Preparation of activated carbon from *Salvadora persica* for the removal of Cu(II) ions from aqueous media

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ABSTRACT

The *Salvadora persica* (Pilu) a cost effective material, is recently being used as adsorbent for the removal of highly toxic Cu(II) ions from polluted water. In this study, three comparative studies, untreated adsorbent (UTSP) and microwave and activating agents mediated activated adsorbent (ACSP) were investigated simultaneously and parallels were drawn between them for validating removal efficiency. Characterization analysis including Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) have been utilized for adsorbent. Factors affecting the adsorption of copper including pH, adsorbent dose, exposure time, and the temperature were investigated. Results showed that ACSP required less extreme conditions for effective working as compared to UTSP. Kinetic studies showed this adsorption reaction was endothermic, feasible, and spontaneous. Additionally, the results clearly showed that both adsorbents exhibited the best correlation with the Langmuir and Freundlich model of adsorption. Hence, a novel, economical and facile biomaterial has been reported in this study for Cu(II) ions removal from aqueous media.

Keywords: Copper; Heavy metals; Adsorption; Biomaterial; Wastewater; Activated carbon

1. Introduction

For the last few decades, due to uncontrolled anthropogenic actions accumulation of heavy metals in rivers and streams has adversely affected aquatic life [1]. Among heavy metals, copper (a brownish-orange malleable, soft and ductile metal) is also considered to be a hazardous trace metal and is generally known as a major water pollutant. Its introduction into the aquatic medium can be from several sources including electroplating, fertilizer or paper industry, paints or pigments, and refineries [2]. However, a large dose of copper intake by humans leads to capillary damage, kidney and liver failure, gastrointestinal irascibility, esophageal mucosal irritation and severe effects on the central nervous system leading to depression [3]. Additionally, it has been reported that 2 mg/L is the maximum non-hazardous limit for human intake in drinking water [2]. Hence, removal of copper from an aqueous medium is the need of the hour and efforts should be made in designing effective removal methodologies. In literature, many techniques for removal of copper including precipitation [4], biosorption [3,5], sedimentation techniques [6], and electrochemical approaches [7], etc. have been reported but these methods possess some limitations. However, among

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all the techniques for the removal of copper, adsorption through activated carbon has gained huge interest due to its cost-effective and eco-friendly approach. Recently, the use of activated carbon obtained from biomaterials has become the center of attention for the removal of toxic pollutants. Various adsorbents such as pomegranate peel [8], hazel nutshell [9], *Cinnamomumcamphora leaves* [10], straws from barley [11], sesame husk [12], molasses activated carbon [13], macroalgae consortium [14], pinewood sawdust activated carbon [15], date seeds biochar [16], olive stone and pinion shell [17], etc. have been employed for the uptake of toxic copper from the aqueous medium. In this research study, the biomass of the plant *Salvadora persica*, also known as Pilu, has been taken as a precursory material for the formation of activated carbon and the applicability of this adsorbent is investigated for the eradication of Cu(II) ions from polluted water.

The objective of this research is the analysis of adsorption isotherms, kinetics and adsorption parameters for Cu(II) ions adsorption over activated carbon exclusively derived from the plant Pilu as the adsorbent. This work provides valuable insights regarding ion adsorption over biomaterial with respect to kinetics and equilibrium studies. Moreover, the optimization of adsorption parameters is also carried out for proposing the best economical design for enhanced removal. Hence, this novel and facile study is directed at evaluating optimized adsorption parameters, isotherm studies, and kinetics associated with inactivated and activated adsorbents generated from *Salvadora persica* for Cu(II) ion adsorption. To the best of our knowledge, the use of such a material as bioadsorbent for the removal of copper has not been reported previously.

2. Experimental

2.1. Materials and methods

The chemicals including copper sulfate ($CuSO_4 \cdot 5H_2O$), sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) used in these experiments were provided by Sigma-Aldrich. All chemicals possess 98% purity and used without further purification processes. Double deionized ultra-pure water was used for solution preparation and washing purposes.

2.2. Biomaterial collection

The biomaterial used in this research work is the plant of Pilu (*Salvadora persica*) locally known as 'miswak' (twigs employed for teeth cleaning as a natural and outdated alternative to modern day toothbrushes). It was acquired from the local market of Lahore. The outer hard surface of the sticks was peeled off. Acquired yellowish colored sticks were then oven-dried at 70°C for 3–4 d after which the material was washed to remove any impurities. The material was then ground to fine powder by using an electric grinder (Phillips) and was screened through the standard 60-mesh for acquiring the particles of 100–275 µm. Plastic bags were utilized for storage of the untreated *Salvadora persica* (UTSP) until further use.

2.3. Preparation of ACSP

Preparation of ACSP for this study was carried out according to the procedure as previously reported by Gupta et al. [18] with major modifications. An amount of 10 g of Pilu was taken in a china dish and digested with concentrated H_2SO_4 which acts as an oxidizing/activating agent here. This wet digestion results in the production of the activated carbon from Pilu. The activated carbon-*Salvadora persica* (ACSP) was then cooked in a commercial microwave oven (Dawlance DW-142 G: frequency, 2.45 GHz) at 200°C for 2 d after which the activated carbon was removed and ground into fine particles by using the similar process mentioned above for untreated adsorbent. The irradiation of ACSP to microwave radiation structurally modifies the surface of the ACSP by re-construction and makes it more mesoporous. As a result of this structural modification, the surface area of the material is enhanced, which allows for the removal of the adsorbate from the system to be more easy and feasible. Fig. 1 represents the ACSP in different forms while Eq. (1) summarizes the whole modification process performed over the adsorbent.
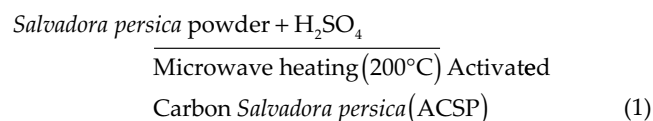
$$Salvadora\ persica\ powder + H_2SO_4 \xrightarrow{Microwave\ heating\,(200°C)} Activated\ Carbon\ Salvadora\ persica\,(ACSP) \quad (1)$$

Fig. 1. ACSP (*Salvadora persica* activated carbon) (A) ACSP before grinding and (B) ACSP after grinding.

2.4. Characterization techniques

FTIR (Model Cary-630) was carried out to determine the structural characteristics of both UTSP and ACSP before and after adsorption. Both samples were dried at 378 K for 24 h and analysis was performed over the range 4,000–400 cm⁻¹ using KBr disc. SEM model Hitachi S-4700 operated at 30 kV has been utilized to understand the morphology of the dried sample. PerkinElmer instrument 2400 Series II elemental analyzer was also used. Additionally, Brunauer–Emmett–Teller (BET) surface area of the sample was determined by interpreting N_2 adsorption isotherm at 77 K in the range of comparative pressure of 10–6 up to 1.0 with the help of pore size and surface area analyzer. However, prior to analysis prepared sample was de-gassed at 300°C/2 h.

