

Adsorption of copper metal ion from aqueous solution by using low cost materials

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Abstract

In this study the matki (*Vigna aconitifolia*) seed husk was tested for removal of Cu metal ion from solution. Batch adsorption techniques were administered to measure the adsorption characteristics of the matki seed husk for Cu (II) metal ion removal from aqueous solutions. The adsorption isotherms, thermodynamic parameters, kinetics, effect of pH were examined. The results show that the utmost adsorption capacity of matki seed husk was approximately 80.39 % Cu (II) at temperature 305 K and at the initial Cu (II) metal ion concentration of 100 mg/L and at 5.1 pH. Adsorption isotherm data might be well fitted by Freundlich isotherm equation. Thermodynamic studies confirmed that the method was spontaneous and endothermic. The adsorption amounts of Cu (II) metal ion tend to extend with the rise in of pH. The relatively low cost and high capability of the matki seed husk make it potentially attractive adsorbent for the removal of Cu (II) metal ions from waste water.

Keywords: matki seed husk, Cu (II) metal ion removal, adsorption capacity, adsorption isotherm adsorption kinetics.

Introduction

Water may be a basic source of life, energy and thus is an important element to all or any things on earth. If water is in pure form, then it's colorless, tasteless and odorless in nature. Level of contaminants has increased because of discharge of industrial effluents in aquatic ecosystems which pollute and contaminate the water streams naturally [11]. Heavy metals generate serious environmental distresses because their non-biodegradable and persistent nature [17]. Many toxic heavy metals are discharged into the environment as industrial wastes causing significant issue of soil and water pollution. Pollution raises an excellent concern nowadays due to rapid industrialization e.g., metal mining operations, fertilizers, agricultural wastes, sewage, domestic wastes, alloy and leather industries, metal galvanization paper industries and pesticides which have largely discharged various sorts of pollutants into environment and cause disorder into an ecosystem [2]. The effluents from mining, mineral extraction, metal processing, metal polishing, cleaning, paint manufacturing and battery manufacturing industries and acid rain contribute for the increasing metal loads within the water bodies. The sources of copper metal in industrial effluents include cleaning of metals also as plating baths, pulp, paper and paper board mills, wood-pulp production, fertilizer industry, etc. Excessive intake of copper leads to in an accumulation within the liver. Copper is released into the environment during a number of various ways; it finds its way into water-streams leading to environmental contamination that poses threat to humans, animals, and plants. This will cause serious and sophisticated problem [15 & 16]. Similarly, another heavy metal like copper in very bit is important for all times process. However, with higher concentrations of this element within the environment and therefore consequent increase in human intake, copper concentrations have reached toxic levels causing various diseases and disorders like liver damage, Wilson disease and insomnia [12]. However, there are several methods for the treatment of wastewater containing Cu (II), including ion exchange, adsorption, precipitation and membrane separation [1 & 13]. During last decades, the method of adsorption using activated charcoal has been found to be an efficient technology for the removal of Cu (II) from the wastewater. Though the removal of Cu (II) through adsorption is sort of effective,



its use is sometimes restricted due to the most cost of activated carbon and difficulties related to regeneration. Attempts have therefore been made to utilize natural also as waste materials as alternative adsorbents like, green gram seed husk [4], Adlai Shell [10], Natural Saponins-Clay [14], and black gram seed husk [7], etc. Although many of those adsorbents can effectively remove Cu (II), most of them present some disadvantages like poor adsorption capacity, low efficiency/cost ratio and ineffectiveness for low metal concentrations.

In the present paper matki seed husk powder was employed for adsorption of Cu (II) and used as an efficient adsorbent within the wastewater treatment. The adsorption technique was found to be very useful and pries effective for a far better adsorption of metal ion.

The objective of this work was to review the feasibility of using matki seed husk as adsorbents for the removal of Cu (II) from aqueous solution. Matki seed husk was chosen due to its insolubility in water, chemical stability and native availability. During this work, batch experiments were administered guage out to evaluate the adsorption characteristics of the modified matki seed husk for Cu (II) removal from aqueous solutions. The adsorption isotherms, thermodynamic parameters, kinetics, contact time, dosage of bio-adsorbent, initial concentration and pH were also investigated.

Material and methods:

Preparation of adsorbent:

The well-developed crop of matki seeds were purchased from neighborhood market and washed thoroughly by utilizing distilled water to wash them from dirt. Then, seeds are keeping into distilled water up to 24 hours. The then husk, was isolated from the pulses and washed with distilled water, after washing husk was dried in shade region. After complete drying, the husk was ground by using processor. The homogeneous powder was obtained by passing through mesh of desired particles size (60 micron) of matki seed husk (MtSH). The fine powder of MtSH adsorbent was stored in an air tight glass bottle prepared for further experimental process.

