

Adsorption performance of rice husk towards copper ions from wastewater

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Received 3 October 2021; Accepted 21 March 2022

ABSTRACT

This work reports the adsorptive discharge of copper ion (Cu(II)) from wastewater by using rice husk (RH) at ambient temperature. The RH was characterized by using scanning electron microscopy, energy-dispersive X-ray spectroscopy and Fourier-transform infrared spectroscopy. The percentage removal of Cu(II) from wastewater was increased from 33% to 62%, 31% to 67% and 49% to 66% with contact time, mass of RH, and temperature respectively whereas decreased from 68% to 52% with increasing initial concentration of solution. Adsorption isotherm study demonstrated that experimental data fitted well to non-linear Freundlich isotherm. Kinetics study showed that experimental data fitted well to non-linear pseudo-second-order model. Adsorption thermodynamic investigations represented that adsorption of Cu(II) was an endothermic process because the value of enthalpy ($\Delta H = 9.453$ kJ/mol) was positive. Contrary, the negative value of Gibb's free energy represented that adsorption of Cu(II) was spontaneous process. Moreover, the influence of diverse ions on adsorption Cu(II) was also elucidated.

Keywords: Rice husk; Adsorption; Copper ions; Non-linear kinetics; Spontaneous process; Non-linear isotherms

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1. Introduction

Heavy metal ions are harmful and largely present in environments and can be dangerous to humans and the environment. As heavy metal cannot be biodegradable and thermal degradation, it can indelible stay in the environment, and assemble to reach dangerous levels [1]. Copper is one of significant elements. Drinking water with copper eclipse acceptable amount for longer time could cause kidney or liver issue and harm of copper is irreversible and curtain. So treatment of wastewater possessing Cu(II) is significant in the field of environmental protection.

Many techniques such as chemical ion exchange [2], precipitation [3], floatation [4], solvent extraction [5], coagulation [6], membrane processes [7], and adsorption [8–10] were utilized to discharge heavy metals from wastewater. Usually, adsorption is the physico-chemical method that involves the collection of soluble substances in liquid phase to a suitable interface; therefore, the synthesis of novel and competent adsorbents has been appeared as hotspot in wastewater treatment process [11,12]. Rapid adsorption and high capacity, derived from high specific surface area and overabundance of adsorption sites, are the main threats for an energetic adsorbent [13–15]. Materials science, environmental science, chemistry, and nanotechnology have helped in synthesizing several new adsorbents. Common adsorbents such as silica, resins, activated carbon and zeolites but either the low adsorption capacity or the expensiveness is their main disadvantage [16–19]. To overcome these issues, we will use rice husk (RH) as an effective adsorbent for the removal of Cu(II) from wastewater.

Pakistan is one of the major producers of rice (5.2 million tons annually) and its husk which forms 20%–23% of the whole rice grain is expressed as waste material that really posture a disposal issue for mill owners [20]. The main contents of RH are proteins, cellulose, hemicellulose and lignin, containing hydroxyl and carboxyl functional groups available to interact with cations [20–22]. Moreover, adsorption of Cu(II) onto RH has not been reported so far to the best knowledge of the authors.

In this manuscript, we reported the application of rice husk (RH) for the batch removal of Cu(II) from wastewater at room temperature. Non-linear pseudo-first-order and pseudo-second-order models were employed on experimental data for adsorption of Cu(II) onto RH. Experimental data was also subjected to non-linear Langmuir, Freundlich and Dubinin–Radushkevich isotherms. Thermodynamics for adsorption of Cu(II) onto RH was also revealed. The RH was also characterized by utilizing techniques such as Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) before and after adsorption of Cu(II) onto it. Moreover, the effect mass of RH, temperature, contact time and initial concentration of solution on the removal of Cu(II) from wastewater was also discussed. Effect of diverse ions on adsorption Cu(II) was also studied.

2. Experimental

2.1. Materials

The temperature of solution was restrained by immersing the culture tube into the water bath of Gallen kamp

thermo stirrer (UK) for thermodynamic evaluation. The fealty of the temperature in the water bath was $\pm 0.1^\circ\text{C}$. All the chemicals used were of analytical grade and employed as received. Distilled water was used throughout the work.

2.2. Adsorbent

The rice mills of Punjab, Pakistan provided rice husk (RH) of basmati rice. Initially, the RH were thoroughly cleaned with water to remove dust particle and then dried at 80°C . Obtained RH was stored in a pre-cleaned airtight container and was utilized without any further physical or chemical pre-treatment. The chemical analysis of RH for their trace metal contents was carried out by using neutron activation analysis (NAA) and atomic adsorption spectrometry (AAS). Results of these analyses exhibited that the amount of metals such as Na, K, Pb and Fe were present in $\mu\text{g/g}$ of sample. Silica contents were found to be 18.27 (0.62%) of RH. The small amount of elements present in RH was studied by employing standard methods.

