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Removal of Cu^{2+} from aqueous solution by activated carbon prepared from sawdust and nutshells

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ABSTRACT

In this study, activated carbons were prepared from waste biomass and were used for the removal of Cu^{2+} from water. Two sets of activated carbons (10 each): un-oxidized and oxidized were prepared by carrying out the carbonization of the waste biomass in N_2 atmosphere and normal atmospheric air, respectively. Oxidized activated carbons showed high adsorption capacities for the removal of copper ion from aqueous solutions. Surface functional groups (carboxylic, phenol and lactones) were determined quantitatively using Boehm titration method. Langmuir and Freundlich models were used to analyze the adsorption equilibrium data. Best fit was obtained with Langmuir model as the R^2 values were high for almost all the prepared adsorbents in this study. Pseudo-first and pseudo-second order kinetic models were used to analyze the adsorption kinetics data. Best fits were obtained with pseudo-second order kinetic model. The equilibrium time were in range of 30 to 160 min (C_5 = 30 lowest and C_3/C_8 = 160, highest). The adsorption parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ were also determined. The values of $\Delta G°$ and $\Delta H°$ were negative while that of $\Delta S°$ were positive. The negative values of $\Delta H°$ show that the adsorption of Cu^{2+} ions on prepared adsorbents was an exothermic process while the increase in $\Delta G°$ values with temperature shows that the adsorption process is favorable one at high temperature. Amongst the oxidized adsorbents (C_1 to C_{10}), activated carbons prepared from Ber and Poplar were more efficient in removal Cu^{++} from aqueous solutions.

Keywords: Activated carbon; Sawdust; Nutshell; Cu^{2+} adsorption; Surface functional groups

1. Introduction

Over the last few decades due to industrial revolution, the contamination of water bodies with organic and inorganic pollutants has become an issue of great concern. Heavy metals are considered as severe pollutants owing to their toxicity, persistence, bioaccumulative and non-degradable nature in environment. Amongst the heavy metals, copper toxicity also known as copperiedus can occur in human due to intake of excess amount of copper (permissible level in drinking water = 1.3 mg/L) in the body. It can occur through eating acidic foods cooked in uncoated copper cookware, or from exposure to excess copper in drinking water or other environmental sources. The acute symptoms of copper poisoning includes vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), coma, jaundice (yellowish pigmentation of the skin) and gastrointestinal distress, while the chronic symptoms include damage of liver and kidneys [1,2].

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A number of techniques such as chemical precipitation [3], coagulation [4], adsorption [5], ion exchange [6] and membrane filtration [7], have been used for the removal of heavy metals from water. Among aforementioned treatment technologies, adsorption had been reported as the most efficient and economically viable option [8]. Research in water treatment by adsorption has resulted in development of different adsorbents from different materials such as activated carbon prepared from natural products, zeolites, aluminosilicate, peat kaolin, clay, nanomaterials and polysaccharides [9–18].

Owing to the importance of adsorption process, the present study was aimed to prepare low-cost activated carbons from waste biomass. To find out whether or not activation methods affect the adsorption capacities of the adsorbents for particular pollutant, two sets of adsorbents: oxidized and un-oxidized were prepared in presence of normal air and N_2 atmosphere respectively and were used for the removal of copper from aqueous solution.

2. Experimental setup

2.1. Chemicals and power materials

All the chemicals used in this study were of analytical grades, supplied by Merck (Germany), BDH (Lahore, Pakistan) or ACROS (Germany). Sawdust of different woods and nutshells was collected from local market. Sawdust was used as received while the nutshells were grounded to fine powder. The details of various samples used in this study are presented in Table 1.

2.2. Preparation of adsorbents

The collected sawdust and nutshell powders were subjected to carbonization in tube furnace. The two methods [19] described below were used for the activation the adsorbent:

2.2.1. Activation with phosphoric acid

The sawdust/nutshells were mixed in 1:1 ratio with H_3PO_4 (50%) and allowed to stand for 24 h at room temperature. The samples were then shifted to a quarts tube placed in a tube furnace. Samples were heated at a temperature of 170°C (±5°C) for 45 min under nitrogen flow (flow rate 40 mL/min). After this the temperature was raised to 450°C (±5°C) and heated for 45 min in nitrogen atmosphere. The treated samples were cooled down to room temperature in nitrogen flow. These activated samples were washed in a soxhlet extractor at 100°C with double distilled water until the rinsed water pH become neutral. No precipitate of free or loosely bound phosphate was observed when the rinsed samples were treated with lead acetate. These samples were kept in an oven for 5 h at 110°C. The dried samples were passed through 100 mesh (U.S. Standard Sieve) and was retained on 400 mesh.