Preparation of adsorbate:

The copper stock solution (1000 mg/L) was prepared using analytical grades of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, which was purchased from Sd. Fine Chemicals Pvt. Ltd. Mumbai. Necessary dilutions were done to get 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L of copper solution. Standard concentrations were also prepared for calibration processes. The concentrations of Cu (II) metal ion was measured at the wavelength of their maximum's absorbance (λ max) that was determined by UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). The pH of the Cu (II) metal ion solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution and measurement was done by digital pH-meter (Elico: LI 615).

Adsorption experiments:

The adsorption of Cu (II) metal ions from aqueous solution was investigated in batch adsorption techniques. The MtSH with different adsorbent dose (0.25, 0.50, 0.75 and 1.0 g) were added in each separate conical flask containing 50 mL of 100 mg/L Cu (II) solution. After adsorption timed, solution was filtered and 10 ml of sample solution was transferred to 100 mL beakers; and 5 mL of 25 % aqueous citric acid solution was added thereto. The solution were made slightly alkaline by the addition of dilute ammonia solution then boiled to remove excess of ammonia. 15 mL of 4% EDTA solution was added then it had been cooled to room temperature and transferred to a separating funnel. 10 mL of 0.2 % aqueous sodium diethyl dithiocarbamate solution was added with constant shaking for 45 seconds. A yellow brown color was developed into the solution. 20 mL of butyl acetate (ethanoate) was added into the funnel and therefore the solution shakes for 30 seconds. The organic layer acquires yellow coloration. The content agitated for 15 seconds the phase obtained were allowed to separate. The lower aqueous layer was removed. 20 mL of 5 % sulphuric acid (v/v) was added with constant shaking for 15 seconds, it had been cooled thus separate organic phase. The absorbance was determined at 560 nm against blank was determined.



The quantity of Cu (II) metal ions adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm, and then the kinetic adsorption parameters were calculated.

$$q = \frac{V(C_0 - C_t)}{M} \quad (1)$$

Where, q is that the amount of Cu (II) metal ions adsorbed from the solution (mg/g), C_0 is the concentration before adsorption (mg/L), and C_t is concentration after adsorption. V is the volume of adsorbate (L) and M is the weight of the MtSH adsorbent (gm).

The percentage adsorption of Cu (II) metal ions was calculated by following equation;

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

Where, C_0 and C_e are the initial and equilibrium concentrations respectively.

Results and discussion

Effect of contact time and initial concentration:

The effect of contact time was studied at different initial concentration of Cu (II) metal ion with time. The time is varies in the parameter for the adsorption of Cu (II) metal ion on MtSH is shown in Fig.1.

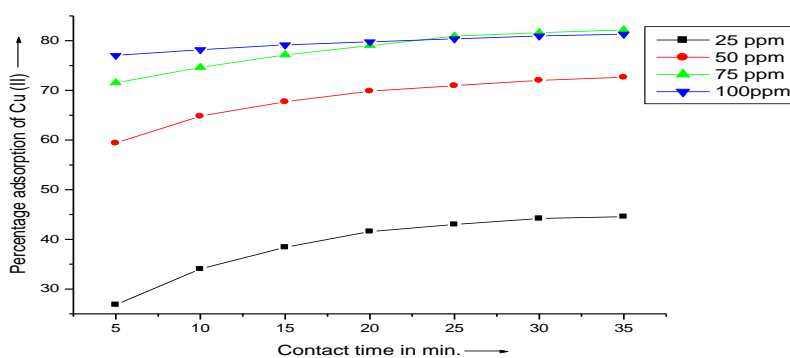


Fig.1: Effect of contact time at various initial concentration of Cu(II) metal ion on Percentage adsorption. [Adsorbent dose.=0.50 g, Temp=298.7K, pH=5.1]

The experimental results of adsorptions of Cu (II) metal ion on MtSH investigates that the percentage adsorption capacity increased with increase in contact time due to availability of more number of active sites on the surface of the MtSH adsorbent. As increase the initial concentration of Cu (II) ion, increase the percentage adsorption capacity due to higher probabilities of collision between Cu metal ion and MtSH adsorbent. Similar observation was reported in literature [13].

Effect of adsorbent dose:

The relation of percentage adsorption efficiency with time at varied MtSH adsorbent dosages is depicted in Fig 2.

