOI) was determined by heating a pre-weighed dry sample (left at 105°C in an oven and then cooled in desiccators) to 600°C over a period of 2 h [28]. The Point of Zero Charge (PZC) was determined using the solid addition method [29] viz: a series of 100mL conical flasks, 45mL of 0.1M KNO_3 solution was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 10 by adding either 0.1N HNO_3 or NaOH . The total volume of the solution in each flask was made exactly to 50mL by adding the KNO_3 solution. The pH_0 of the solutions were then accurately noted. WS (1g) was added to each flask and securely capped, immediately. The suspension was then manually agitated. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_i) values ($\Delta\text{pH} = \text{pH}_0 - \text{pH}_i$) was plotted against the pH_0 . The point of intersection of the resulting curve at which pH_0 gave the PZC. The FTIR spectra of WS (before and after sorption of copper) were used to determine the vibrational frequency changes in the functional groups in the adsorbents. FTIR spectra of the samples were also recorded on PerkinElmer Model System 2000 using KBr pellet method.

Chemicals: Stock solution were prepared in distilled water from salts of Cu(II). For 1000 mg/L solution preparation, dried salts of 3.801 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 1000 mL of distilled water. Analytical grades of HCl and NaOH (Merck) solutions were used for pH adjustment. The resulting stock solutions were stored in air tight bottle.

Batch Studies: A stock solution of copper (1000 mg/L) was prepared in deionized double distilled water using copper nitrate. All working solutions of varying concentrations were obtained by successive dilution (AR grade). The pH of the solution was adjusted to required value by adding either 0.01M HCl or 0.01M NaOH using pH meter. The clear supernatants (10 mL) after filtration were analyzed for copper ion concentrations using an Atomic Absorption Spectrometer (AAAnalyst 300, India) at a wavelength of 312 nm.

The batch mode operation was used to study the removal of Cu(II) from synthetic wastewater. Adsorption experiments were carried out using 50 mL of copper solution of desired concentration (10 mg/L), adsorbent dosage 0.001 g/50 mL in 150 mL Erlenmeyer flasks at temperature $26 \pm 1^\circ\text{C}$ and agitation speed of 150 rpm on orbital shaker (Scigenics Biotech Orbitek, India) for 210 min. At predetermined time interval, the samples were separated by centrifugation at 4000 rpm for 10 min. Residual Cu(II) concentration in the supernatant was determined as stated above.

The amount of Cu(II) adsorbed per unit of WS (mg copper per g WS) was calculated according to a mass balance on the copper concentration Eq (1).

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

Where, C_i and C_e were the initial and final concentration of Cu(II) in the solution, respectively. The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume V is often used to acquire the experimental adsorption isotherms .and m is the mass of adsorbent (in g) used.

The percentage removal of the copper was calculated using the following equation:

$$\text{Percentage of removal (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

The prologue investigations were carried out in batches in different conditions of pH, concentration, time, amount of adsorbent, temperature, etc., to check the propensity of adsorption process. After undergoing meticulous experimental procedures, concentration 10 mg/L was chosen. Thereafter supernatant liquid was filtered through Whatman filter paper No. 42 and the amount of copper adsorbed was determined by Atomic Absorption Spectrometer (AAS).

RESULTS AND DISCUSSIONS

Characterization of Adsorbent: The detailed values of physical characteristics of adsorbent are given in Table 1. The high LOI values indicate that WS contains more organic matter. The results of the zero point of charge of the WS which is the point of intersection of the resulting curve ($\text{pH}_{\text{PZC}} = 6$) is presented in Fig. 1. From Fig. 1, it was observed that at pH less than 6 the surface of the WS is predominated by positive charges while at pH greater

Table 1: Physical characteristics of adsorbent

Properties	Values
Moisture content	2.8%
Specific gravity	1.23
Loss on Ignition	70.5%
Point of zero charge	6

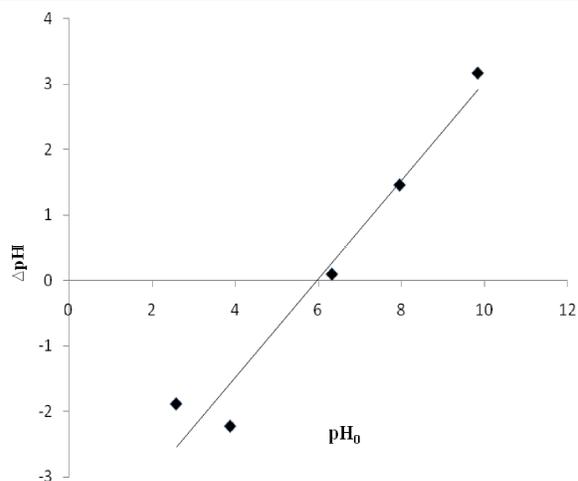


Fig. 1: Point of Zero Charge for Water melon

than 6 the surface is predominated by negative charges [30]. Thus, below pH 6, the surface has a high positive charge density; uptake of positively charged copper would be low. With increasing pH, i.e., beyond the PZC, the negative charge density on the surface of the adsorbent increases, resulting in an enhancement in the removal of copper.