2.5. Adsorption experiment

All the solutions were of analytical grade and prepared in double-distilled water. Cu(II) ions were selected as a model adsorbate for investigatory purposes in the context of this study. A 1,000 mg/L stock solution of Cu(II) ions were prepared by adding 2.51 g of $CuSO_4$ in water and then making the solutions up to the mark using deionized water. Further solutions were prepared from the stock solutions by performing successive dilutions. However, Atomic Absorption Spectroscopy (AAS) using a Perkin Elmer Analyst Model number 100AAS was used for the determination of Cu(II) concentration. All the experiments were performed in a flask with a stopper to avoid any evaporation during reaction progress to attain maximum efficiency. Additionally, the effect of different parameters including pH, dose, contact time and temperature on the removal of Cu(II) ions on synthesized adsorbent were studied. For the effect of pH on adsorption of Cu(II) ions on UTSP and ACSP was investigated at different pH values from 1 to 6 in the presence of H_2SO_4 or NaOH. The effect of adsorbate was investigated at a different concentrations between 10 to 100 mg/L concentration. And the contact time of adsorption of Cu(II) ions on UTSP and ACSP was performed from 10 to 80 min. respectively. For each experiment, one factor was varied while keeping all other factors constant.

3. Results and discussion

3.1. Characterization analysis of UTSP and ACSP

A total of four analytical techniques including FTIR, SEM, BET and elemental analysis were employed for characterizing the different adsorbents. FTIR analysis provides information about the presence of functional group moieties in the sample. Fig. 2 shows the comparison of FTIR analysis of UTSP and ACSP before and after the uptake of Cu(II) ions with the change in functional moieties of adsorbent. Additionally, the comparative FTIR analysis before and after adsorptions facilitate in an understanding of the presence of the binding site in both adsorbent. However, the attachment of Cu(II) ions to the specific functional group of adsorbent indicates significant variation in electron density that produces a shift in the band from the original position. Additionally, the UTSP FTIR spectra showed a characteristic broad band of the hydroxyl group at 3,312 cm⁻¹ in

Fig. 2A. However, a single small peak at 2,919 cm⁻¹ is due to the presence of stretching C–H bond vibrations while the band at 1,602 cm⁻¹ corresponds to the carbonyl group of aldehyde and ketone. Additionally, the band/peak at 1,702 cm⁻¹ corresponds to the vibrations of the C=O bond of esters or the carboxylic group. The peaks observed at 1,509; 1,332 and 1,032 cm⁻¹ indicate the presence of N–H, C–N groups, and C–O stretching, respectively. However, in ACSP spectra minor shift in peaks was observed as compared to UTSP. In Fig. 2B the characteristic broad band centered at 3,355 cm⁻¹ shows the presence of hydroxyl functional groups. However, the sharp peak at 1,720 cm⁻¹ specifies the presence of carboxyl functional groups. And two peaks at 1,014 and 1,104 cm⁻¹ are credited to the presence of primary alcohol and the C–O group. The amide functional group peak appeared at 1,509 cm⁻¹. Additionally, the peak appeared at 859 cm⁻¹ assigned to the bending of CH bonds of four methylene groups. Yuen and Hameed [19] also proposed similar finding that microwave irradiations induce surface modifications. Fig. 2C and D provide valuable information about the functional group's moieties in UTSP and ACSP responsible for the uptake of Cu(II) ions. It has been clearly observed that peaks of C=O, N–H, C–N, C–H, and OH peaks slightly shifted or displaced from 1,024; 1,507; 1,321; 2,919 and 3,331 cm⁻¹ to 1,015; 1,509; 1,332; 2,922 and 3,312 cm⁻¹. The FTIR analysis of Cu(II) loaded ACSP showed the shift of peak or bands for a number of functional groups including C=O, N–H, C–H, and OH groups. These shifts are from 1,720; 1,509; 12,114 and 3,355 cm⁻¹ to 1,701; 1,587; 2,119 and 3,362 cm⁻¹ respectively. Damping or widening of adsorbents peaks as a result of metal ions uptake from the aqueous environment has already been previously reported in the academic literature [20].

Scanning electron micrographs enables us to observe the changes occurring on surface microstructures of the adsorbent owing to chemical surface modifications, adsorption, and desorption. In UTSP (Fig. 3A), settled frames with round edges and homogenous surfaces were observed while in the micrograph of ACSP (Fig. 3B), bold frames with elliptical shaped units that appeared in the wrinkled biomass surface can be subsequently observed on its micrographic structural surface. Increased roughness directly contributes to improving the adsorptive capacities of the ACSP as a large number of entrapping and attachment sites will be now accessible to the adsorbate for incapacitation. The importance of textural configuration and super-facial roughness for adsorptive uptake of copper is also narrated by Macías-García et al. [21] their research work as well. The modifications acquired in the treated adsorbent are attributed to the activation and microwave irradiation treatment provided to ACSP before carrying out the adsorption of Cu(II) ions [19]. Moreover, elemental analysis of both the adsorbents also establishes that the surface of ACSP has been significantly modified by sulfuric acid activation and microwave irradiation. Results acquired by the elemental analysis are summarized in Table 1. Table 1 shows that elemental analysis of UTSP and ACSP possesses higher content of C, H and low amount of S and N which make it appropriate for adsorption process. The treated adsorbent showed significant increase in carbon content from 38.94% of UTSP to 52.3% of ACSP. BET surface analysis was also studied
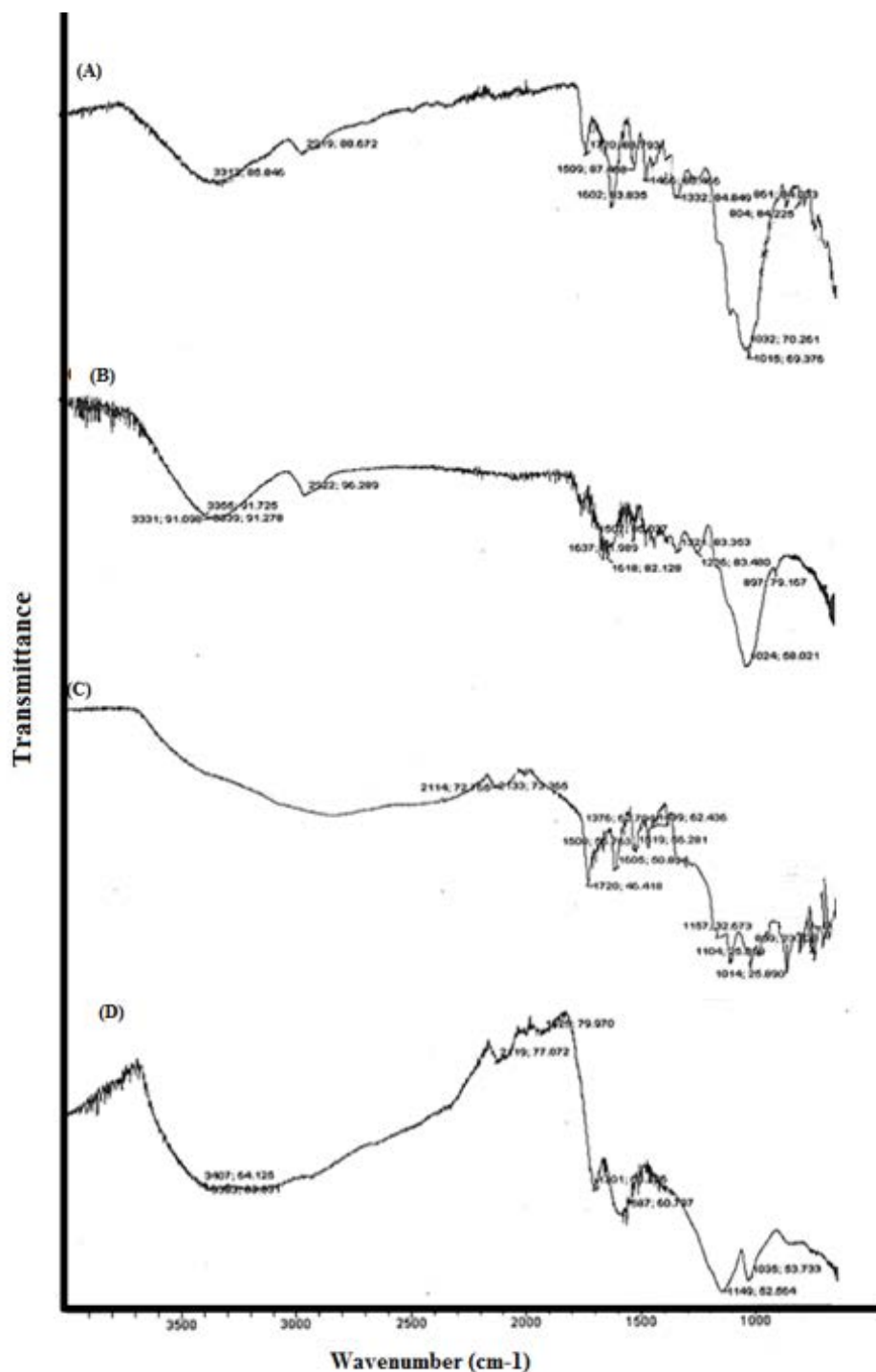
Fig. 2. FTIR spectra of (A) simple UTSP, (B) simple ACSP, (C) Cu(II) loaded UTSP and (D) Cu(II) loaded ACSP.