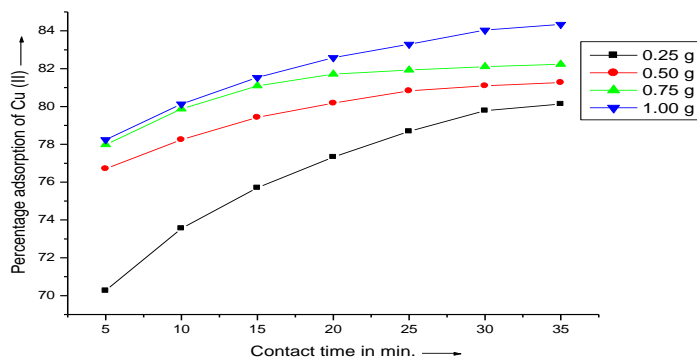


Fig.2: Effect of various adsorbent dose of MtSH with contact time on adsorption of Cu (II) metal ion. [Initial conc.=100 mL, Temp=298.7K, pH=5.1]

Fig 2: shows the plot of percentage adsorption against time for a fixed Cu (II) metal ion concentration (100 mg/L), and varied adsorption dose of MtSH. It is often clearly observed that the percentage adsorption is higher at beginning time for the all dosage used. This is due to the large surface area of MtSH available during the initial time. Because the surface adsorption sites become exhausted, the adsorption rate is slow. The percentage adsorption was found to be 76.36, 78.90, 80.22, and 81.05 for MtSH dose of 0.25 gm, 0.50 gm, 0.75 gm, and 1.0 g respectively. From the adsorption dose of MtSH experiments, 1.0 g. was found to be an optimal dose for the 100 mg/L concentration of Cu (II) metal ion used.

Effect of pH:

The pH of the adsorbate solution is taken in accounting one among the foremost important factors affecting the adsorption process. The pH effect of solution was studied between 2 and 11 pH shown in **Fig. 3**.

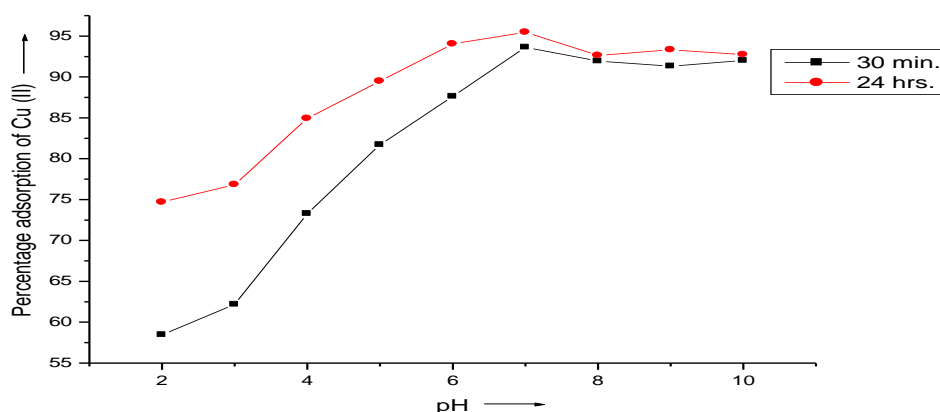


Fig.3: Effect of pH on percentage adsorption of Cu (II) metal ion on MtSH adsorbent. [Initial conc.=100 ppm, Adsorbent dose=0.5 g., Temp=298.7K]

Adsorption of Cu (II) metal ion increases appreciably with increase of pH from 2 to 7 at 30 min. and according to results obtained by others. The rise is partly attributed to the formation of varied hydroxo species with the rise in solution pH. It is supported the hydrolysis constants of metal ions as defined in



and taking just for primary metals expected to be formed within the working pH ranges into consideration. Cu (II) and its monohydrate species are the predominating species up to pH~7. Since maximum adsorption copper ion was achieved at pH~7.0, it's going to safely be stated that the removal of copper ion was mostly due to adsorption and precipitation.

Effect of Zero point pH:

The pH at which the worth of ΔpH is adequate to zero is known as zero point pH (pH_{pzc}). At pH 8.0, zero point charge was found in adsorbents utilized in present work. Cationic adsorption on MtSH adsorbent are going to be favorable at $pH > pH_{pzc}$. The surface of the adsorbent gets negatively charged and favors uptake of Cu (II) metal ion to increased electrostatic force of attraction. Thus, Cu (II) metal ion removal favored at higher pH ($pH > 6.0$). At lower pH ($pH < pH_{pzc}$), adsorbent surface is positively charged, concentrations of H^+ were high and that they compete with positively charged Cu (II) metal ion cations for empty adsorption sites causes decrease in adsorption of dye.