2.3. Adsorption of Cu(II) onto RH

Adsorption of Cu(II) onto RH was carried out as reported in our previous research [20,23–25] (S1 in supporting information for detail).

2.4. Characterization

2.4.1. Instrumentation

Morphology of RH before and after adsorption of Cu(II) was evaluated by using field emission scanning electron microscope (FE-SEM, Sirion200, FEI Company, USA). Before and after adsorption of Cu(II) onto RH, its FTIR spectrum was taken by attenuated total reflectance (ATR) with FTIR spectrometer (Vector 22, Bruker) having resolution of 2 cm^{-1} and total spectral range of $4,000\text{--}400\text{ cm}^{-1}$. Adsorption of Cu(II) onto RH was also proved by using EDX analysis.

2.5. Adsorption kinetics

The Lagergren's pseudo-first-order kinetic equation is shown as [25]:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \quad (1)$$

The pseudo-second-order kinetic rate equation is represented as [25]:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (2)$$

where Q_t is amount of Cu(II) adsorbed at time " t " (mg/g), Q_e is amount of Cu(II) adsorbed at equilibrium (mg/g), t is time (min), k_1 is rate constant of pseudo-first-order model (min^{-1}), k_2 is rate constant of pseudo-second-order model (g/mg min).

Non-linear pseudo-first-order

$$Q_t = Q_e(1 - e^{-kt}) \quad (3)$$

Non-linear pseudo-second-order

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

To compare the applications of different models, Chi-square test ' χ^2 ' was employed as determining tool for the best-fit of kinetic equations which is calculated by following equation:

$$\chi^2 = \sum \frac{(Q_e - Q_{e,m})^2}{Q_{e,m}} \quad (5)$$

where Q_e is equilibrium capacity calculated from experimental data (mg/g), and $Q_{e,m}$ is equilibrium capacity measured from model (mg/g).

2.6. Non-linear adsorption isotherms

Non-linear Langmuir adsorption isotherm is expressed as [26]:

$$C_{\text{ads}} = \frac{Q_m k_L C_e}{1 + k_L C_e} \quad (6)$$

where C_e shows the concentration of Cu(II) solution (mol/L) at equilibrium. The constant Q_m is monolayer adsorption capacity (mol/g) and k_L (L/mol) is related to energy of adsorption. In general Q_m and k_L are functions of pH, ionic media and ionic strength.

Non-linear Freundlich isotherm is given as [26]:

$$C_{\text{ads}} = K_f C_e^{1/n} \quad (7)$$

where ' K_f ' and ' n ' are Freundlich constants denoting adsorption capacity and adsorption intensity respectively.

Non-linear Dubinin–Radushkevich equation can be given as [26]:

$$C_{\text{ads}} = C_m \exp(-\beta \epsilon^2) \quad (8)$$

where C_{ads} is the quantity of Cu(II) adsorbed onto RH, C_m (mol/g) is the maximum quantity of Cu(II) that can be adsorbed onto RH under the optimized experimental conditions, β is a constant related to adsorption energy and ϵ (Polanyi potential) = $RT \ln \left(1 + \frac{1}{C_e} \right)$ where R is the universal gas constant (kJ/mol K), and T is absolute temperature (K).

The mean adsorption energy (E) can be calculated by utilizing value of β as [26]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

2.7. Adsorption thermodynamics

Herein, adsorption thermodynamics was also evaluated. The values of change in Gibb's free energy (ΔG°), enthalpy

(ΔH°) and entropy (ΔS°) were calculated by employing below relationships:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$K_c = \frac{C_a}{C_e} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

where K_c , ΔG° , ΔH° and ΔS° are denoting equilibrium constant, change in Gibb's free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K) respectively.

3. Results and discussion

3.1. SEM and EDX studies

Before and after adsorption of Cu(II) onto RH, its structure was studied by utilizing SEM and attained result is represented in Fig. S1. It was found that the surface of RH become smooth as a result of adsorption of Cu(II) from wastewaters. The radius of Cu(II) was 0.091 nm which was much smaller than the pore sizes of RH, so it may adsorbed through diffusion into pores.

To confirm presence of Cu(II) onto RH, EDX analysis of Cu(II) loaded RH was employed and result is denoted in Fig. S2. The metal ion peaks at different energy levels ranging 0.550–8.80 keV showing its adsorption onto RH.