FT-IR Spectroscopy: The FT-IR technique was an important tool to identify some important functional groups, which are capable of adsorbing pollutant ions [31, 32]. The FT-IR spectrum of water melon, before and after Cu adsorption, is shown in Fig. 2. The FTIR spectra before and after sorption of Cu(II) were used to determine the vibrational frequency changes in the functional groups in the adsorbent. The spectra of adsorbents were measured within the range of $400\text{--}4000\text{ cm}^{-1}$ wave number. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents before and after adsorption. The FTIR spectra of the adsorbent display a number of absorption peaks, indicating the complex nature of the studied adsorbent. The peaks of WS are given in our previous work [26].

Effect of Contact Time: The contact time affected the extent of adsorption of the Cu(II). Fig. 3 shows the variation in the extent of adsorption (%) of Cu(II) on WS

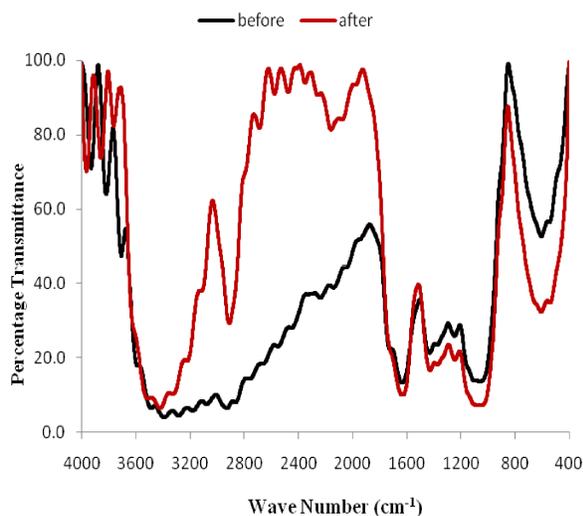


Fig. 2: FT-IR Spectrum of WS before and after Cu(II) Adsorption

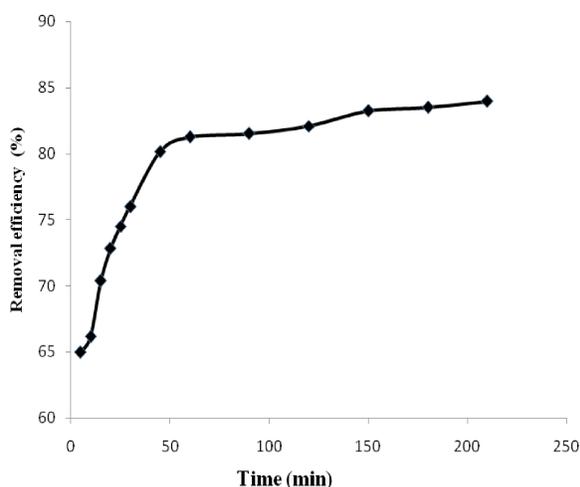


Fig. 3: Effect of contact time on Cu(II) removal by WS

at 30°C with time for constant metal concentration. As it can be seen from Fig. 3, the amount of the adsorbed Cu(II) onto the WS increases with time and, at some point of time, it reaches a constant value beyond which no more is removed from solution. At this point, the amount of the Cu(II) desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the metal being adsorbed onto the WS [33]. The time required to attain this state of equilibrium is termed the equilibrium time and the amount of Cu(II) adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions [33]. After 5 min, it has a removal efficiency of 64% and a maximum of 84% at equilibrium time of 120 min.

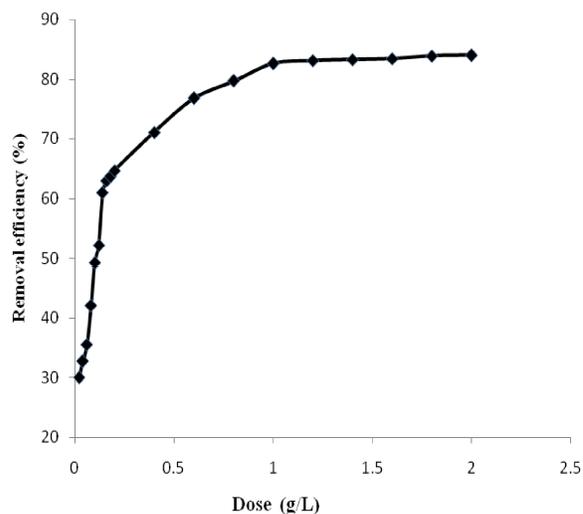


Fig. 4: Effect of Dose on Cu removal by water melon

Effect of Dose of Adsorbent: The adsorption of Cu(II) on WS was studied by changing the quantity of WS in the test solution while keeping the initial Cu(II) concentration (10 mg/L) and temperature as constant at equilibrium time. Increase in adsorbent dosage increased the percent removal of Cu(II), as shown in Fig 4, which is due to the increase in adsorbent surface area of the adsorbent [21]. But after a particular dose the change in concentration is very less. This is due to high WS concentration; there is a very fast superficial adsorption onto the WS surface that produces a lower solute concentration in the solution than when WS dose is low. Thus with an increase in adsorbent dose, the amount of Cu(II) adsorbed per unit mass of bottom ash is reduced; thus caused a decrease in equilibrium uptake value [35]. The maximum removal was found to be 84% at the dose of 0.002 g/L.