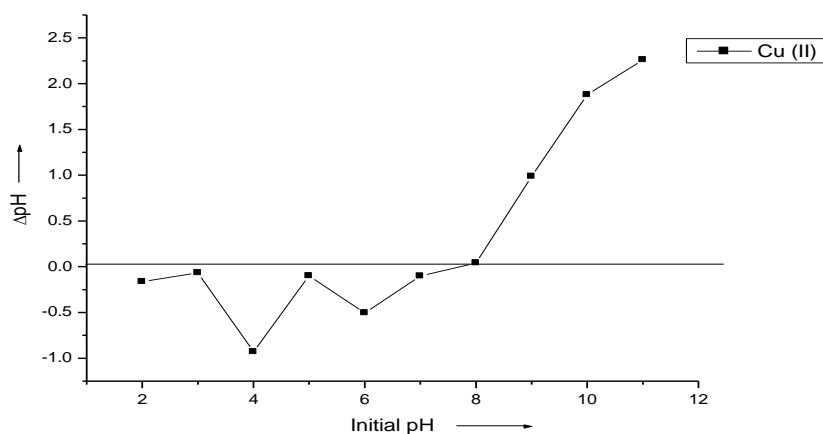


Fig.4: Effect of zero point pH on percentage adsorption of Cu (II) metal ion.

Effect of temperature:

It's one among the important factor influencing separation in most of the processes. To look at the effect of temperature on Cu (II) metal ion adsorption five different temperatures were selected. Experiments were carried out at 305, 310, 315, 320, and 325 K. Within present work percentage removal of Cu (II) metal ion to decrease from 80.39 % to 77.32 % by increase in temperature from 305 to 325 K. The percentage adsorption of Cu (II) was found to decrease with increase in temperature as shown in Fig.5.

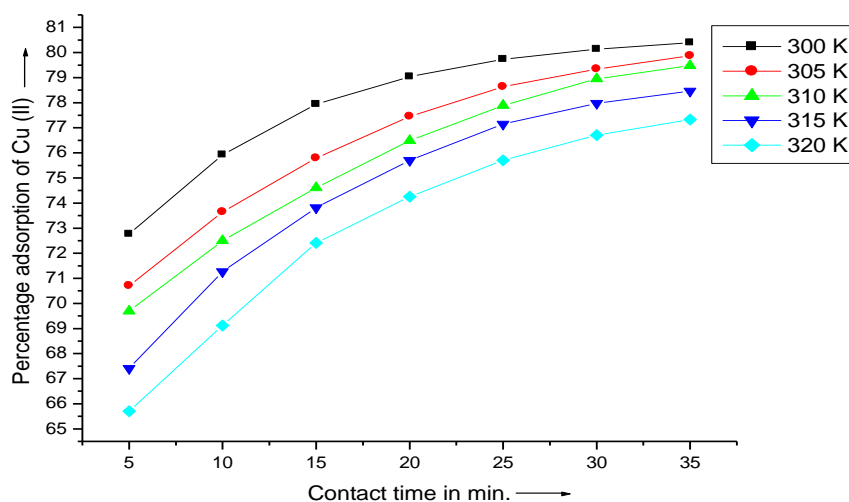


Fig.5: Effect of temperature on percentage adsorption of Cu (II) metal ion on MtSH adsorbent. [Initial conc.=100 ppm., Adsorbent dose=0.5 g., pH=5.1]

It reveals that the adsorbate-adsorbent system is exothermic in nature that the evaluation of thermodynamic parameters.

Thermodynamic Parameters like Gibb's free energy change ΔG^0 , enthalpy change ΔH^0 and entropy change ΔS^0 were determined using the subsequent equations.

$$K_c = \frac{C_{ad}}{C_e} \quad (3)$$

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

$$\text{Where, } \Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (6)$$

Where, K_c is the equilibrium constant, C_{ad} is that the amount of metal ion adsorbed per liter of the solution at the equilibrium, C_e is the equilibrium concentration (mg/L) of the metal within the solution, T is the temperature in Kelvin and R is the universal gas constant (8.314 J/mole). The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plot of $\log K_c$ against $\frac{1}{T}$ respectively. Thermodynamic parameter values are shown in Table 1.

Table: 1. Thermodynamic parameter values of Copper metal ion solution.