3.2. FTIR study

FTIR spectrum of virgin RH is shown in Fig. S3. The peaks at 1,737.8; 1,435.6 and 1,365.4 cm^{-1} are associated to C=O stretching, OH bending of the adsorbed H_2O and aliphatic C–H bending respectively [27]. The characteristic absorption band at 3,400–3,200 cm^{-1} is due to surface O–H stretching whereas aliphatic C–H stretching had a broad band at 2,921–2,851 cm^{-1} . The peak at 1,074.0 cm^{-1} attributes to anti-symmetric stretching vibration of Si–O whereas at 476.2 cm^{-1} showing bending vibration of Si–O–Si bond [28–30]. The peaks at 1,217.0; 1,365.4; 1,737.8 and 1,027.4 cm^{-1} were because of carboxyl group on RH whereas the peaks at 1,208–1,230; 1,367–1,371; 1,740 and 1,029 cm^{-1} for carboxyl group [28,31].

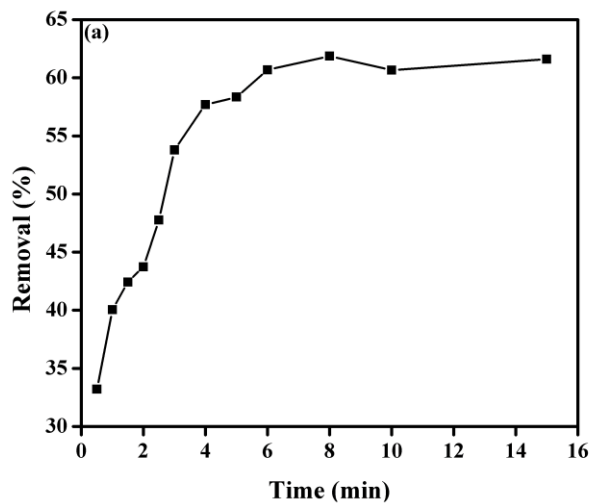
FTIR spectrum of Cu(II) loaded RH is shown in Fig. S3. After adsorption of Cu(II) onto RH, the shifting of peaks to 1,730.6; 1,501.4; 1,037.3 and 500.8 cm^{-1} and the decrease in the intensities of 1,216.3 and 1,367.3 cm^{-1} for RH which indicated that less stretching occurs because of the binding of Cu(II) with carboxyl and silanol groups present in RH. It was also observed that new peaks at 467 cm^{-1} has been observed after the adsorption of Cu(II) onto RH.

3.3. Effect of operating parameters on the discharge of Cu(II)

The effect contact time, mass of RH, initial concentration of Cu(II) solution, and temperature on the removal of Cu(II) was investigated. Its details are reported below:

3.3.1. Effect of contact time

The influence of contact time on the percentage removal of Cu(II) from wastewater was investigated keeping mass of RH, initial volume of solution, concentration of Cu(II) solution, temperature and shaking speed constant. Fig. 1a indicates the influence of contact time on the percentage removal of Cu(II) at room temperature. The percentage removal of Cu(II) was found to be 33%–62% which was enhanced with contact time. In the beginning, the percentage discharge of Cu(II) was rapid. Table 1 provides an interesting comparison of adsorption capacity of copper ions for different adsorbents. It was because of existence of maximum number of empty sites onto RH and interaction was developed between adsorption sites and Cu(II) [32,33]. After it, the removal of Cu(II) was not fast. Then the equilibrium was achieved and no significant increase in adsorption was occurred with contact time. Due to movement of Cu(II) into interior pores of RH, it was slowed down when all empty sites were covered.



3.3.2. Effect of mass of RH

Fig. 1b denotes affect of the mass of RH onto the percentage discharge of Cu(II) from wastewater. It was studied keeping other operating endowments constant at ambient tempertaure. The percentage discharge of Cu(II) from wastewater was found to be increased from 31% to 67% with increasing mass of RH from 0.1 to 0.5 g. Similar results were attained in our previous work [34,35]. From this, the optimized mass of RH was attained to be 0.25 g because there was very small increase in percentage removal of Cu(II) from wastewater at room temperature after this mass of RH (0.25 g). It was used in further research.