Effect of Initial Concentration: Adsorption experiments were conducted to study the effect of the initial concentration of Cu(II) in the solutions on the rate of metal adsorption on water melon. The experiments were carried out at a fixed adsorbent dose (0.002 g) and at different initial Cu(II) concentrations (6, 10 and 20 ppm) for different time intervals at 30°C as shown in Fig. 5. It was observed that Cu(II) uptake is rapid for the first 20 min and there after it proceeds at a slower rate and finally attains saturation. This may be explained by a rapid adsorption on the outer surface, followed by slower adsorption inside the pores [36]. As the initial Cu(II) concentration increases from 6, 10 and 20 ppm the equilibrium removal of Cu(II) decreases. This may be due to the fact that at lower concentrations almost all

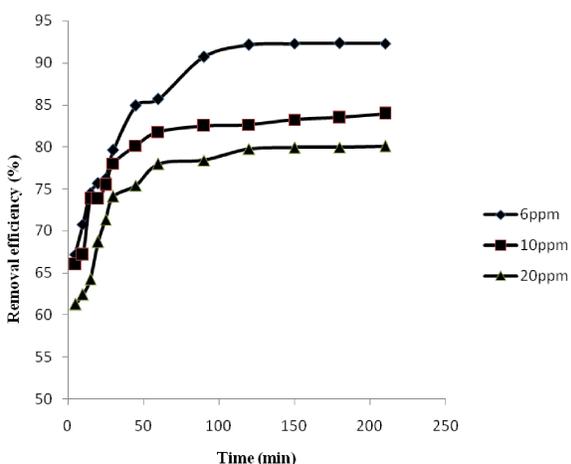


Fig. 5: Variation of removal efficiency with the variation in the initial Cu concentration

the Cu(II) molecules were adsorbed very quickly on the outer surface, but further increases in initial Cu(II) concentrations led to fast saturation of WS and thus most of the Cu adsorption took place slowly inside the pores [37].

Adsorption Kinetics: To determine the applicability of the adsorption processes in wastewater treatment, kinetic studies were also carried out. To evaluate the performance of unit processes utilizing adsorption, it is necessary to have an understanding of the time dependence of the concentration distribution of the solute in both the bulk solution and solid adsorbent phases and to identify the rate-determining step [38]. The kinetics of Cu(II) sorption was investigated using various different models: Pseudo-first order, Pseudo-second order kinetics, Elvoich kinetics and Power model. The best-fit model was selected based on the linear regression correlation coefficient, R^2 , values.

Pseudo First-Order Equation: The pseudo first-order equation is generally expressed as [39],

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \quad (3)$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg/g), k_1 is the rate constant of pseudo first-order adsorption (1/min). The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot (Fig. 6) of $\log(q_e - q_t)$ vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

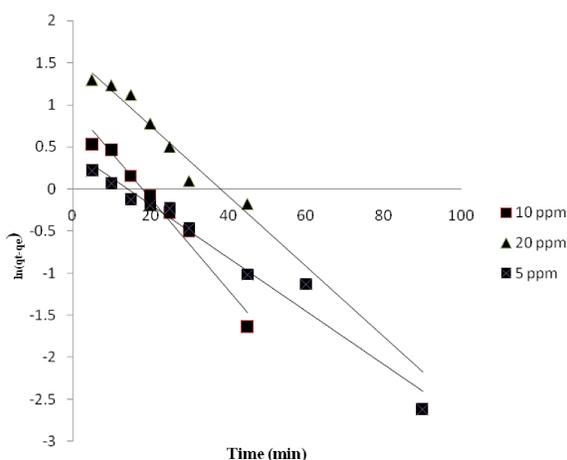


Fig. 6: Pseudo First-Order Plot for Cu(II) Removal by WS

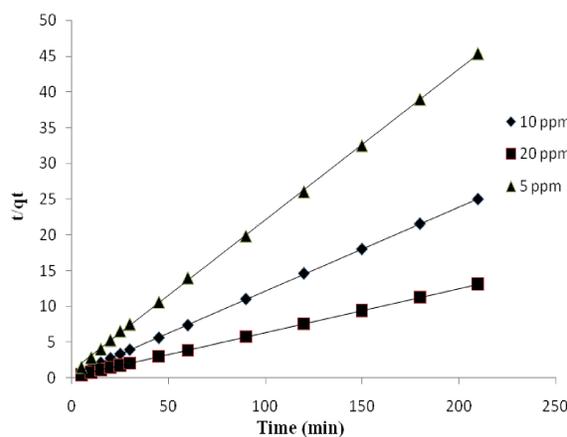


Fig. 7: Pseudo Second-Order plot for Cu(II) Removal by WS

Pseudo Second-Order Equation: The second-order Lagregren equation was given by [40]. It is expressed as

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (4)$$

Where, k_2 is the rate constant of pseudo second-order adsorption (g/mg/min). The plot (Fig. 7) of (t/q_t) and t of Eq. 4 should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

It can be seen from the results listed in Table 2 that the linear correlation coefficients for first-order and second-order model are good and based on the comparison between experimental and theoretically calculated q_e values, it was found that the pseudo second order model fitted better than pseudo first order model for removal of Cu(II) by water melon.