Temp (K)	ΔG^0 KJ/mole	ΔH^0 KJ/mole	ΔS^0 KJ/mole
305	- 26.943	- 29.280	- 0.0075
310	- 26.951		
315	- 26.918		
320	- 26.880		
325	- 26.843		

The negative value of ΔG^0 (Table 1) confirms that the feasibility of the reaction and spontaneous nature of the adsorption. The ΔG^0 values obtained in this study for the Cu (II) metal ions are > -10 KJ/mole, which indicate that physical adsorption wasn't predominant mechanism in the adsorption process. The negative value of ΔH^0 suggests that the adsorption to be in agreement within the exothermic nature of interaction. [6]. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorbent while the adsorption there are some structural changes within the Cu (II) ion and therefore the adsorbent occurs.

Adsorption kinetic models:

Kinetic studies are significant for any kind of adsorption process. Pseudo-first order also as pseudo-second order kinetic models are often suggested for an adsorption. Pseudo-first order kinetics is especially to explain the rate of adsorption techniques in liquid-solid phase. The pseudo-first order rate equation is given as,

$$\frac{dq}{dt} = K_1(q_e - q_t) \quad (7)$$

After definite integration by applications of the conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$; Equation (7) becomes,

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (8)$$

Where, q_e (mg/gm) is the amount of adsorption at equilibrium, q_t (mg/gm) denotes the quantity of adsorption at time t (min.) and K_1 (min^{-1}) is the rate constant of the pseudo-first order model. Supported experimental results, linear graphs were plotted between $\log(q_e - q_t)$ versus t , to calculate K_1 , q_e and R^2 .

The pseudo-second order equation are often written as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (9)$$

Where, K_2 ($\text{gm} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant of the pseudo-second order.

The linear form of equation is

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

K_2 and q_e are often obtained from the intercept and slope of plotting t/q_t against t . Kinetic parameter values are given in table (2)

Table: 2. Comparison of the experiments and the kinetic model of Cu (II) metal ion on MtSH adsorbent.

Metal ion	Pseudo-First order			Second order			
	K_1	(min^{-1})	q_e (mg/gm)	R^2	K_2 (gm./mg.min)	q_e (mg/gm)	R^2
Cu (II)	7.659×10^{-2}		1674.94	0.982	6.284×10^{-5}	16284.94	0.999

Present work investigates that the adsorption of Cu (II) on all adsorbents was better represented by pseudo second order kinetics as presented in Table.2.

Adsorption isotherms:

The foremost widely used isotherms for solid-liquid adsorption are the Langmuir and Freundlich adsorption isotherms. Langmuir isotherm model is valid for monolayer adsorption on to surface containing a finite number of identical sites.

The linear sort of the equation is given by,

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0}\right) C_e + \frac{1}{bQ_0} \quad \text{or} \quad \frac{1}{q_e} = \left(\frac{1}{Q_0}\right) + \frac{1}{bQ_0 C_e} \quad (11)$$



Where, C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/gm) is the amount of adsorbate adsorbed per unit mass of adsorbent, at equilibrium, Q_0 (mg/gm) and b (L/mg) are Langmuir constants associated with maximum monolayer adsorption capacity and energy of adsorption respectively. The values of Q_0 and b are calculated from the slope and intercept of plot of $\frac{C_e}{q_e}$ against C_e respectively. The graphical representation is shown in fig.6. The separation factors of the Langmuir isotherm could also be expressed in terms of equilibrium parameter (R_L). It is a dimensionless constant factor.

$$R_L = \frac{1}{1+bC_0} \quad (12)$$

Where, C_0 is initial concentration in ppm and b is Langmuir constant related to the energy of adsorption. R_L Value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if, $R_L = 0$ [5].

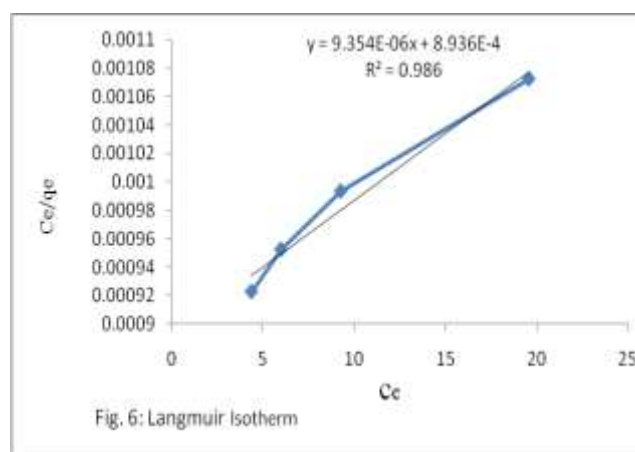
Freundlich presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces also as multi layer sorption and is also expressed as