Table 1
Precursor material and BET surface area of the adsorbents

Sample no.	Botanical name	Common/ local name	BET surface area (m^2/g)
C_1	*Acacia modesta*	Phulai	132
C_2	*Dalbergia sissoo*	Sheeshum	135
C_3	*Pinus excelsa*	Kail	133
C_4	*Prunus amygdalus*	Almond	198
C_5	*Juglans regia*	Walnut	205
C_6	*Melia azedarach*	Dhrek	188
C_7	*Cedrus deodara*	Deodar	194
C_8	*Morus alba*	Mulberry	220
C_9	*Populus ciliata*	Poplar	235
C_{10}	*Ziziphus jujuba*	Ber	266

2.2.2. Air activation method

Half amount of the collected samples were subjected to carbonization in the presence of normal atmospheric air (flow rate 40 mL/min) at 450°C for 45 min in furnace. The prepared samples were then cooled to room temperature.

2.3. Determination of densities and pore volume

To calculate the apparent density, a calibrated cylinder was filled with a given mass of activated carbon and tapped till there was no change in volume. It was recorded as the minimum volume. From mass and volume, the density was calculated which was adsorbent's tapping or bulk density. For calculation of the apparent density, pycnometer's method was used, in which a pycnometer is filled with activated carbon and then solvent is added (water in this case) to fill the void [20,21]. From weight and volume, the apparent density was calculated which was termed as real density. For the determination of total pore volume of activated carbon, water sorption is generally accepted method [20]. Using the following equation, the pore volume of the prepared adsorbents was determined.

$$\frac{1}{d_b}-\frac{1}{d_a}=V_p \tag{1}$$

where d_b, d_a and V_p are bulk density, apparent density and pore volume, respectively.

Table 2 shows the bulk and apparent densities, and total pore volume of all the oxidized and un-oxidized samples.

Table 2
Densities (bulk, d_b and apparent, d_a) and pore volume (V_p)

Sample	Oxidized			Un-oxidized		
	d_b (g/cm^3)	d_a (g/cm^3)	V_p (g/cm^3)	d_b (g/cm^3)	d_a (g/cm^3)	V_p (g/cm^3)
C_1	0.60	1.50	1.00	0.67	1.21	0.66
C_2	0.58	1.55	1.08	0.60	1.16	0.81
C_3	0.48	1.06	1.13	0.53	0.83	0.67
C_4	0.40	1.70	1.89	0.43	1.08	1.39
C_5	0.48	1.96	1.58	0.50	1.43	1.30
C_6	0.37	2.19	2.28	0.47	1.05	1.19
C_7	0.54	3.43	1.56	0.57	1.91	1.23
C_8	0.45	1.85	1.67	0.38	1.13	1.78
C_9	0.36	2.12	2.28	0.37	1.66	2.08
C_{10}	0.57	1.45	1.07	0.60	1.01	0.66

The BET surface area was also determined and is shown in Table 1.

2.4. Determination of titrable surface functional groups

Boehm's titrations method [19,22] was used to determine the number of titrable surface functional groups on the prepared activated carbons. In this method, 0.2 g of carbon was added to 40 mL of 0.05 M NaOH or 0.05 M $NaHCO_3$ solutions in 100 mL titration flask and was shaken in an end-to-end shaker water bath at 25°C for 24 h. After this the solutions were filtered and 10 mL from this filtrate were mixed with 15 mL of 0.05 M HCL solution. This solution was back titrated with 0.05 M solution of sodium hydroxide. The quantity of sodium hydroxide needed for neutralizing the solution was converted to titrable surface functional groups (m mol/g).

2.5. Metal ions adsorption

The $CuCl_2.2H_2O$ solution was prepared in sodium acetate 0.07 M/acetic acid (0.03 M) buffer (pH = 4.9). 0.2 g of activated carbon samples were added to 40 mL of copper solutions in a series of 100 mL titration flasks and were shaken at 25°C for 24 h. Standard sodium EDTA solution was used to determine the amount of the remaining copper in solution.

The amount of copper adsorbed was determined by using the formula:

$$X = \frac{(C_i - C_f)}{m} V \qquad (2)$$

where X is the amount of copper adsorbed/g of activated carbon; C_i and C_f are initial and final concentrations of copper; V is the volume of the test solution where m is the amount of activated carbon. Giles, Langmuir and Freundlich isotherms were applied to describe the adsorption equilibrium data.

2.6. Adsorption kinetics

To determine the adsorption parameters, 80 ppm copper solutions were contacted with known amount of adsorbent and at different time intervals samples were taken out which were then filtered, and the remaining amount of copper ions in solutions was determined through the above-mentioned method.