3.3.3. Effect of initial concentration

Fig. 1c shows influence of initial concentration of Cu(II) on the percentage discharge of it from wastewater. It was studied by keeping other operating factors constant. The percentage removal of Co(II) was declined from 68% to

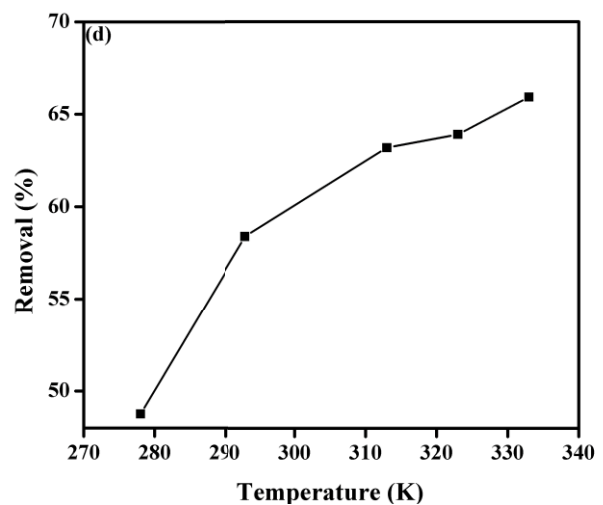
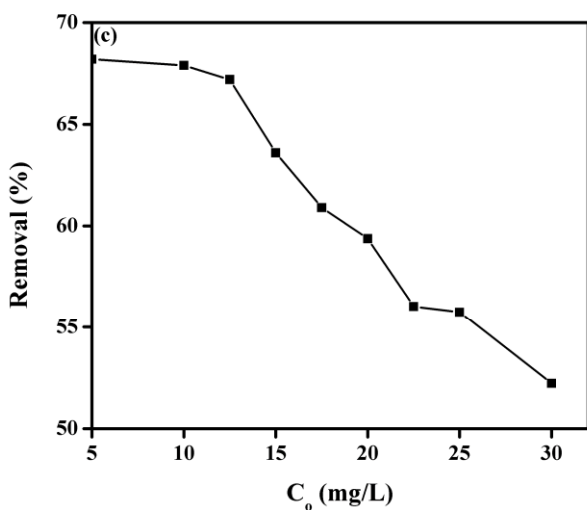
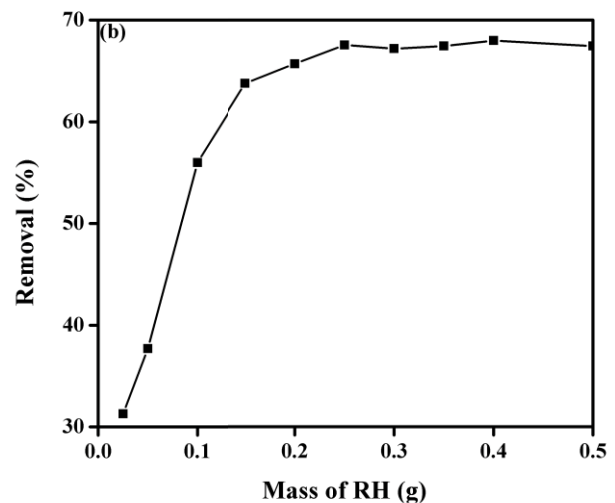


Fig. 1. (a) Effect of contact time, (b) mass of RH, (c) initial concentration of Cu(II) solution, and (d) temperature on the percentage removal of Cu(II) from aqueous solution.

52% with increasing initial concentration of Cu(II) which is similar to our previous work [23–25]. Some of Cu(II) were left unabsorbed because of saturation of adsorption sites at higher initial concentration [25]. At low concentration of metal ions, the maximum numbers of binding spaces were present. With increasing in the concentration of metal ions in an aqueous solution, the number of ions competing for present binding sites onto RH was enhanced.

3.3.4. Effect of temperature

The effect of temperature on the percentage removal of Cu(II) by using RH was also revealed by keeping other operating endowments constant and attained results are represented in Fig. 1d. The percentage discharge of Cu(II) from wastewater by using RH was increased from 49% to 66% with increasing temperature. It may be either because of acceleration of some initially slow adsorption stages or to the establishment of some new active sites onto surface of the RH with rise in temperature [20,33].

3.4. Adsorption isotherms

Non-linear Langmuir isotherm for adsorption of Cu(II) onto RH is denoted in Fig. 2. We used Wave Metrics IGOR Pro 6.1.2 software for determination of isotherm endowments. The values of Langmuir isotherm parameters are given in Table 2. The measured values of R_L are also given in Table 2 which represented that adsorption of Cu(II) onto RH was favorable process.