Table 2: Kinetic co-efficient for Pseudo first order and Pseudo second-order kinetic model

Concentration (ppm)	Theoretical q_e (mg/g)	Pseudo first order kinetic model			Pseudo second-order kinetic model		
		q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2
5	4.608	2.786	0.043	0.9702	4.73	0.047	0.9997
10	9.49	8.4	0.025	0.9712	9.38	0.044	0.9999
20	15.92	14.9	0.024	0.9458	16.2	0.04	0.9999

Table 3: Kinetic co-efficient for Power model and Elvoich equation kinetic model

Concentration (ppm)	Power model kinetic model			Elvoich equation kinetic model		
	a	b	R^2	β (mg/g.min)	α (g/mg)	R^2
5	5.38	0.1408	0.9503	0.385	2.62	0.9726
10	6.73	0.1113	0.965	0.195	1.82	0.9438
20	8.98	0.099	0.9475	0.144	0.869	0.9379

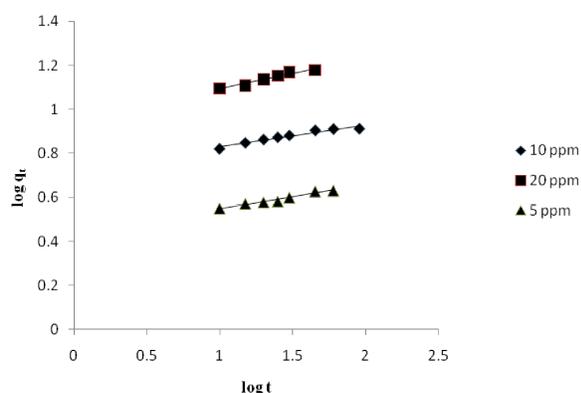


Fig. 8: Power model plot for Cu(II) Removal by WS

Power Function Equation: The power function kinetic equation develops a relation between metal uptake on to the adsorbent and time t , the equation [41] is given as

$$\log q_t = \log a + b \log t \quad (5)$$

A linear plot (Fig. 8) between $\log q_t$ vs. $\log t$ gives the constants of power functions a and b . The constant a represents the initial rate and refers to y -intercept of the straight-line plot of $\log q_t$ vs. $\log t$. The rate constant of the reaction b is given by slope of the plot.

Elvoich Equation: One of the most useful models for describing such activated chemisorptions is the Elvoich equation [42]:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (6)$$

Where α and β are constants during any experiment. α is the initial adsorption rate (mg/g min) and β the desorption constant (g/mg) during any one experiment. To simplify the Elvoich equation, Chien and Clayton [43] assumed a $\beta t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (6) becomes:

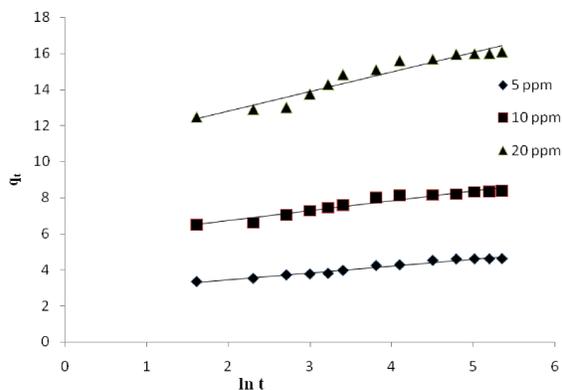


Fig. 9: Elvoich equation plot for Cu(II) Removal by Water Melon

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (7)$$

According to Eq. (7), the plot (Fig. 9) of q_t vs. $\ln t$ gives a slope, $1/\beta$ value is indicative of the number of sites available for adsorption [28]. This equation predicts the behavior over the whole range of variable studied. This fact strongly supports its validity and suggests that the adsorption is rate-determined by a chemisorption step [44].