to investigate the extent of modification. The surface area of the treated adsorbent was enhanced from 2.11 m²/g of untreated adsorbent to 381 m²/g of ACSP. Additionally, the single point technique also showed similar results in the presence of UTSP at 0.88 m²/g while ACSP showed a prominent increase in value at 217.14 m²/g. Similar results has been reported by Radwan et al. [22,23] respectively. Hence, it has been observed in all techniques that the

applied approach successfully modified the surface of the treated adsorbent.

3.2. Adsorption parameter studies

In this study, the effect of UTSP/ACSP dose, solution pH contact time, and temperature on the adsorption of Cu(II) ions were studied to obtain excellent results. The optimum
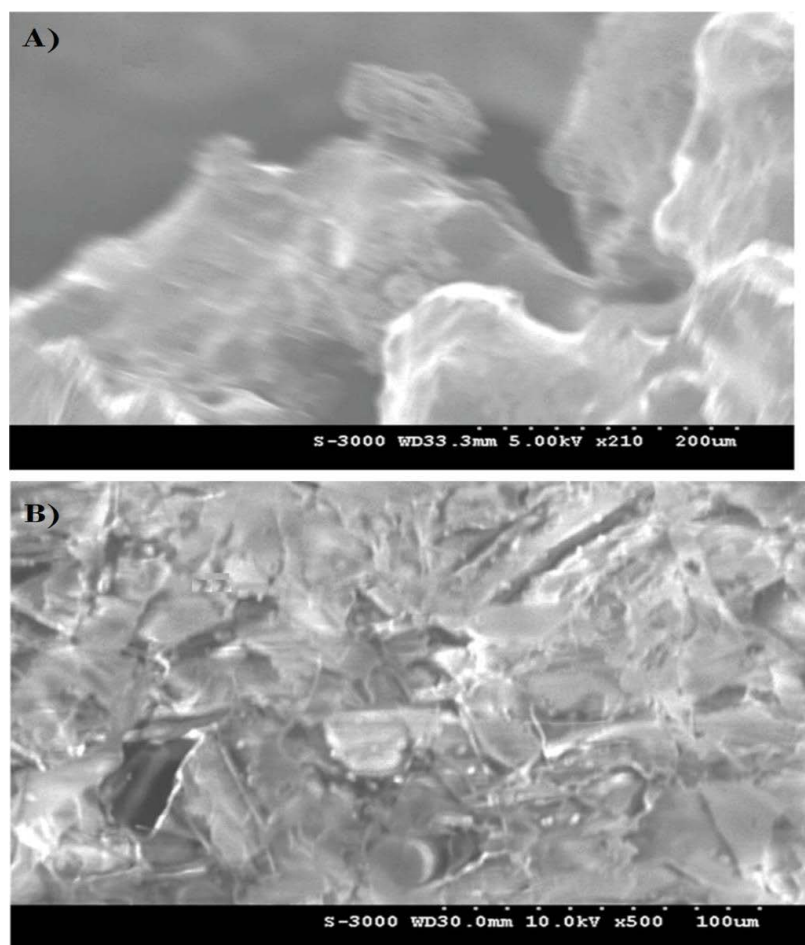
Fig. 3. SEM micrographs (A) untreated-*Salvadora persica* (UTSP) and (B) activated adsorbent-*Salvadora persica* (ACSP).

Table 1
Elemental analysis of UTSP and ACSP

Elements	UTSP	ACSP
C%	38.84%	52.3%
H%	5.8%	3.0%
S%	1.7%	1.1%
N%	0.54%	0.3%

solution pH was studied for the uptake of Cu(II) ions (initial concentration = 50 mg/L) and 0.3 g/L of ACSP. Fig. 4A shows an insignificant change in adsorption of Cu(II) ions at different pH values for both UTSP and ACSP. However, a slight variation at pH value from 5 to 6 was observed due to two reasons (a) high hydronium ion concentration at low pH and (b) competition for the Cu(II) ions increases which restrict their approach to the function group due to electrostatic repulsive forces [24]. The results showed that pH has insignificant effect on adsorption of Cu ions. The effect of adsorbent dose on the removal efficiency of Cu(II) ions was also studied as shown in Fig. 4B. The R (%) value for ACSP was higher (96.67%) as compared to UTSP (82%). The results showed that the value of R (%) increases the

amount of ACSP increases up to 0.3 g/L with a removal efficiency of 96.67% and then insignificantly decreases. Increasing the UTSP and ACSP amount to 0.5 and 0.3 g/L provides more surface area and high availability of active sites for the Cu(II) ions which increase the R (%) efficiency. However, on increasing the dose of adsorbents beyond the optimum limit the chance of aggregation in adsorbents increase which reduce the available surface area and increase diffusional path length. A similar trend for the effect of the adsorbent dosage on the adsorption of brilliant green dye was reported by Rehman et al. [25]. Hence, the dose of 0.3 and 0.5 g/L for ACSP and UTSP at pH 5.5 was considered for further investigation respectively.