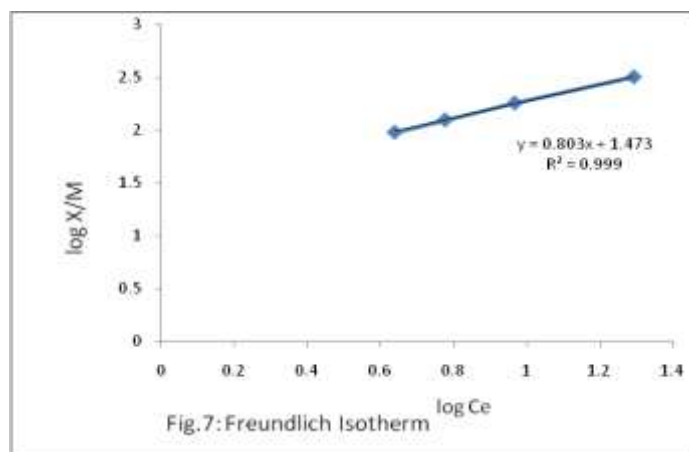
$$\frac{x}{m} = K_f C_e^{1/n} \quad (13)$$

Where C_e is the equilibrium concentration of adsorbate (mg/L), The constants K_f and n are often obtained by taking \log on both sides of equation (13) as follows,

$$\log \frac{x}{m} = \frac{1}{n} \log C_e + \log K_f \quad (14)$$

K_f is adsorption capacity of indicator, while $\frac{1}{n}$ is a function of the strength of adsorption in the adsorption process. If $n = 1$ then the partition between the two phases are independent of the concentration. If value of $\frac{1}{n} < 1$, it indicates a traditional adsorption, on the other If value of $\frac{1}{n} > 1$ indicates the adsorption is favored and new adsorption sites are generated [8]. A plot of $\log \frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis is shown in fig. 7.





The value of n and $\log K_f$ can be obtained from the slope and the intercept of the linear plot respectively. Isotherm parameter values are shown in Table 3.

Table: 3. Isotherm parameter values with Copper [Cu (II)] metal ions

Adsorbent	Langmuir constants				Freundlich constants		
	$Q_0 \cdot 10^5$ (mg/gm)	$b \cdot 10^{-2}$ (L/gm)	R_L	R^2	n	K_f (mg/gm.(L/gm.)) ^{1/n}	R^2
MtSH	1.069	1.046	0.488	0.986	1.24	29.72	0.999

Since R_L values lies between 0 and 1 for Cu (II) metal ion studies indicates that the adsorption of Cu (II) metal ion is favorable. The info reveals that the Langmuir model yields better fit than the Freundlich model. The values of n suggests that deviation from linearity, if $n = 1$ the adsorption is homogeneous and there's no interaction between adsorbed species. The values of n greater than unity, ($1 < n < 10$), that means favorable adsorption [9].

Conclusion

The study reveals that MtSH can act nearly as good adsorbents for the adsorption of Cu (II) metal ion. The optimum pH for adsorption is 7.0. On the idea of above studies the subsequent conclusions could also be drawn.

1. Matki seed husk may be a non-toxic agricultural material has been successfully used adsorption of Cu (II) metal ion from aqueous solutions.
2. Adsorption of Cu (II) metal ion decreased with increasing temperature, with maximum adsorption of Cu (II) metal ion 80.39 % at 305 K.
3. Process of adsorptive separation was exothermic in nature and thus lower temperature favors adsorption of Cu (II) metal ion from aqueous solutions.
4. The kinetics of the adsorption of Cu (II) metal ion was the best described by the second order model.
5. The negative value of ΔG° confirms that the feasibility of the reaction and spontaneous nature of the adsorption.
6. The negative value of ΔH° suggests that the adsorption to be in agreement with the exothermic nature of interaction.

7. The negative value of ΔS° suggests that the decreased disorder and randomness at the solid solution interface with adsorbent.
8. The experimental data for the adsorption of Cu (II) metal ion on MtSH fits well for the Freundlich adsorption isotherm model than Langmuir adsorption isotherm.
9. The investigation showed that MtSH adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which could be used as a potential adsorbent for adsorption of Cu (II) metal ion from aqueous solution and polluted water.

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