2.7. Effect of temperature on adsorption

About 80 ppm solutions were contacted with adsorbents at different temperature, that is, 25°C, 35°C, 40°C and 50°C in order to determine the effect of temperature on adsorption.

3. Results and discussion

In this study, two sets of 10 activated carbons each were prepared from wastes biomass. One set was prepared in the presence of normal atmospheric air (oxidized) and the other set was prepared in presence of inert atmosphere of nitrogen (un-oxidized). The BET surface area and other detail about biomass have been shown in Table 1.

Table 2 shows the densities and pore volumes of the adsorbents. It is obvious from the table that there is no significant difference (densities and pore volumes) between the oxidized and un-oxidized activated carbons. Except from sample C_8 where there is a slight decrease in the pore volume in the oxidized form, in the rest of samples with oxidation there is an increase in the pore volume.

Fig. 1 shows the amount of copper ions adsorbed by oxidized and un-oxidized activated carbons. From the figure, it is evident that the amount of copper (in concentration range of 0.78–2.15 m mol/g) adsorbed by oxidized activated carbons were higher than the corresponding activated carbon prepared in inert atmosphere of nitrogen. Highest adsorption capacity was exhibited by C_{10} which was derived from Ber; the common name of *Ziziphus jujuba* followed by poplar sawdust derived activated carbon C_9 and C_8 (prepared from mulberry sawdust). Amongst the samples derived from nutshells, the highest adsorption capacity was shown by activated carbon C_5 (oxidized) derived from walnut shell.

The adsorption capacities of activated carbons are usually related to the pore volumes and presence of acidic and basic functional groups on their surfaces [19–22]. Less importance has been given to the effect of oxidation of functional groups towards the enhancement of adsorption capacities of adsorbent for a particular pollutant. The most important aspect of this study is the high adsorption capacities shown by the activated carbons in the oxidized form (Fig. 1) as compared with un-oxidized activated carbon samples which were derived from the same starting material. The least active activated carbon sample C_1 (0.46 m mole/g) in the oxidized form has a much higher capacity even from the highest capacity activated carbon sample C_8 (0.046 m mole/g) in the un-oxidized group.

Fig. 2 shows dependency of Cu^{2+} adsorption on NaOH titrable surface charge for both un-oxidized and oxidized carbons. Sodium hydroxide is a strong base which is capable of neutralizing all weak and strong acids present in aqueous media. Titration with NaOH is used to measure the surface charges resulting from carboxylic acid, phenols and lactones. The surface charges on oxidized activated carbons were more than on the un-oxidized carbons indicating that the functional groups initially present have been successfully oxidized. The highest capacities of oxidized activated carbons for copper ions was due to the fact that the surface has now more surface

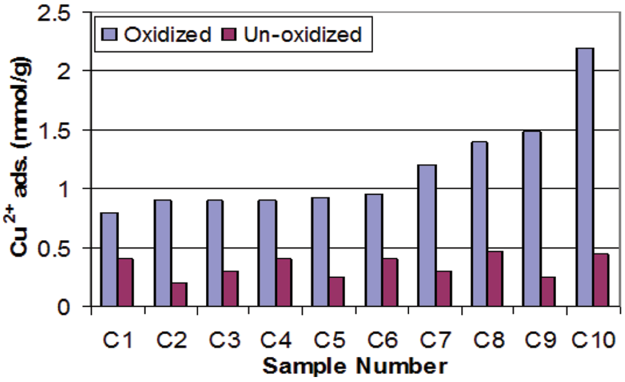


Fig. 1. Cu^{++} adsorption on oxidized and un-oxidized activated carbons.

negative charge resulting in favorable interaction with the positively charged copper ions.

Fig. 3 shows the dependence of Cu^{2+} adsorption on $NaHCO^3$ titrable surface functional groups for both un-oxidized and oxidized activated carbons. $NaHCO_3$ is a weak base capable of neutralizing only relatively strong acids such as carboxyl group on the carbon surface. A similar co-relation observed in case of NaOH was observed for oxidized and un-oxidized activated carbons.

The Giles et al. [23] isotherms for the adsorption of copper ion on prepared activated carbons have been shown in Fig. 4. For all adsorbents, the isotherms are L type. In L type isotherms, the ratio between the concentration of the compound remaining in solution and adsorbed on the solid decreases when the solute concentration increases, providing a concave curve.

The Langmuir [24] and Freundlich [25] isotherms are shown in Figs. 5 and 6 while the values of constants calculated from following equations are presented in Table 3.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

In this relation, q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_m (mg/g) and K_L (L/mg) are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively.