Fig. 2 shows Freundlich isotherm for adsorption of Cu(II) onto RH and the calculated values of K_f and n are given in Table 2. The value of “ n ” was employed to indicate heterogeneous surface of the RH. The values of ‘ n ’ ranges from 2–10 exhibiting good adsorption, 1–2 moderate adsorption and less than one represents poor adsorption [26,32].

Dubinin–Radushkevich isotherm for adsorption of Cu(II) onto RH is represented in Fig. 2. The values Dubinin–Radushkevich constants are given in Table 2 along with their respective (χ^2) values. The small value of ‘ χ^2 ’ shows that experimental data fitted well to Dubinin–Radushkevich isotherm. The value of adsorption free energy (E) was 10.324 ± 0.42 kJ/mol exhibiting that adsorption of Cu(II) onto RH was chemical adsorption [24].

3.5. Kinetics study

Non-linear pseudo-first-order and pseudo-second-order models were applied on the time dependent adsorption data of Cu(II) onto RH. IGOR Pro 6.1.2, Wave Metrics software was used for the calculation of kinetic parameters by utilizing non-linear method. Non-linear plots of pseudo-first-order and pseudo-second-order models for adsorption of Cu(II) onto RH are denoted in Fig. 3. The measured values of constants and theoretically calculated Q_e for adsorption of Cu(II) onto RH are given in Table 3. The computed values of ‘ χ^2 ’ are also given in Table 3. The computed lower values of non-linear ‘ χ^2 ’ test analysis of Cu(II) adsorption onto RH for pseudo-second-order

Table 1
Adsorption capacities of copper for different adsorbents

Adsorbents	Capacity (mg g ⁻¹)	References
N-(2-Carboxybenzyl) grafted chitosan	0.027	[36]
Chitosan–GLA beads	6.210	[37]
Chitosan beads	21.55	[37]
Chitosan–alginate beads	27.44	[37]
Activated carbon	540.14	[38]
Untreated fruit peel	0.137	[39]
Treated fruit peel	0.486	[39]
Palm nut	2.667	[40]
Chestnut	3.247	[41]
Palm shell activated carbon	0.228	[42]
Coconut husk	0.668	[43]
Low-cost mineral	33.18	[44]
Sludge pyrolysis	0.620	[45]
Modified <i>Gmelina arborea</i> leaves	3.971	[46]
<i>Gmelina arborea</i> leaves	5.176	[46]
AC <i>Ceiba pentandra</i> hulls	9.060	[47]
Rice bran	7.130	[48]
Sawdust	1.347	[49]
Dehydrated wheat bran	14.10	[50]
Cone biomass	5.110	[51]
Chitosan/sisal/banana fiber hybrid composite	1.885	[52]
Rice husk	53.123	This work

Table 2
Measured parameters of Langmuir, Freundlich and Dubinin–Radushkevich isotherms by non-linear method

Adsorption isotherms	Isotherm parameters	
Langmuir isotherm	Q_m	1.92×10^{-5}
	k_L	6,515
	R_L	0.220–0.629
	χ^2	4.21×10^{-13}
Freundlich isotherm	K_f	$(8.555 \pm 1.44) \times 10^{-3}$
	n	1.979 ± 0.074
	χ^2	1.54×10^{-13}
Dubinin–Radushkevich isotherm	C_m	$(8.945 \pm 0.811) \times 10^{-5}$
	β	$(4.69 \pm 0.192) \times 10^{-3}$
	E	10.324 ± 0.42
	χ^2	9.1×10^{-13}

Q_m : mol/g; k_L : L/mol; K_f : (mg/g) (L/mg)^{1/n}; C_m : mol/g; β : mol²/J²; E : kJ/mol.

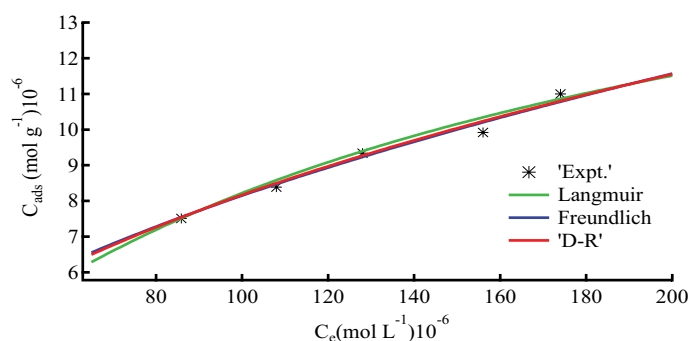


Fig. 2. Non-linear plots of Langmuir, Freundlich and Dubinin–Radushkevich isotherms for adsorption of Cu(II) onto RH.