The % removal efficiency of Cu(II) ions with respect to contact time was studied as shown in Fig. 4C. The adsorption contact time varied from 10 min to 80 min. It has been observed that the percentage removal values first increase (up to 50 min for UTSP and 40 min for ACSP) then after attaining optimum contact time value a slight decrease or constancy in removal with respect to increasing contact time was observed (Fig. 4C). Additionally, in both cases, it was observed that after optimum value the curve becomes parallel to the time axis. Hence, with the passage of time, almost all the available active sites were covered that significantly increasing the contact time for further diffusion
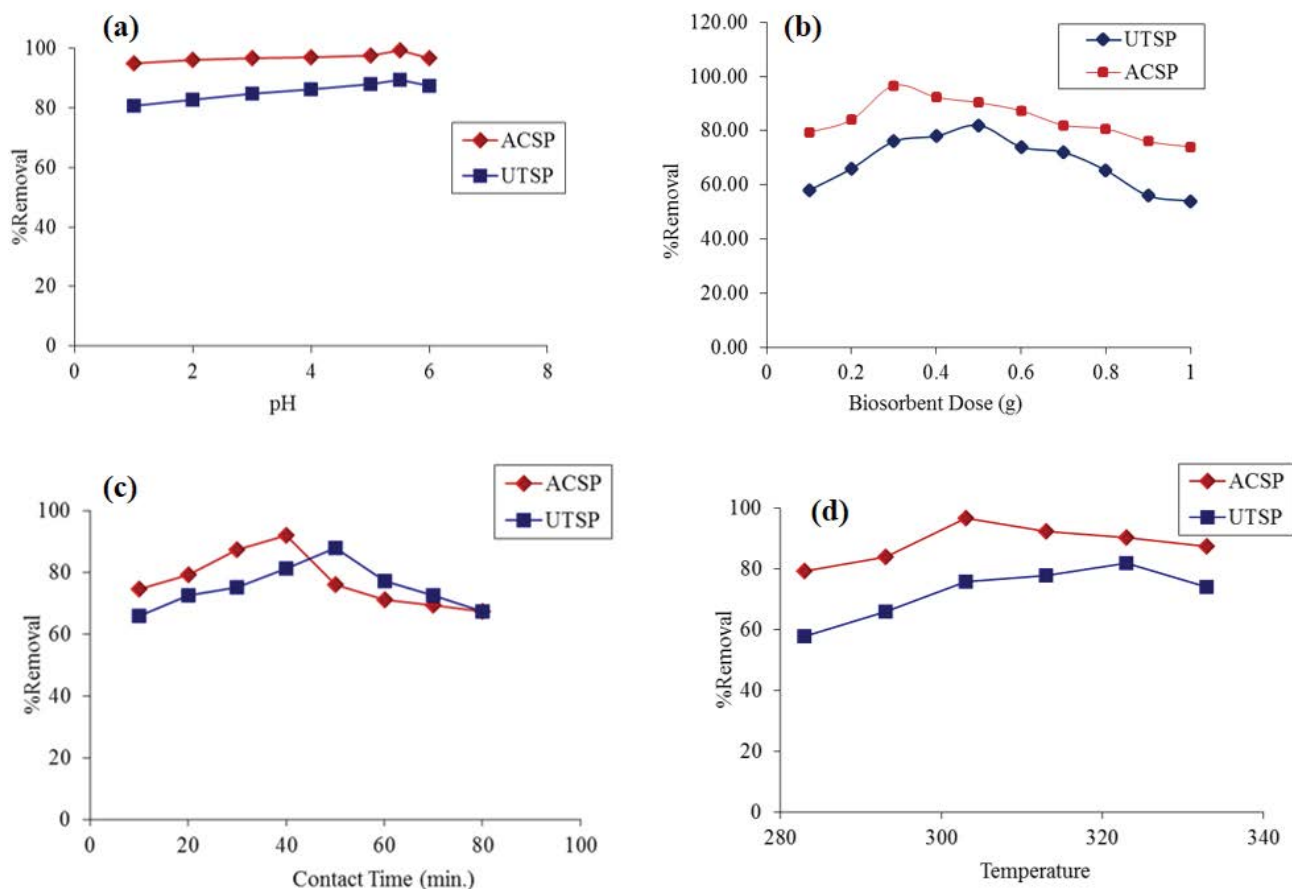
Fig. 4. (A) Effect of pH (dose of UTSP = 0.5 g/L; dose of ACSP = 0.3 g/L, at 30°C contact time for UTSP = 50 min; contact time for ACSP = 40 min), (B) effect of adsorbent dosage (contact time for UTSP = 50 min; contact time for ACSP = 40 min at 30°C pH of both adsorbents = 5.5), (C) effect of contact time (dose of UTSP = 0.5 g/L; dose of ACSP = 0.3 g/L; pH of both adsorbents = 5.5) and (D) effect of temperature (dose of UTSP = 0.5 g/L; dose of ACSP = 0.3 g/L; contact time for UTSP = 50 min; contact time for ACSP = 40 min pH of both adsorbents=5.5) with 50 mg/L initial concentration of Cu(II) ions.

of the adsorbate. The diffusional barrier causes hindrance in absorbance which makes the curve parallel to the time axis [26]. This contact time for both adsorbents is comparatively smaller as compared to the already reported adsorbent [27].

Temperature is another important factor affecting the removal efficiency of Cu(II) ions on the adsorbent. As temperature not only facilitates the determination of thermodynamic quantities but also informs about the nature or feasibility of reaction progress. Fig. 4D shows that the effect of temperature varied from 10 to 60°C. It has been observed that the maximum % removal efficiency of Cu(II) ions was found to be 97.36% for UTSP and 99.54% for ACSP at 30°C. Hence, an increase in adsorption capacity related to Cu(II) ions with the rise in temperature was indicative of an increase in kinetic energy that favored the endothermic nature of adsorption. Similar findings in this regard have been reported by Bajpai and Vishwakarma [28]. However, the results clearly indicate that both UTSP and ACSP adsorbents work exceptionally well as an adsorbent for Cu(II) ion adsorption as compared to others reported in the literature [27].

3.3. Adsorption isotherm studies

To understand the mechanism of adsorption various equilibrium models have been utilized. In this study, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms have been used separately to have an understanding of the mechanism of Cu(II) adsorption on UTSP and ACSP (Fig. 5). For this purpose different parameters of equilibrium models were determined from plotted graphs (Table 2).