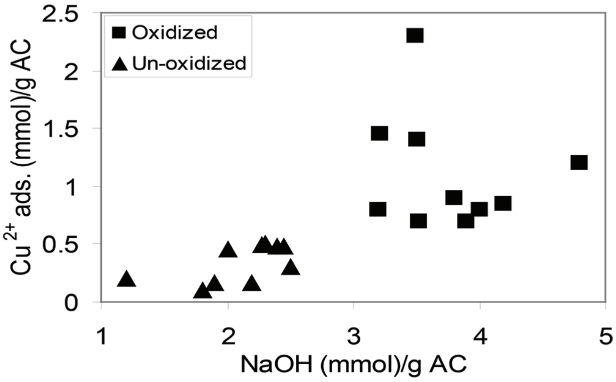


Fig. 2. NaOH-titrable surface charge vs. Cu^{++} uptake by oxidized and un-oxidized activated carbons.

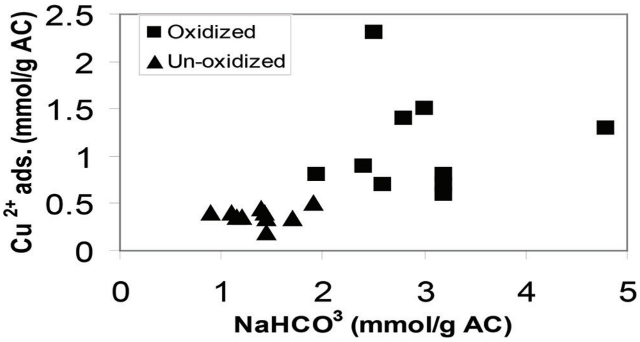


Fig. 3. $NaHCO_3$-titrable surface charge vs. Cu^{++} uptake for oxidized and un-oxidized activated carbons.

$$\ln q_e = \ln k + \ln \frac{C_e}{n} \tag{4}$$

In relation shown above, C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed (mg g^{-1}), k and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

Looking at Table 3, the R^2 values are higher for Langmuir isotherm as compared with Freundlich model. So with the exception of C_5, the isotherms data are fitted well to Langmuir model. High adsorption capacities were shown by C_{10}, C_9 and C_8 oxidized activated carbons.

The equilibrium time is an important parameter in the kinetics studies (Fig. 7). The equilibrium times for the prepared adsorbents are given in Table 4 which are in the range of 30–160 min showing these adsorbents have high affinities for copper adsorption.

The Lagergren first and pseudo-second order models are often successfully used to describe the removal of pollutants from aqueous solution by adsorbents [26,27]. These equations are given as follow as:

$$\ln(q_e - q_t) = \ln q_e - \ln K_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{K_2} + \frac{t}{q_e} \tag{6}$$

where q_t (mg/g) in Eq. (5) is the amount of copper adsorbed at time t, while, q_e (mg/g) is the amount adsorbed at equilibrium time, K_1 (min^{-1}) is the rate constant of pseudo-first order kinetics. In Eq. (6), K_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption for pseudo-second order kinetics, q_e (mg g^{-1}) is the amount of copper adsorbed at equilibrium, while q_t is the amount of copper adsorbed at time t. The kinetic data in forms of plots have been shown in Figs. 8 and 9 while values of kinetic rate constants and R^2 are given in Table 5. The R^2 values are higher for pseudo-second order model as compared with pseudo-first order model.

The effect of temperature on adsorption was determined at four different temperatures; 25°C, 35°C, 40°C and 50°C. The Van't Hoff equation was used to determine the values of $\Delta H°$ and $\Delta S°$ of the adsorption process.