Table 3
Measured parameters of pseudo-first-order model and pseudo-second-order model by non-linear method

Kinetic models	Parameters	
Pseudo-first-order model	$Q_{e(\text{exp.})}$	0.616
	Q_e	0.582
	k_1	1.0103
	% Error	5.440
	χ^2	0.022
Pseudo-second-order model	Q_e	0.643
	k_2	2.456
	% Error	–4.3442
	χ^2	0.0083

Q_e : mg/g; k_1 : (min^{–1}); k_2 : g/mg min.

represented that pseudo-second-order model fitted well to experimental data for adsorption of Cu(II) onto RH.

3.6. Adsorption thermodynamics

The plot of $1/T$ vs. $\ln K_c$ for adsorption of Cu(II) onto RH is represented in Fig. 4. The calculated values of Gibb's

Table 4
Measured thermodynamic parameters for adsorption of Cu(II) onto RH

Temp. K	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
278.16			–0.055
293.16			–0.568
313.16	9.453	34.201	–1.252
323.16			–1.594
333.16			–1.936

free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) for adsorption of Cu(II) onto RH are given in Table 4. The attained negative value of Gibb's free energy for adsorption of Cu(II) onto RH exhibited that adsorption of Cu(II) onto RH was spontaneous in nature [24]. The decrease in Gibb's free energy with increase in temperature showed decrease in feasibility of adsorption at elevated temperature. The measured positive value of entropy (ΔS°) showed increase in randomness during adsorption of Cu(II) onto RH at adsorbent–adsorbate interface. The positive value of enthalpy ($\Delta G^\circ = 9.453$ kJ/mol) indicated that adsorption of Cu(II) onto RH was an endothermic process [24].

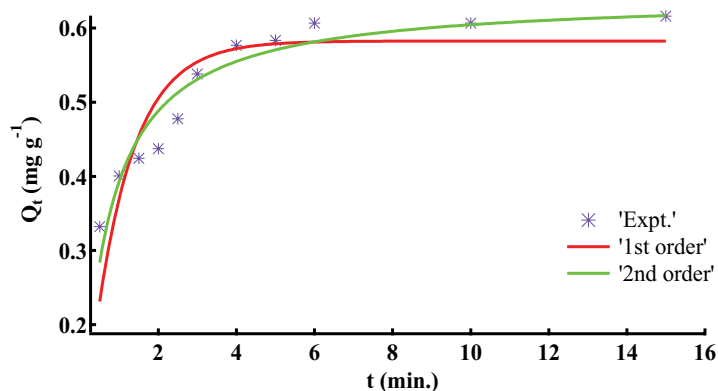


Fig. 3. Non-linear plots of pseudo-first-order and pseudo-second-order kinetics models for the adsorption of copper ions on rice husk.

Table 5
Effect of diverse ions on adsorption of Cu(II) by RH

Cations	Concentration (mol/L × 10 ⁻³)	% Adsorption	Anions	Concentration (mol/L × 10 ⁻³)	% Adsorption
None	–	64.45	None	–	64.45
K ⁺	2.56	00.00	CO ₃ ²⁻	1.67	53.00
Cd ²⁺	0.89	09.85	PO ₄ ³⁻	1.05	64.55
Mg ²⁺	4.12	25.90	NO ₃ ⁻	1.61	66.35
Fe ³⁺	1.79	08.90	OH ⁻	5.88	46.80
Pb ²⁺	0.48	09.80	Cl ⁻	2.82	57.80
Cu ²⁺	1.57	10.95	I ⁻	0.78	69.75
Na ⁺	43.50	52.55	C ₁₀ H ₁₆ N ₂ O ₈	0.34	06.55
Ca ²⁺	2.50	12.60	C ₆ H ₅ O ₇ ³⁻	0.53	27.25

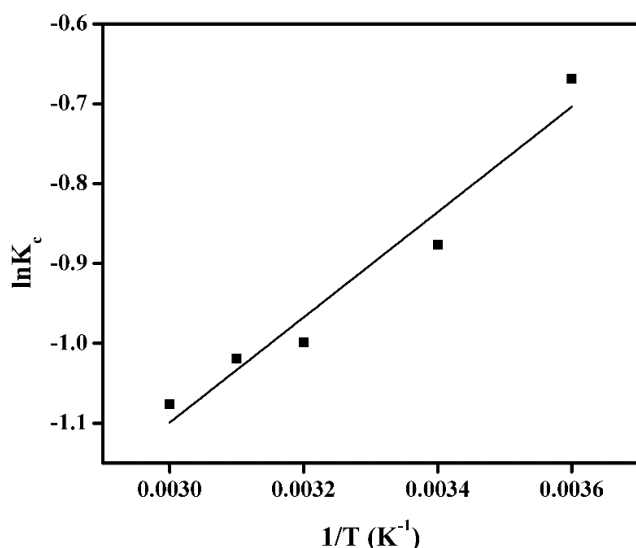


Fig. 4. Plot of $1/T$ vs. $\ln K_c$ for adsorption of Cu(II) onto RH.