The Langmuir isotherm predicts that adsorption occurs only at specific homogenous sites on the adsorbent surface and a single layer of adsorbent is formed. However, it has been reported that numerous researchers have employed this adsorption isotherm in their research for removal of pollutants [29,30]. The linear plot equation of Langmuir adsorption isotherm is shown in Eq. (2).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{2}$$
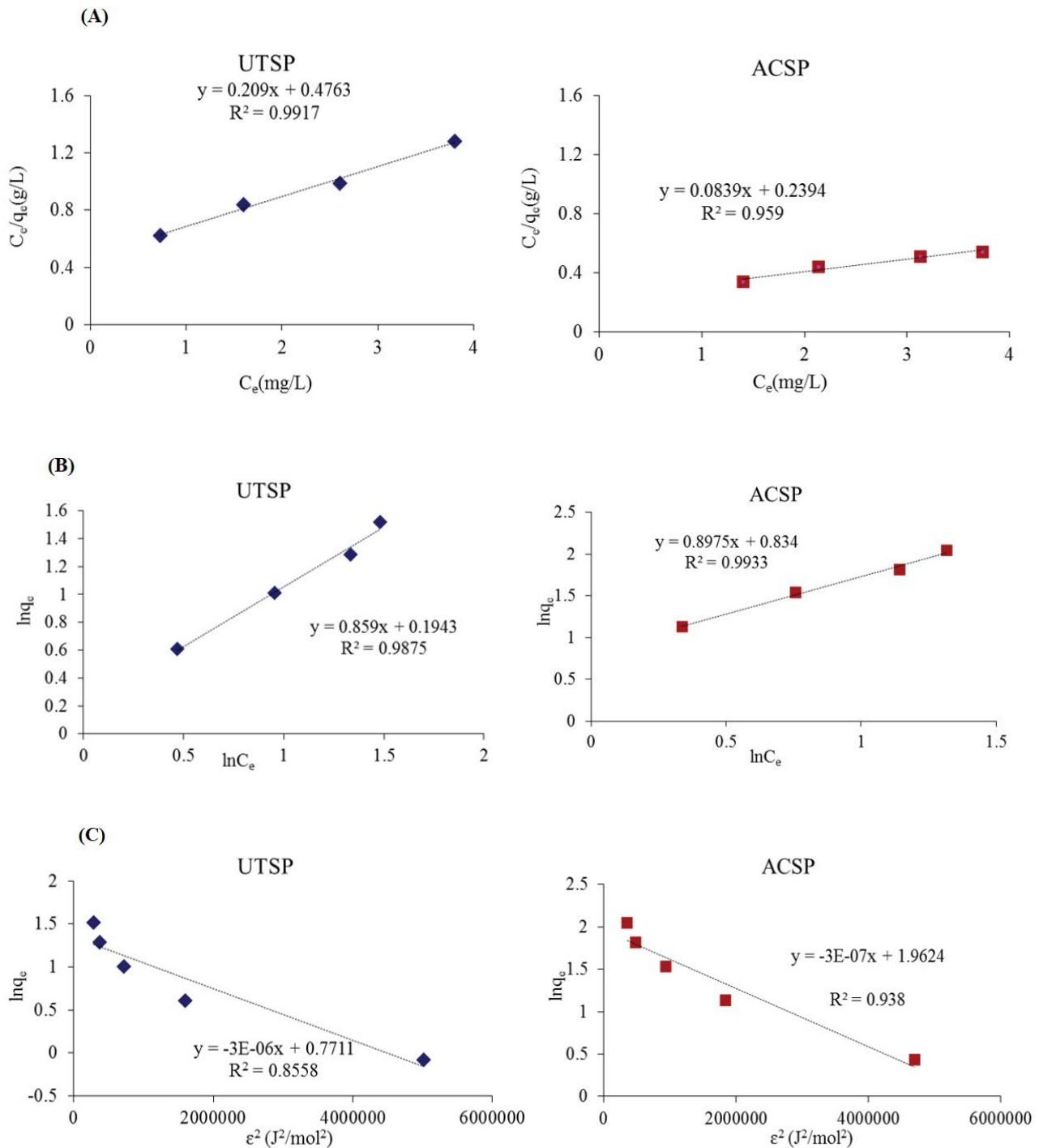
(A)

(B)

(C)

Fig. 5. (A) Langmuir adsorption isotherm, (B) Freundlich adsorption isotherm and (C) D–R adsorption isotherm for sorption of Cu(II) ions on UTSP (0.5 g/L) at 50 min and for ACSP (0.3 g/L) at 40 min contact time with pH = 5.5 and temperature 30°C.

where the q_m (mg/g) and K_L (L/mg) represent the Langmuir adsorption isotherm constant [31]. The q_m value in the Langmuir model was found to be significantly higher for ACSP than UTSP. Additionally, the R^2 value in the Langmuir model for UTSP and ACSP was found to be 0.9917 and 0.959 respectively. The results clearly showed that the adsorption of Cu(II) ions on UTSP and ACSP followed Langmuir adsorption isotherm. However, the q_m value for Cu-UTSP was 4.78 mg/g while a three-time increase of 11.91 mg/g was observed in the case of Cu-ACSP. The increase in q_m value showed the higher Cu(II) adsorption by ACSP mainly due to the higher surface area that provides more adsorption sites [31]. Hence, the adsorption capacity for ACSP was higher as compared to UTSP for the removal of Cu(II) ions. The results

Table 2
Adsorption isotherms parameters study on UTSP and ACSP

Adsorption isotherms	Parameters		
Untreated adsorbent (UTSP)			
Langmuir isotherm	q_m = 4.78 mg/g	K_L = 0.43 L/mg	R^2 = 0.9917
Freundlich isotherm	K_f = 1.21 L/mg	n = 1.16	R^2 = 0.9875
D–R isotherm	q_m = 2.16 mg/g	β = 3 × 10^{-6}	R^2 = 0.85
Modified adsorbent (ACSP)			
Langmuir isotherm	q_m =11.91 mg/g	K_L =0.35 L/mg	R^2 = 0.959
Freundlich isotherm	K_f =2.30 L/mg	n = 1.12	R^2 = 0.9933
D–R isotherm	q_m = 7.12 mg/g	β = 3 × 10^{-7}	R^2 = 0.93

also proved that UTSP adsorbent best fits for the Langmuir adsorption isotherm as compared to ACSP.

The adsorption phenomena in the heterogeneous system can be explained by the Freundlich adsorption isotherm model. The linear equation of the Freundlich model is shown in Eq. (3).

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3}$$

The graph has been plotted between $\ln q_e$ and $\ln C_e$ and constant of equations including the K_f extent of adsorption (L/mg) and n degree of non-linearity are the Freundlich adsorption isotherm constants. However, the value of n provides information on whether the reaction is feasible or not feasible under a given set of conditions [8]. In the present study, the value of n was found to be greater than 1 for both UTSP and ACSP adsorbents which indicates favorable adsorption in a heterogeneous system. The R^2 value in the Freundlich isotherm was 0.9875 for UTSP and 0.9933 for ACSP which proved that that Freundlich adsorption model best fit for ACSP adsorbent.

The D–R model is mathematically represented as shown in Eq. (4).

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{4}$$

where ε denotes the Polanyi potential while β (mol^2/kJ^2) is a constant representing the mean free energy of adsorption per unit mole of Cu(II) ions. However, in D–R model the value of R^2 for adsorption of Cu(II) on UTSP and ACSP was less than 0.98 which proved that this adsorption did not follow this model. The values of D–R models parameters derived from Fig. 5C are provided in Table 2. The uptake of Cu(II) ions on UTSP and ACSP followed both Langmuir and Freundlich adsorption isotherms. However, the R^2 values were also found to be very close for other adsorption models respectively. The results obtained were comparable with the work of Din et al. [32].