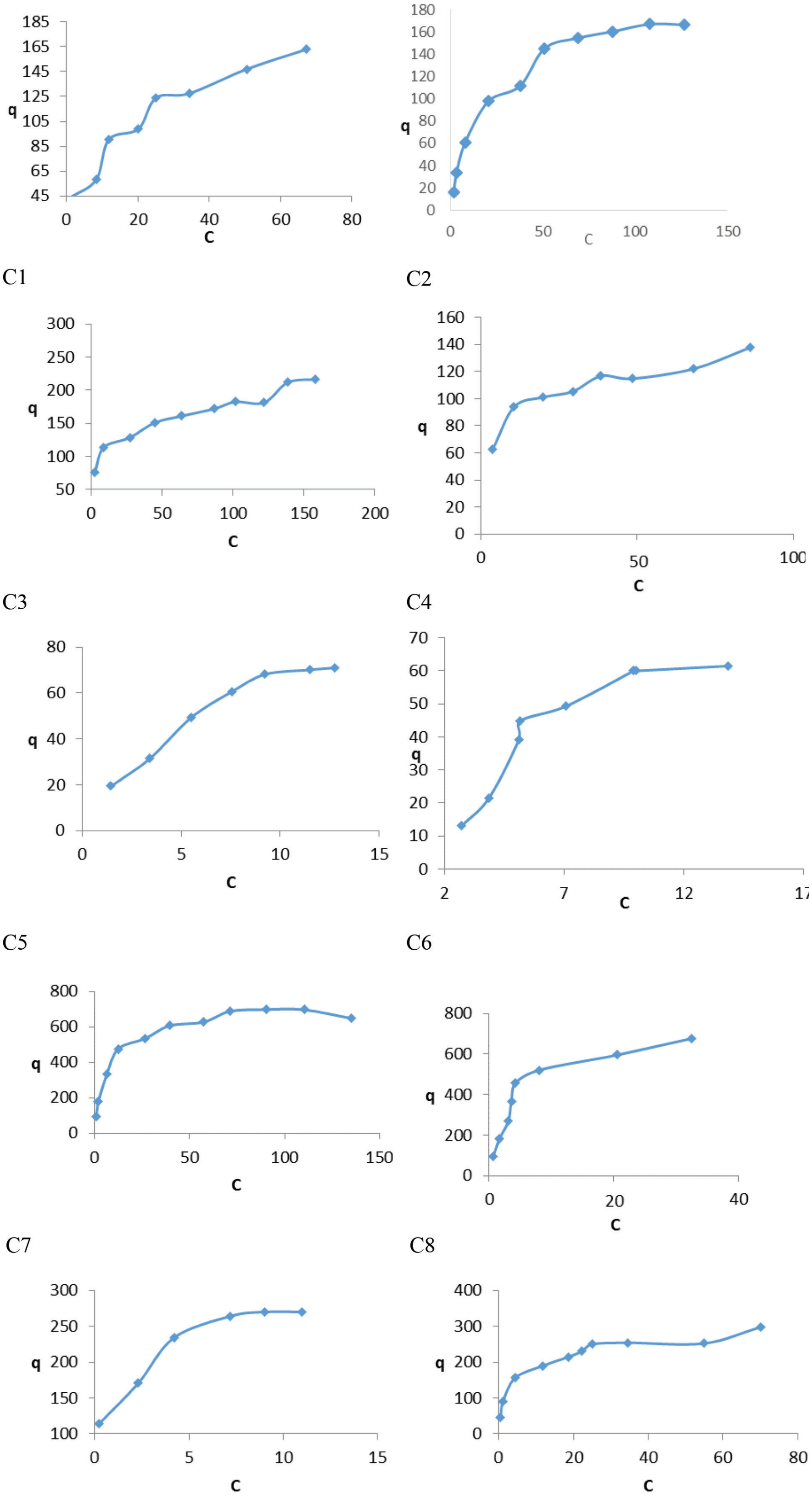
$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H}{RT} \tag{7}$$

K is the distribution constant of adsorption, $\Delta H°$ is the enthalpy change, $\Delta S°$ is the entropy change, T is the temperature in kelvin while R is universal gas constant.

The value of $\Delta H°$ was calculated from the slope while $\Delta S°$ value was calculated from intercept of the ln$K$ and 1/T plot (Fig. 10). The values of $\Delta H°$ and $\Delta S°$ are given in Table 6.

The positive value of $\Delta S°$ indicated that there is an increase in the randomness of the solid/solution system interface whereas the negative values of $\Delta H°$ show that the processes were exothermic.

The values of standard free energy $\Delta G°$ are given in Table 6 and were calculated from the following equation:



C1

C2

C3

C4

C5

C6

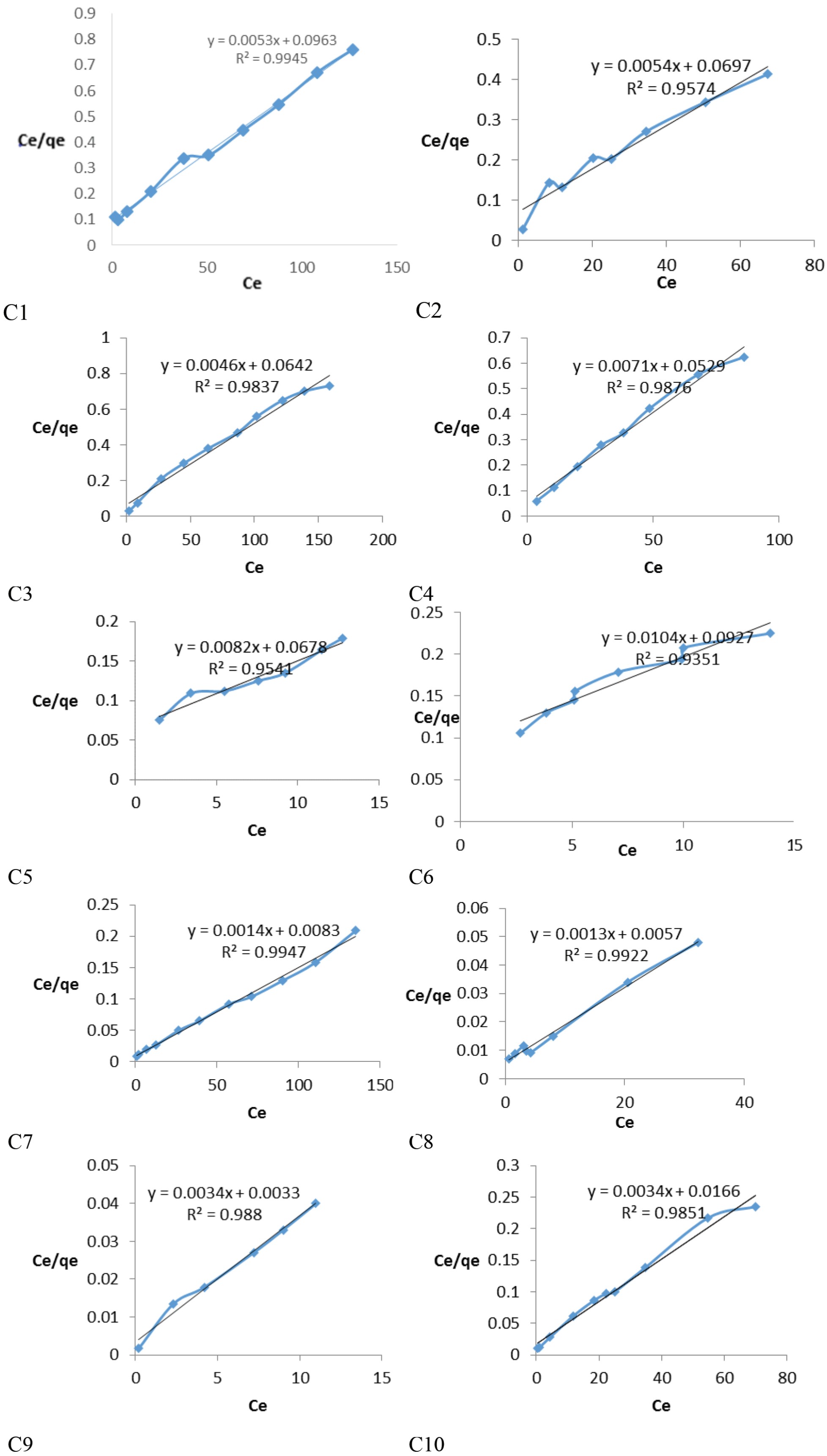
C7

C8

C9

C10

Fig. 4. Giles isotherms for copper adsorption on prepared adsorbents.