The detailed results are presented in Table 3. The constants "a" and "b" of the power function and Elvoich model represent the intercept and the slope of the linear plots resulting from plotting the adsorbed Cu(II) vs. time. When adsorbent uptake does not positively correlate with the β value, this may represent the adsorbent's inability to hold the Cu(II) by the adsorbent. On the other hand, a high positive correlation can be an indication of adequate Cu(II) adsorption from the medium. In the Table 3, the Elvoich equation which demonstrated the best fit (R^2) and displayed the better b values than the power equation. The β values (also referred to as rate

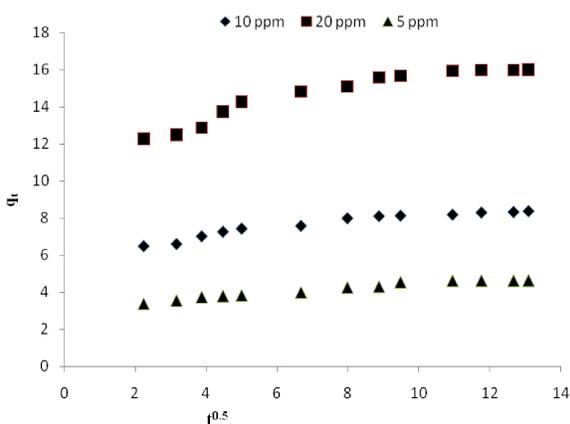


Fig. 10: Intra particle diffusion model for Cu(II) Removal by WS

constant, k) of the Elvoich equation were at least third order of magnitude greater than those shown by the power function equation. This may present a strong favor of Elvoich equation than the power function model.

Intra-Particle Diffusion Equation: In a rapidly stirred batch adsorption, the diffusive mass transfer can be related to an apparent diffusion coefficient, which may fit the experimental sorption-rate data [45]. Generally, the process is diffusion controlled if its rate is dependent upon the rate at which components diffuse towards one another. The overall rate of sorption may be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever is the case, external diffusion is involved in the sorption process. The possibility of intra-particle diffusion was explored using intra-particle diffusion model [46].

$$q_t = k_i t^{0.5} + C \quad (8)$$

Where q_t refers to the amount of phenol adsorbed in mg/g at time, t ; intercept C , indicating the boundary layer effect (Weber and Morris, 1963) and k_i , the intra-particle diffusion rate constant (mg/g. min^{0.5}).

It is shown in Fig. 10 the plots of mass of Cu(II) adsorbed per unit mass of adsorbent vs. $t^{0.5}$ for all the adsorbents. In Fig. 10 the data points are related by two straight lines (—) the first straight portion depicting macropores diffusion and the second representing micro-pore diffusion [47]. This shows only

the pore diffusion data. Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts, which provide the measure of the boundary layer thickness i.e., the larger the intercept, the greater the boundary layer effect [48].

Adsorption Isotherms: The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [33]. Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the sorbent sorption [49]. Equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface [49]. Equilibrium isotherm is described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the sorbent sorption. Equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that at the sorbent interface [35]. In order to quantify the affinity of WS for the Cu(II) studied, widely used isotherm models (Langmuir, Freundlich and Temkin isotherm models) were used to analyze the data obtained from the sorption process.

Langmuir Isotherm: The monolayer coverage of the sorbate on a sorbent surface at a constant temperature is described by Langmuir isotherm [50]. The basic assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one sorbed molecule [50]. The Langmuir isotherm is expressed as [51].

$$q_e = \frac{X}{M} = \frac{q_{\max} b C}{1 + b C} \quad (9)$$

Where

- b = Constant that increases with increasing molecular size
- q_{\max} = Amount adsorbed to form a complete monolayer on the surface (mg/g)
- X = Weight of substance adsorbed (mg)
- M = Weight of adsorbent (g)
- C = Concentration remaining in solution (mg/L)

The above equation can be recast in a linear form as

$$\frac{1}{X/M} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b} \frac{1}{C_e} \quad (10)$$

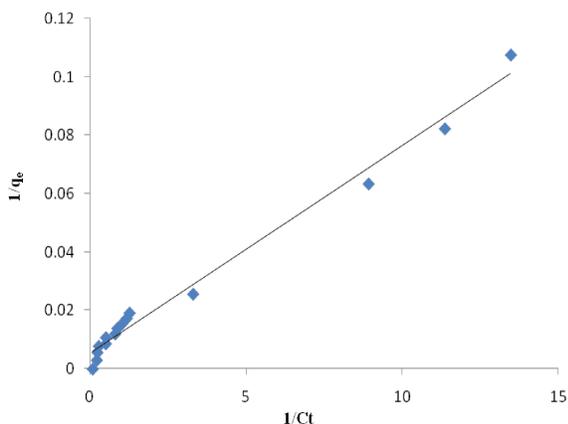


Fig. 11: Langmuir Isotherm for Cu(II) Removal by WS

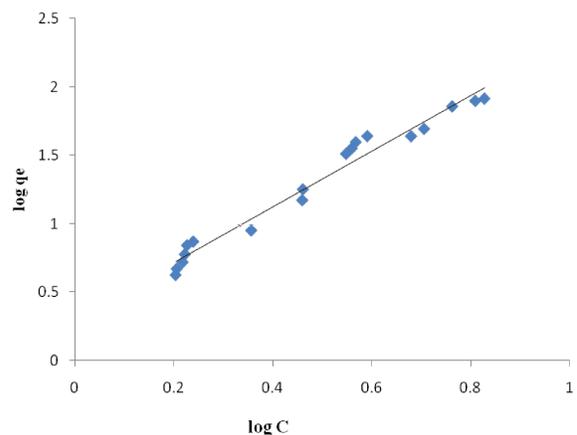


Fig. 12: Freundlich Isotherm for Cu(II) Removal by WS

Table 4: Isotherms Constants

Langmuir Coefficients			Freundlich Coefficients		
$q_{max}(mg/g)$	$b(l/mg)$	R^2	$K(mg/g)$	n	R^2
111.1	0.789	0.9859	107.94	1.10	0.9713