3.4. Adsorption kinetics

To further understand the adsorption mechanism of Cu(II) on ACSP and UTSP, kinetics studies were carried out. For this purpose, pseudo-first-order or pseudo-second-order along with intraparticle diffusion model were employed. In the case of UTSP and ACSP, the plots between the variables of $\ln(q_t - q_e)$ as a function of the time interval for studying pseudo-first-order reactions are given in Fig. 6A. For exploiting pseudo-second-order kinetics, Fig. 6B depicts the dependency of the Cu(II) ion adsorption over the involved rate by representing the plot between the variables of t/q_t against the same independent variable of time respectively for UTSP and ACSP. The linear plot shown in Fig. 6C similarly portrays the intraparticle diffusion model for both adsorbents. The mathematical equations for pseudo-first-order, pseudo-second-order and diffusion model are given in Eqs. (5)–(7), respectively [33].

$$\ln\left(q_e - q_t\right) = \ln q_e - k_f t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \tag{6}$$

$$q_t = k_{ID}\sqrt{t} + C \tag{7}$$

where q_t and q_e (mg/g) are indicative of adsorption values at any time t (min) and at equilibrium, respectively while k_f (1/min) k_s (mg/g min) and k_{ID} (mg/g min$^{1/2}$) are the rate constants of kinetic models. However, the kinetics models plots are given in Fig. 6 while kinetics parameters are given in Table 3 respectively. The correlation coefficient (R^2) for the plot of t/q_t vs. t was found to be 0.9452 and 0.9997 for UTSP and ACSP respectively which is higher than the values recorded for the other two models. Hence, from the data, it is inferred that the adsorption process of Cu(II) ions followed pseudo-second-order kinetic model. Foo et al. [20] reported similar findings while removing copper metal ions from water media. The intraparticle diffusion model was employed for determining the slowest step of adsorption. Fig. 6C indicates that no intra-jumping occurs over the adsorbent surfaces in both UTSP and ACSP. This assumption was also justified by the fact that the linear line acquired in the plots did not pass through the origin which is a requirement for this model to be valid [34].
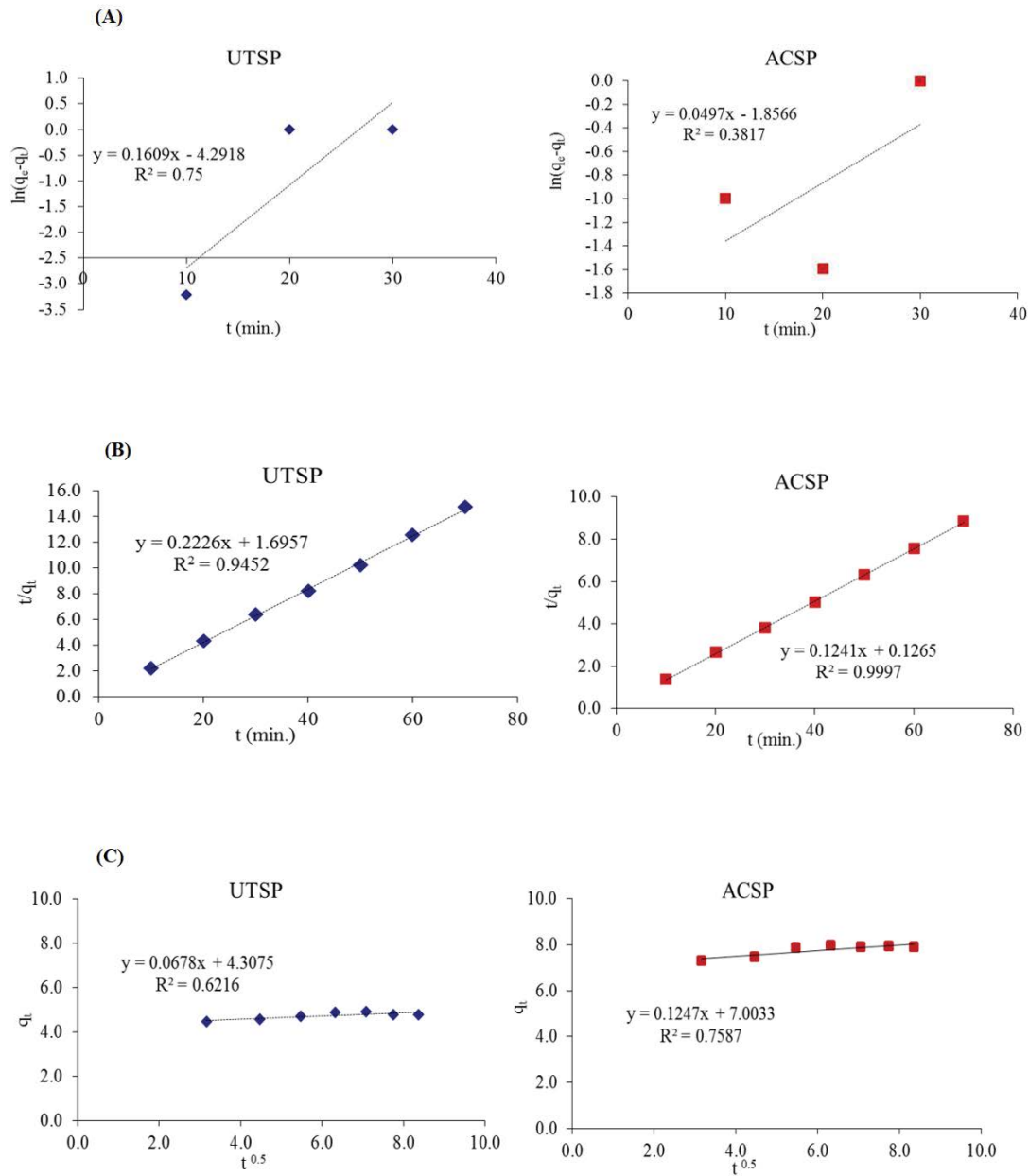
(A)

(B)

(C)

Fig. 6. (A) Pseudo-first-order kinetics, (B) pseudo-second-order kinetics and (C) intraparticle diffusion model for sorption of Cu(II) ions on UTSP (0.5 g/L) at 50 min and for ACSP (0.3 g/L) at 40 min contact time with pH = 5.5 and temperature 30°C.

3.5. Thermodynamics studies

To investigate the thermodynamic parameters in adsorption studies the mathematical Eq. (8) have been utilized [35].

$$\ln k_D = -\frac{\Delta G°}{RT} = \frac{\Delta S°}{R} - \frac{\Delta H°}{R}\frac{1}{T} \tag{8}$$

Positive values of ΔS for both adsorbents support the increase in the randomness of the overall system brought about by the interaction of Cu(II) ions with UTSP and ACSP. Additionally, with the rise in temperature, the value of $\Delta G°$ decreases. Hence, the lower $\Delta G°$ values at higher temperature indicate the endothermic nature of Cu(II) removal process. Additionally, the negative value of free energy also indicates the thermodynamic feasibility and spontaneous nature of reaction progress. Moreover, the positive enthalpy values indicate that this adsorption reaction is not only feasible but also endothermic in nature. Thermodynamics revealed in this study correspond with the work of Shi et al. [27]. The plots regarding thermodynamic parameters for UTSP and ACSP are given in Fig. 7, respectively. Extensive academic literature has been reported on the use of various biomaterials employed for use as an adsorbent for the efficient removal of Cu(II) ions [27,36].