C1 C2

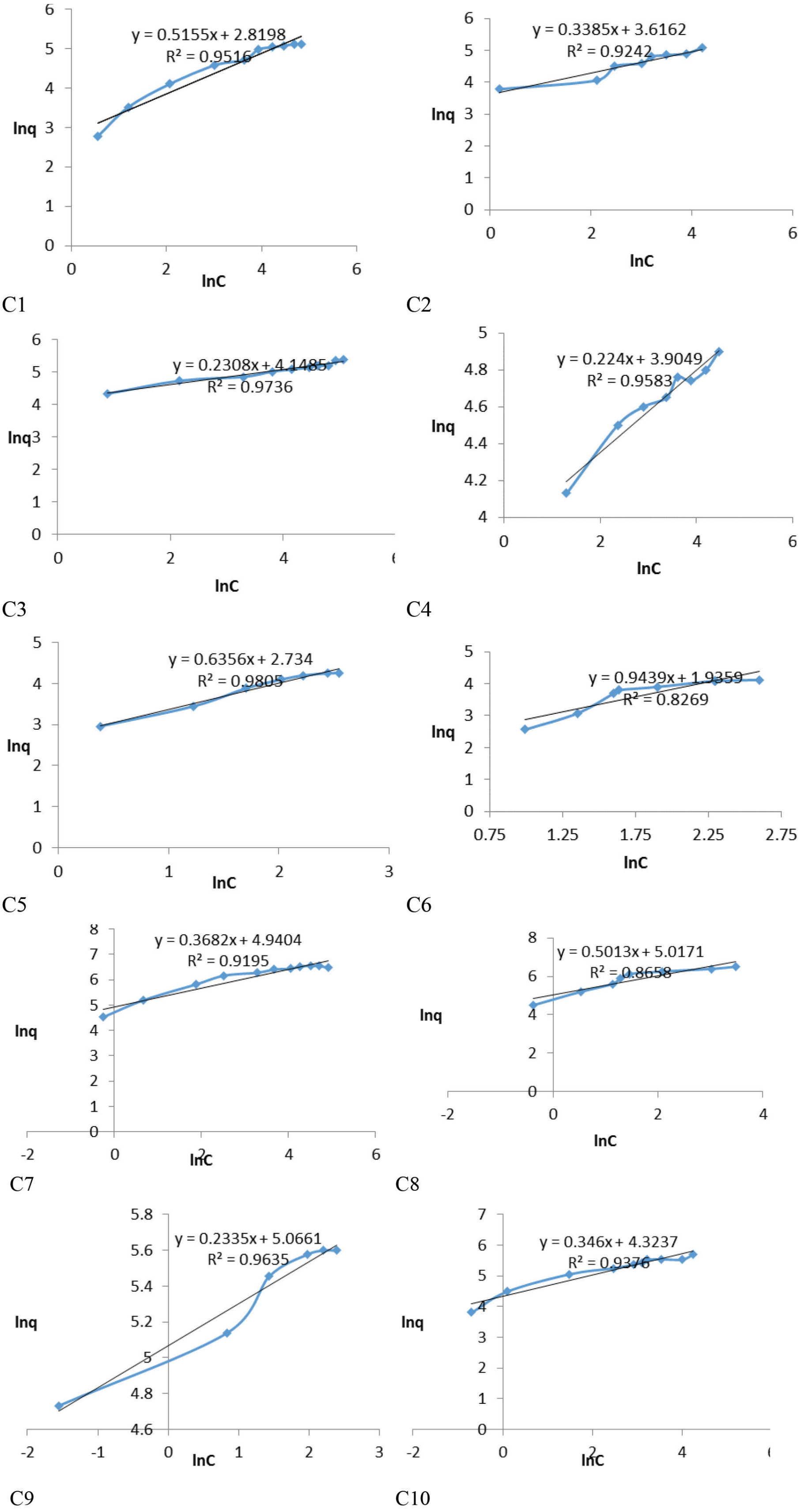
C3 C4

C5 C6

C7 C8

C9 C10

Fig. 5. Langmuir isotherms for copper adsorption on prepared adsorbents.



C1 C2

C3 C4

C5 C6

C7 C8

C9 C10

Fig. 6. Freundlich isotherms for copper adsorption on prepared adsorbents.

Table 3
Adsorption isotherm parameters for copper adsorption on different adsorbent

Model	Constants	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Langmuir	q_m (mg/g)	188.7	185.2	217.4	140.8	121.9	96.15	714.2	769.2	294.1	294.1
	K_L (L/mg)	0.005	0.077	0.072	0.134	0.121	0.112	0.169	0.228	1.030	0.205
	R^2	0.994	0.957	0.983	0.987	0.954	0.935	0.994	0.992	0.988	0.985
Freundlich	K (mg/g (L/mg)$^{1/n}$)	16.77	37.19	63.33	49.65	15.39	6.93	139.8	150.9	158.5	75.46
	$1/n$	1.67	1.40	1.26	1.25	1.89	2.57	1.45	1.65	1.26	1.41
	R^2	0.951	0.924	0.973	0.958	0.980	0.826	0.919	0.865	0.963	0.937

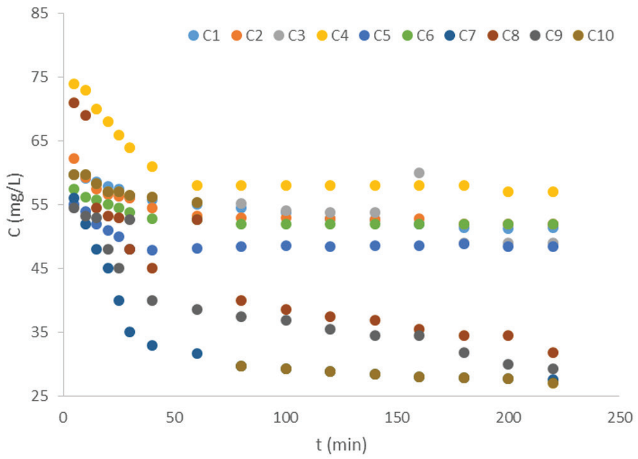


Fig. 7. Equilibrium times for copper adsorption on prepared adsorbents.

Table 4
Equilibrium time for copper adsorption on different adsorbent

Adsorbent	Equilibrium time
C_1	120
C_2	80
C_3	160
C_4	60
C_5	30
C_6	40
C_7	80
C_8	160
C_9	120
C_{10}	120

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

The spontaneous character of the process is evident from the negative values of ΔG° at different temperatures. For all the adsorbents, there was an increase in ΔG° values with increase in temperature showing that at high temperature the adsorption process is more favorable. It was concluded that the adsorbent prepared from different biomass can be used as alternative of the activated carbon for the removal of copper from water.