Freundlich Isotherm (Van Bemmelen Equation):

Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [52]. The Freundlich equation is an empirical equation that is very useful as it accurately describes much adsorption data [53]. The Freundlich isotherm is expressed as

$$q_e = \frac{X}{M} = KC^{1/n} \tag{11}$$

Where,

$K, n =$ constants depending on temperature. The above equation can be recast in a linear form as Eq.12.

$$\log q_e = \log K + \frac{1}{n} \log C \tag{12}$$

The coefficients K and n can be estimated from slope and intercept from a line fitted to a graph of $\log (X/M)$ versus $\log C$.

From Fig. 11 and 12, regression values (R^2) indicates that the adsorption data for Cu(II) onto WS fitted well with the Langmuir and Freundlich isotherm. From Table 4, the ‘ n ’ value of Cu(II) was observed to be more than the value of 1, thus indicating that the adsorption is favorable for removal of Cu(II) by WS.

Tempkin Isotherm: Tempkin is considered as the effect of some indirect adsorbate/adsorbate interaction on adsorption isotherms and suggested that because of interaction the heat of adsorption of all the molecules

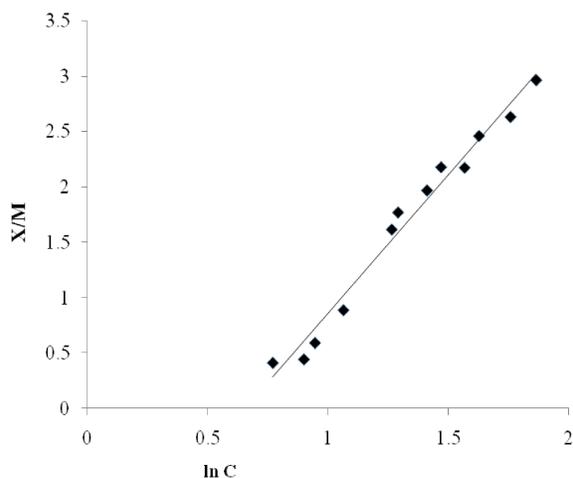


Fig. 13: Tempkin Isotherm for Cu(II) Removal by WS

in the layer would decrease linearly with coverage [54]. The amount of adsorbate can be given as below:

$$q_e = \left(\frac{RT}{b}\right) \ln AC_e \tag{13}$$

Eq. 13 can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \tag{14}$$

With

$$B = \frac{RT}{b} \tag{15}$$

The adsorption data can be analyzed according to Eq. 14 and a plot of q_e versus $\ln C_e$ (Fig. 13) enables

Table 5: Isotherms Constants for Temkin model

Concentration (mg/L)	Temkin isotherm model		
	A(l/g)	B(J/mg)	R ²
10	9.92	0.249	0.9795

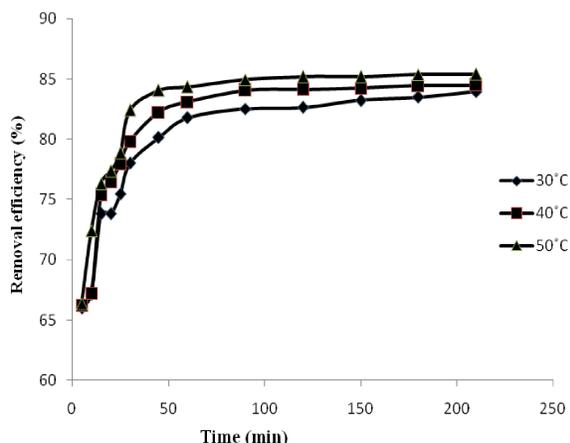


Fig. 14: Variation of removal efficiency with variation in temperature

the determination of the isotherm constant, A and B. It would be worth noting that the constant B is related to heat of adsorption.

From Fig. 13. the isotherms A and B can be determined. From Table 5, WS has maximum binding energy 9.92 J/g, which is uniformly distributed. the value for constant B is 0.249 J/mg which is related to heat of adsorption.

Effect of Temperature: The effect of temperature on the Cu(II) adsorption experiment has been investigated at three different temperatures (30, 40 and 50°C) for WS. The temperature of adsorption medium could be important for energy dependent mechanisms in metal adsorption by adsorbent [55]. For an increase in temperature, an increase in the adsorption of Cu(II) was observed in Fig.14. Increase in adsorption with an increase in temperature indicated endothermic nature of the adsorption process. The increase in sorption with temperature may be attributed to either increase in number of active surface sites available for sorption on the adsorbent or due to decrease in the boundary layer thickness surrounding the sorbent; so that the mass transfer resistance of adsorbate in the boundary layer decreased [56].