3.7. Effect of diverse ions

The existence of several ions in the adsorbing medium may change the chemistry and environment of the metal of interest in solution which changes adsorption efficiency of any adsorbent. The influence of existence of the

other ions in the adsorbing media was studied by adding higher concentration of diverse ions by employing the optimized experimental endowments for adsorption of Cu(II) onto RH. All the cations were employed as their nitrate salts whereas for anions sodium salts were used. Table 5 represents results of copper adsorption onto RH in the presence of counter ions. The results exhibited that biosorption of copper onto RH was declined in the presence of OH⁻, citrate ions and Ca²⁺ up to 24.42%, whereas EDTA, Cd²⁺, Fe³⁺ and Pb²⁺ decreased the adsorption largely.

4. Conclusions

In summary the adsorptive discharge of Cu(II) by employing RH was studied. The discharge of Cu(II) from wastewater was enhanced with contact time, mass of RH, and temperature whereas declined with initial concentration of solution. Results of adsorption isotherm showed that experimental data fitted well to non-linear Freundlich isotherm. Kinetics study showed that adsorption of Cu(II) onto RH followed non-linear pseudo-second-order model. Adsorption thermodynamic study indicated that adsorption of Cu(II) was endothermic and spontaneous process. Therefore, the RH could be utilized as outstanding adsorbent for the discharge of Cu(II) from wastewater at ambient temperature.

Acknowledgement

The authors are highly thankful to Higher Education Commission (HEC), Pakistan for financial support.

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Supplementary information

S1. Adsorption of Cu(II) onto rice husk

In a typical procedure, a known amount of rice husk (RH) was taken into a 25 cm³ secured cap culture tube along with 4 cm³ of standard acid solution and a fixed quantity of stock radiotracer with known quantity of Cu(II) solution was added. Consecutively, the contents were equilibrated on a wrist-action mechanical shaker (Vibromatic, USA) at a rate of 500 rpm for specific intervals of time. Then, it was centrifuged at 5,000 rpm for phase separation and the supernatant solution was withdrawn for activity measurement. The radioactivity of solutions before (A_i) and after

(A_f) equilibrium was recorded with a NaI well type scintillation counter (Canberra Inc.) coupled with a counter-scaler (Nuclear Chicago). A volume of 1.0 cm³ was normally used to measure the activity. All experiments were performed at ambient temperature. The percentage adsorption of Cu(II) onto RH was calculated by using below relationship:

$$\% \text{ adsorption} = \frac{A_i - A_f}{A_i} \times 100 \quad (1)$$

where A_i and A_f show initial and final adsorption of Cu(II) (counts/min) into respectively.

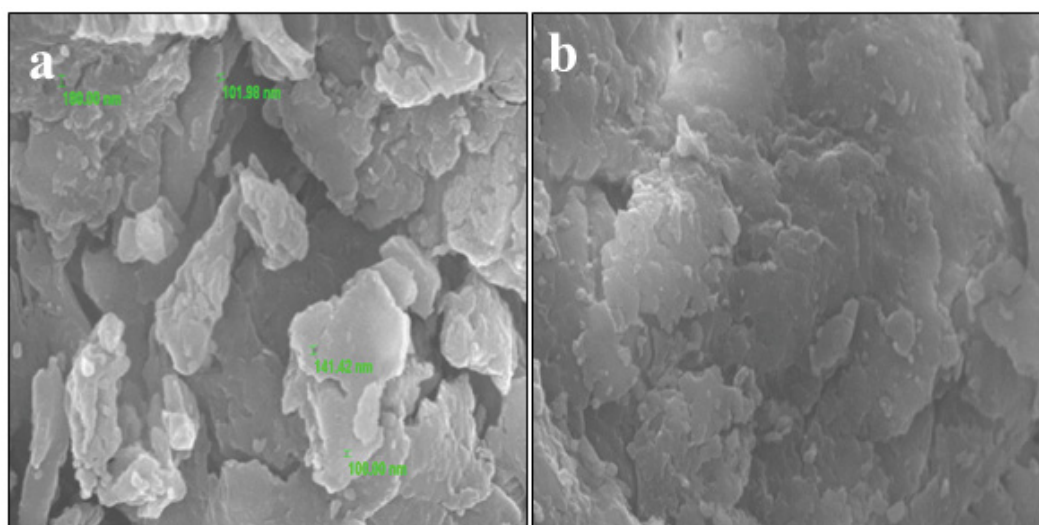


Fig. S1. SEM images of (a) virgin RH and (b) Cu(II) loaded RH.