Table 3
Adsorption kinetics for adsorbents UTSP and ACSP

| Kinetics	Parameters		
Untreated adsorbent (UTSP)			
Pseudo-first-order	q_e = 0.013 mg/g	K_f = 0.1609 min^{-1}	R^2 = 0.75
Pseudo-second-order	q_e = 4.49 mg/g	k_s = 0.13 g/mg min	R^2 = 0.9452
Intraparticle diffusion	C = 4.307	k_{ID} = 0.0678 mg/g min$^{1/2}$	R^2 = 0.6216
Modified adsorbent (ACSP)			
Pseudo-first-order	q_e = 0.15 mg/g	K_f = 0.0497 min^{-1}	R^2 = 0.3817
Pseudo-second-order	q_e = 8.05 mg/g	k_s = 0.95 g/mg min	R^2 = 0.9997
Intraparticle diffusion	C = 7.0033	k_{ID} = 0.1247 mg/g min$^{1/2}$	R^2 = 0.7587
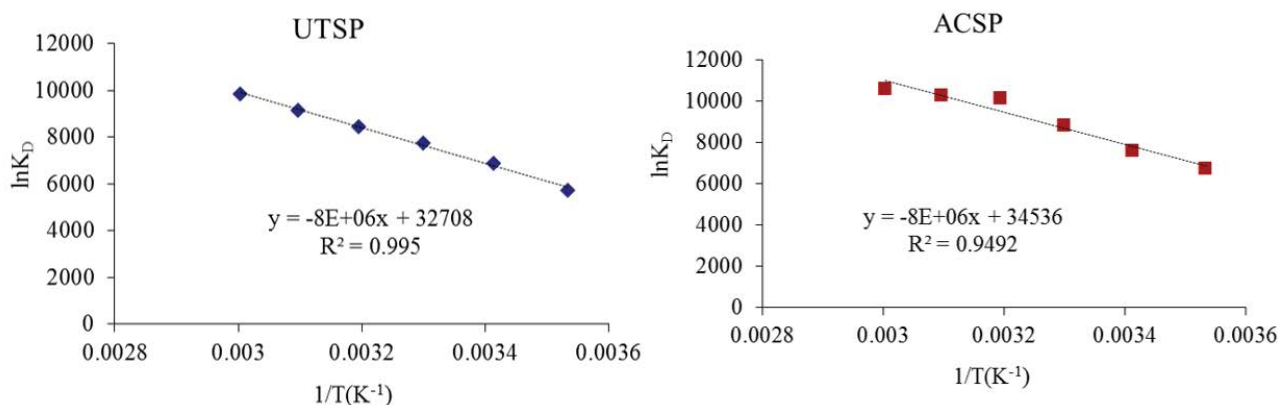
Fig. 7. Thermodynamic parameters study for UTSP (0.5 g/L) and for ACSP (0.3 g/L) at pH = 5.5.

Table 4
Comparison of adsorption capacities of various adsorbents with the engineered activated adsorbent (ACSP) for Cu(II) ion removal from untreated water

Applied adsorbent	Adsorption capacity	Reference
Herbaceous peat	4.84	[37]
Waste peat	5.1	[38]
Oligotrophic peat	6.41	[39]
Sawdust (tree)	6.92	[40]
Reactive orange modified sawdust	8.07	[41]
Jute fibers	8.40	[42]
Peanut husk	10.15	[43]
Cork power	19.0	[44]
Activated carbon (*Salvadora persica*)	40.0	Present work

3.6. Comparison with literature

Comparisons are drawn between the various studies and presented in Table 4. The data highlights the usefulness and applicability of the engineered adsorbent as compared to other adsorbents.

4. Conclusion

The present study clearly shows that activated carbon (*Salvadora persica*) can be used as bioadsorbent for the successful uptake of Cu(II) ions from aqueous media. The FTIR spectra showed that various functional groups present in both adsorbents facilitate the process of adsorption. BET surface area and elemental analysis further confirmed and documented the enhancements brought about by the modification process into the adsorbent by the microwave irradiation method. Morphology was pictorially described by using SEM micrographs. The surface area of ACSP was found to increase from 2.11 to 381 m²/g for UTSP as a result of modification. Optimization of adsorption parameters for ACSP was found to be adsorbent dose 0.3 g/L, pH 5.5, exposure time 40 min and temperature 30°C. Thermodynamic studies showed that the adsorption process was spontaneous, endothermic, and feasible. The kinetic model results clearly showed that adsorption followed pseudo-second-order for both adsorbents. The adsorption of the Cu(II) ions followed Langmuir and Freundlich adsorption models which showed

heterogeneous surface binding. Hence, it can be concluded that ACSP adsorbent is cost-effective, eco-friendly biomaterials and can be a suitable alternative for the removal of Cu(II) ions from wastewater.

Conflict of interest

None

References

[1] M.I. Din, S. Jabbar, J. Najeeb, R. Khalid, T. Ghaffar, M. Arshad, S.A. Khan, S. Ali, Green synthesis of zinc ferrite nanoparticles for photocatalysis of methylene blue, Int. J. Phytorem., 22 (2020) 1440–1447.

[2] S. Golkhah, M.H. Zavvar, H. Shirkhanloo, A. Khaligh, Removal of Pb(II) and Cu(II) ions from aqueous solutions by cadmium sulfide nanoparticles, Int. J. Nanosci. Nanotechnol., 13 (2017) 105–117.

[3] J. Li, B. Jiang, Y. Liu, C. Qiu, J. Hu, G. Qian, W. Guo, H.H. Ngo, Preparation and adsorption properties of magnetic chitosan composite adsorbent for Cu^{2+} removal, J. Cleaner Prod., 158 (2017) 51–58.

[4] E.A. Deliyanni, G.Z. Kyzas, K.A. Matis, Various flotation techniques for metal ions removal, J. Mol. Liq., 225 (2017) 260–264.

[5] E.K. Radwan, A.M. Abdel-Aty, S.T. El-Wakeel, H.H. Abdel Ghafar, Bioremediation of potentially toxic metal and reactive dye-contaminated water by pristine and modified *Chlorella vulgaris*, Environ. Sci. Pollut. Res., 27 (2020) 21777–21789.

[6] Z. Chen and B. Zeng, Characteristics of micro-interface adsorption kinetics between sediments and Cu ions, Int. J. Sediment Res., 32 (2017) 82–89.

[7] S.A. Al-Saydeh, M.H. El-Naas, S.J. Zaidi, Copper removal from industrial wastewater: a comprehensive review, J. Ind. Eng. Chem., 56 (2017) 35–44.

[8] S. Ben-Ali, I. Jaouali, S. Souissi-Najar, A. Ouederni, Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal, J. Cleaner Prod., 142 (2017) 3809–3821.

[9] E. Demirbas, N. Dizge, M.T. Sulak, M. Kobya, Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, Chem. Eng. J., 148 (2009) 480–487.

[10] H. Chen, G. Dai, J. Zhao, A. Zhong, J. Wu, H. Yan, Removal of copper(II) ions by a biosorbent—*Cinnamomum camphora* leaves powder, J. Hazard. Mater., 177 (2010) 228–236.

[11] E. Pehlivan, T. Altun, Ş. Parlayici, Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution, Food Chem., 135 (2012) 2229–2234.

[12] H.A. El-Araby, A.M.M.A. Ibrahim, A.H. Mangood, A.-H. Adel-Rahman, Sesame husk as adsorbent for copper(II) ions removal from aqueous solution, J. Geosci. Environ. Prot. Sci., 5 (2017) 109, doi: 10.4236/gep.2017.57011.