Thermodynamic Studies: The effect of temperature on biosorption of Cu(II) onto WS was investigated under isothermal conditions in the temperature range of 30-50°C.

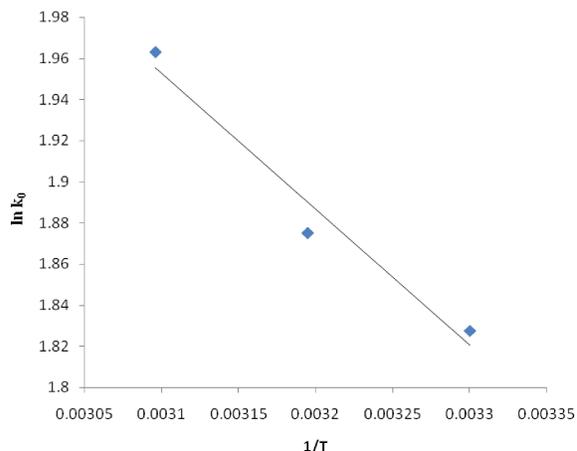


Fig. 15: Von't Hoff plot for effect of temperature on particle biosorption of Cu onto WS.

The temperature dependence of Cu(II) adsorption on WS is shown in Fig. 15. The extent of adsorption of Cu(II) is found to increase with an increase in temperature and time, indicating that the process to be endothermic in nature [56]. Increase in the removal of Cu(II) may be attributed to the increase of mobility of the Cu(II) particles and the swelling of pore structure of the sorbent [57].

Thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. The thermodynamic parameters such as changes in free energy (ΔG) (J/mole), enthalpy (ΔH) (J/mole) and entropy (ΔS) (J/mole.K) were determined using the following equations [26]:

$$K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \tag{16}$$

$$\Delta G = \Delta H - T\Delta S \tag{17}$$

$$\ln k_o = \frac{\Delta G}{RT} \tag{18}$$

$$\ln k_o = \frac{\Delta s}{R} - \frac{\Delta H}{RT} \tag{19}$$

Where K is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/l), C_{liquid} is liquid phase, T is absolute temperature in Kelvin and R is gas constant. ΔH and ΔS values are obtained from the slope and intercept of plot $\ln K$ against $1/T$. Fig. 15 illustrates Von't Hoff plot of effect of temperature on biosorption of Cu(II) on WS.

Table 6: Thermodynamics Constants

T(K)	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/K/mol)
303	-4583.81		
313	-4916.41	5493.97	33.26
323	-5249.01		

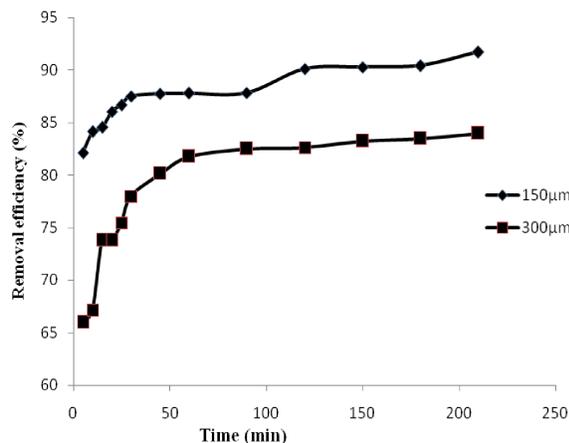


Fig. 16: Variation of removal efficiency with the variation in the particle size.

The observed thermodynamic values are listed in Table 6. “The negative value of ΔG indicates the biosorption is favorable and spontaneous. Also ΔH confirms the endothermic nature of adsorption process. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of Cu(II) with the adsorbent. The increase of adsorption capacity of the biosorbent at higher temperatures was due to enlargement of pore size three and activation of adsorbent surface” [58].

Effect of Particle Size: The results of variation of these particle sizes on Cu(II) adsorption rate are shown in Fig. 16. The effect of altering the adsorbents particle size (150 μm , 300 μm) on the removal efficiency showed that there was a more dominant removal of Cu(II) by the smaller particles. This was most probably due to an increase in total surface area, which is provided more biosorption sites for the metal ions [59]. For larger particles, the diffusion resistance to mass transport is high and most of the internal surface of the particle may not be utilized for adsorption and consequently, the amount of Cu(II) adsorbed is small [60]. Similar trend has been seen in adsorption of chromium onto rice husk [61].