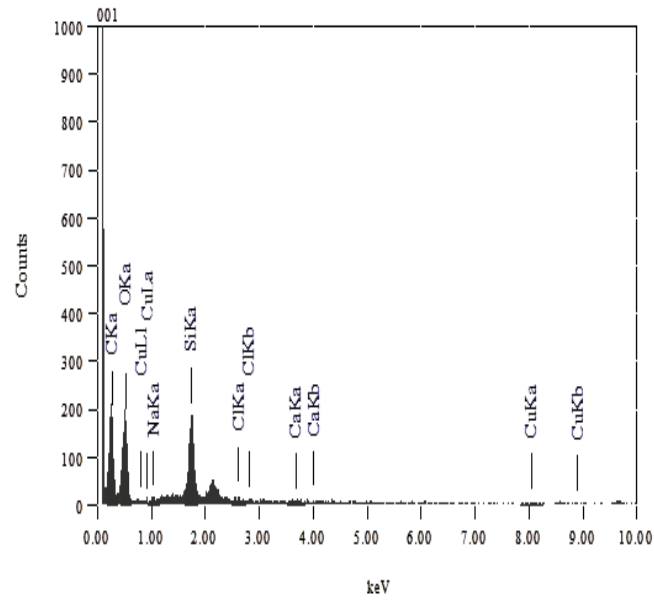


Fig. S2. EDX graph of Cu(II) loaded RH.

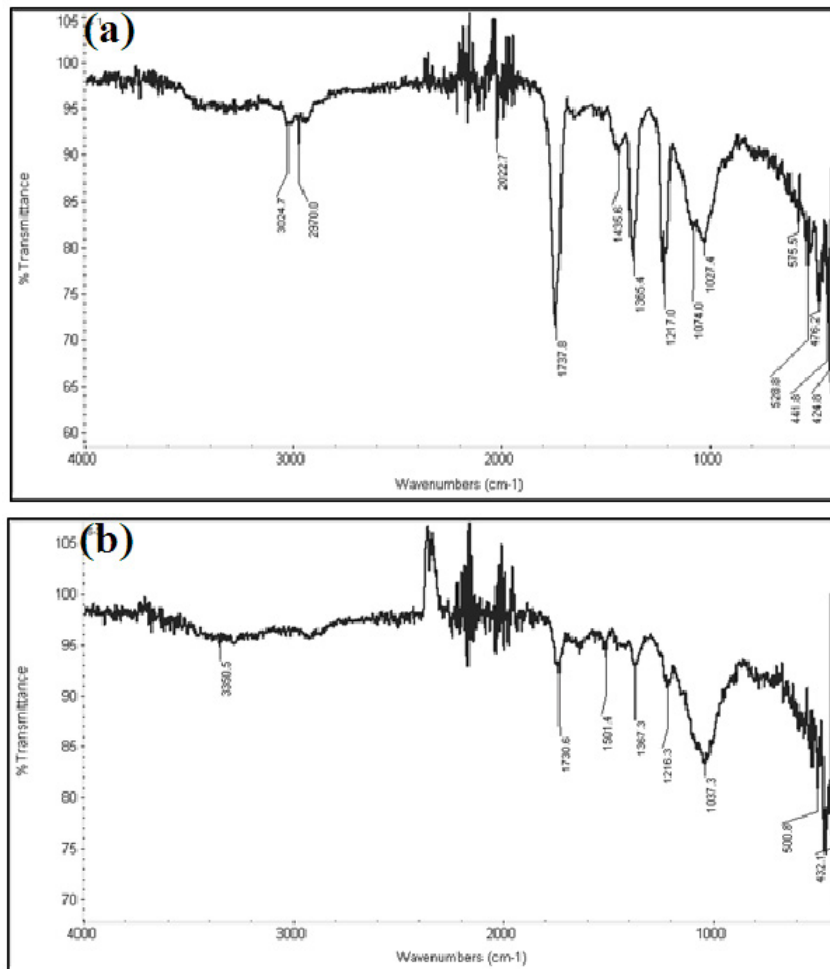


Fig. S3. FTIR spectrum of (a) virgin RH and (b) Cu(II) loaded RH.