[13] K. Legrouri, E. Khouya, H. Hannache, M. El Hartti, M. Ezzine, R. Naslain, Activated carbon from molasses efficiency for Cr(VI), Pb(II) and Cu(II) adsorption: a mechanistic study, Chem. Int., 3 (2017) 301–310.

[14] F. Deniz, E.T. Ersanli, A natural macroalgae consortium for biosorption of copper from aqueous solution: optimization, modeling and design studies, Int. J. Phytorem., 20 (2018) 362–368.

[15] X. Gao, L. Wu, Q. Xu, W. Tian, Z. Li, N. Kobayashi, Adsorption kinetics and mechanisms of copper ions on activated carbons derived from pinewood sawdust by fast H_3PO_4 activation, Environ. Sci. Pollut. Res., 25 (2018) 7907–7915.

[16] Z. Mahdi, Q.J. Yu, A. El Hanandeh, Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar, J. Environ. Chem. Eng., 6 (2018) 1171–1181.

[17] M. Calero, I. Iáñez-Rodríguez, A. Pérez, M. Martín-Lara, G. Blázquez, Neural fuzzy modelization of copper removal from water by biosorption in fixed-bed columns using olive stone and pinion shell, Bioresour. Technol., 252 (2018) 100–109.

[18] V.K. Gupta, D. Pathania, S. Sharma, Adsorptive remediation of Cu(II) and Ni(II) by microwave assisted H_3PO_4 activated carbon, Arabian J. Chem., 10 (2017) S2836–S2844.

[19] F.K. Yuen, B. Hameed, Recent developments in the preparation and regeneration of activated carbons by microwaves, Adv. Colloid Interface Sci., 149 (2009) 19–27.

[20] K. Foo, B. Hameed, Coconut husk derived activated carbon via microwave induced activation: effects of activation agents, preparation parameters and adsorption performance, Chem. Eng. J., 184 (2012) 57–65.

[21] A. Macías-García, M.G. Corzo, M.A. Domínguez, M.A. Franco, J.M. Naharro, Study of the adsorption and electroadsorption process of Cu(II) ions within thermally and chemically modified activated carbon, J. Hazard. Mater., 328 (2017) 46–55.

[22] E.K. Radwan, S.T. El-Wakeel, T.A. Gad-Allah, Effects of activation conditions on the structural and adsorption characteristics of pinecones derived activated carbons, J. Dispersion Sci. Technol., 40 (2019) 140–151.

[23] E.K. Radwan, H.H.A. Ghafar, A.S. Moursy, C.H. Langford, A.H. Bedair, G. Achari, Preparation and characterization of humic acid–carbon hybrid materials as adsorbents for organic micro-pollutants, Environ. Sci. Pollut. Res., 22 (2015) 12035–12049.

[24] L. Wang, Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: kinetic, equilibrium and thermodynamic studies, J. Environ. Manage., 102 (2012) 79–87.

[25] M.S.U. Rehman, M. Munir, M. Ashfaq, N. Rashid, M.F. Nazar, M. Danish, J.-I. Han, Adsorption of Brilliant Green dye from aqueous solution onto red clay, Chem. Eng. J., 228 (2013) 54–62.

[26] S.K. Behera, J.-H. Kim, X. Guo, H.-S. Park, Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon, J. Hazard. Mater., 153 (2008) 1207–1214.

[27] T. Shi, S. Jia, Y. Chen, Y. Wen, C. Du, Z. Wang, R. Qiu, Adsorption characteristics of Cu(II) and Pb(II) ions onto natural manganese ore from aqueous solution, Adsorpt. Sci. Technol., 26 (2008) 613–629.

[28] A. Bajpai, N. Vishwakarma, Adsorption of polyvinylalcohol onto Fuller's earth surfaces, Colloids Surf., A, 220 (2003) 117–130.

[29] A.P. Adornado, A.N. Soriano, O.N. Orfiana, M.B.J. Pangon, A.D. Nieva, Simulated biosorption of Cd(II) and Cu(II) in single and binary metal systems by water hyacinth (*Eichhornia crassipes*) using Aspen adsorption, ASEAN J. Chem. Eng., 16 (2017) 21–43.

[30] C.H.J. Luk, J. Yip, C.W.M. Yuen, S.K. Pang, K.H. Lam, C.W. Kan, Biosorption performance of encapsulated *Candida krusei* for the removal of copper(II), Sci. Rep., 7 (2017) 1–9.

[31] A. Kong, B. He, G. Liu, X. Lu, Y. Hao, F. Yan, J. Li, A novel green biosorbent from chitosan modified by sodium phytate for copper(II) ion removal, Polym. Adv. Technol., 29 (2018) 285–293.

[32] M.I. Din, Z. Hussain, H. Munir, A. Naz, A. Intisar, M.N. Makshoof, M.L. Mirza, Microwave treated *Salvadora oleoides* as an eco-friendly biosorbent for the removal of toxic methyl violet dye from aqueous solution—a green approach, Int. J. Phytorem., 18 (2016) 477–486.

[33] S. Khamparia, D.K. Jaspal, Evaluation of decoloration potential of Xanthium Strumarium seed hull for adsorption of Direct red 81 in aqueous solution, Environ. Dev. Sustain., 19 (2017) 1933–1951.

[34] U. Farooq, M. Khan, M. Athar, *Triticum aestivum*: a novel biosorbent for lead(II) ions, Agrochimica, 51 (2007) 309–318.

[35] S. Madala, S.K. Nadavala, S. Vudagandla, V.M. Boddu, K. Abburi, Equilibrium, kinetics and thermodynamics of cadmium(II) biosorption on to composite chitosan biosorbent, Arabian J. Chem., 10 (2017) S1883–S1893.

[36] O. Moradi, K. Zare, M. Monajjemi, M. Yari, H. Aghaie, The studies of equilibrium and thermodynamic adsorption of Pb(II),

Cd(II) and Cu(II) ions from aqueous solution onto SWCNTs and SWCNT–COOH surfaces, Fullerenes Nanotubes Carbon Nanostruct., 18 (2010) 285–302.

[37] R. Gündoğan, B. Acemioğlu, M.H. Alma, Copper(II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interface Sci., 269 (2004) 303–309.

[38] J. Tummavuori, M. Aho, On the ion-exchange properties of peat. Part I: on the adsorption of some divalent metal ions (Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) on the peat, Suo, 31 (1980) 79–83.

[39] X.-H. Chen, T. Gosset, D.R. Thévenot, Batch copper ion binding and exchange properties of peat, Water Res., 24 (1990) 1463–1471.

[40] F.N. Acar, Z. Eren, Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions, J. Hazard. Mater., 137 (2006) 909–914.

[41] S. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust, Sep. Purif. Technol., 43 (2005) 1–8.

[42] S. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres, Bioresour. Technol., 96 (2005) 1430–1438.

[43] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, J. Hazard. Mater., 141 (2007) 163–167.

[44] N. Chubar, J.R. Carvalho, M.J.N. Correia, Heavy metals biosorption on cork biomass: effect of the pre-treatment, Colloids Surf., A, 238 (2004) 51–58.