Effect of Variation of Orbital Speed: Flasks were agitated on orbital speed at different speeds (50 rpm, 150 rpm and 200 rpm). The influence of orbital speeds in Cu(II)

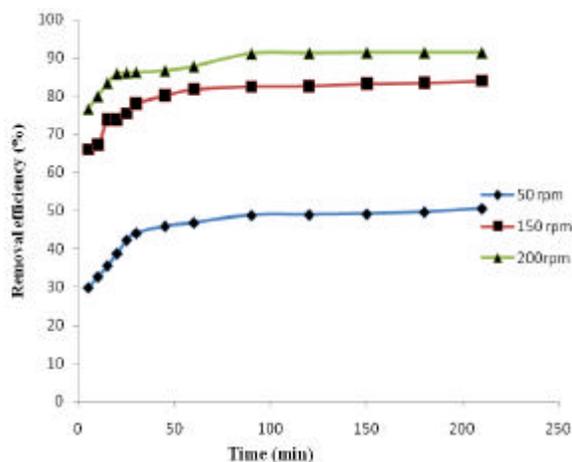


Fig. 17: Variation of removal efficiency with the variation in the agitation speed.

adsorption evident from Fig.17. It shows that removal efficiency is increasing with the increment of orbital speed. It may happen in four steps: (i) migration of adsorbate molecules from the bulk solution to the surface of the adsorbent; (ii) diffusion through the boundary layer to the surface of adsorbent; (iii) adsorption at a site; and (iv) intraparticle diffusion into the interior of the adsorbent [62]. Increasing agitation speed may decrease the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface [62]. Due to this, the adsorbate is forced towards the adsorbent surface and leads to an increase in the diffusion of adsorbate into the surface of the adsorbent [63]. Similar trend has been seen in the adsorption of cadmium onto Tamarind seed [64].

Effect of pH: The pH is amongst one of the important parameters for adsorption process as it controls the protonation of the functional groups on the biomass as well as the metal chemistry [65]. Therefore the influence of pH on Cu(II) biosorption by WS was investigated in the pH range 2.0–10.0.

Biosorption potential of WS for Cu(II) was seen to increase with increase in solution pH appreciably up to pH 8.0 as shown in Fig. 18. The optimum pH for Cu(II) biosorption by WS was found to be 8.0. Lower metal removal at highly acidic pH might be due to the competition for metal binding sites between positively charged Cu(II) ions and hydrogen ions [66]. Also at low pH, the biosorbent surface became more positively charged thus reducing attraction between the WS and metal ions [67]. Further increase in pH (beyond pH 8)

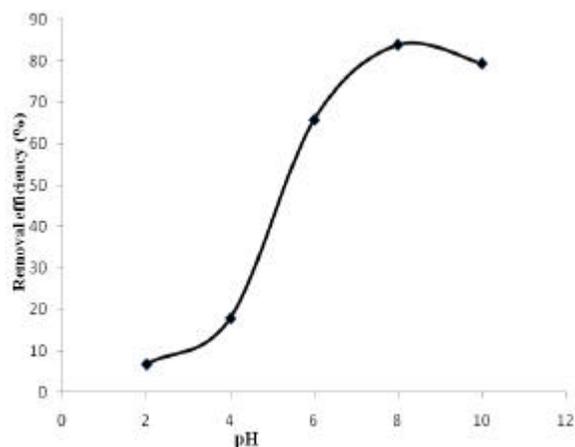


Fig. 18: Variation of removal efficiency with the variation in the pH

Table 7: Comparison of Cu(II) removal by various low cost adsorbents

Adsorbent	Adsorption Capacity(mg/g)	Reference
Ion Exchange Resins	26.73	[69]
Sawdust	71.20	[70]
Banana Peel	1.439	[71]
Teak (<i>Tectona grandis</i> L.f) Leaves	166.78	[72]
Low-grade phosphate rock	14.43	[73]
Newspaper pulp	10.94	[74]
<i>Pseudomonas veronii</i> 2E	54	[75]
WS	111.1	Present study

may be attributed to the precipitation of Cu(II) as Cu(OH)₂ [68]. This reduces the concentration of Cu(II) in the solution and thus decreases the removal efficiency of WS. Similar results have been reported by Bharathi and Ramesh [26].

Comparison of Adsorption Capacity: Adsorption capacity of WS for Cu(II) removal was compared and shown in Table 7. The adsorption capacity of WS is very high compared to ion exchange resins, sawdust, banana peel, phosphate rock, newspaper pulp, etc. But the Cu(II) adsorption capacity of tea leaves is higher than that of WS. The adsorption capacity of WS can increase by activating the adsorbent.

CONCLUSIONS

The WS employed in the adsorption processes is efficient in removing Cu(II) from aqueous solutions. The operating parameters, pH of solution, dosage, contact time, temperature, particle size, agitation speed were effective on the adsorption efficiency of Cu(II).

Adsorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer adsorption capacity of WS for Cu(II) was found to be 111 mg/g. Kinetic examination of the equilibrium data showed that the adsorption of Cu(II) ions onto WS followed well the pseudo-second-order kinetic model. The calculations indicated the adsorption procedure is endothermic and spontaneous in nature. Based on all results, it can be also concluded that the WS is an effective and alternative biomass for the removal of Cu(II) ions from aqueous solution because of its considerable adsorption capacity, being of natural, renewable and thus cost-effective biomass.

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