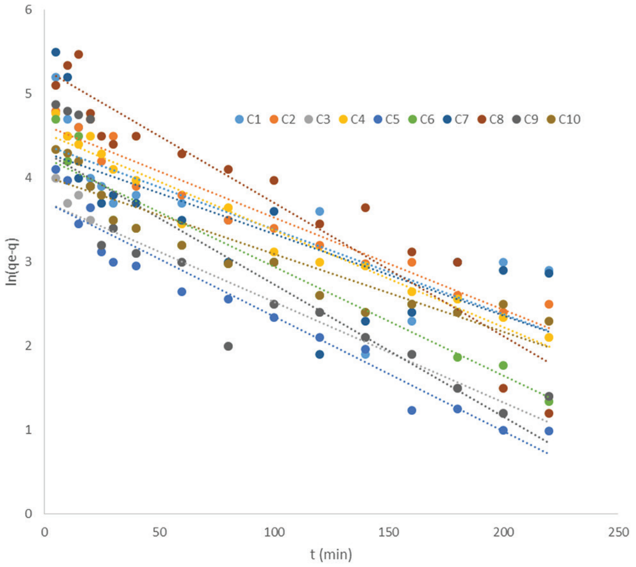


Fig. 8. Pseudo-first order kinetic model plots for copper adsorption on prepared adsorbents.

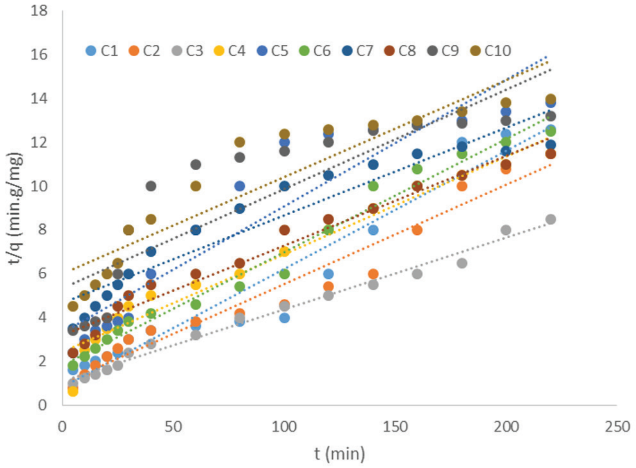


Fig. 9. Pseudo-second order kinetic model plots for copper adsorption on prepared adsorbents.

4. Conclusion

In this study, two sets (oxidized and un-oxidized) of activated carbons (10 each) were prepared from sawdust of different wood and nutshells. Air oxidation and phosphoric

Table 5
Adsorption kinetic models parameters for copper adsorption on different adsorbent

Model	Constants	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Pseudo-first order	K_1 (min^{-1})	0.014	0.056	0.032	0.043	0.012	0.023	0.054	0.067	0.057	0.045
	R^2	0.961	0.976	0.954	0.963	0.976	0.945	0.962	0.973	0.932	0.967
Pseudo-second order	K_2 (g mg^{-1} min^{-1})	0.034	0.076	0.072	0.067	0,037	0.087	0.073	0.091	0.073	0.078
	R^2	0.983	0.987	0.979	0.978	0.983	0.964	0.975	0.984	0.957	0.978

Table 6
Thermodynamic parameters for the adsorption of copper on prepared adsorbent

Adsorbent	$\Delta G°$ (KJ mol^{-1})				$\Delta H°$ (KJ mol^{-1})	$\Delta S°$ (KJ mol^{-1} deg^{-1})
	25°C	35°C	40°C	50°C		
C_1	–12.23	–12.76	–12.98	–13.02	–35.3	42.4
C_2	–10.53	–10.67	–10.77	–10.89	–21.7	45.5
C_3	–15.30	–15.38	–15.87	–15.98	–27.9	67.1
C_4	–9.98	–10.32	–10.44	–10,45	–54.5	89.4
C_5	–8.43	–8.77	–9.54	–9.60	–12.8	32.3
C_6	–13.10	–13.55	–13.78	–13.77	–54.4	34.6
C_7	–22.65	–22.78	–22.83	–22.85	–76.6	54.7
C_8	–24.33	–24.75	–24.78	–24.80	–82.2	56.6
C_9	–8.88	–8.94	–8.98	–9.02	–33.3	23.7
C_{10}	–7.89	–7.92	–7.97	–8.22	–29.4	18.6

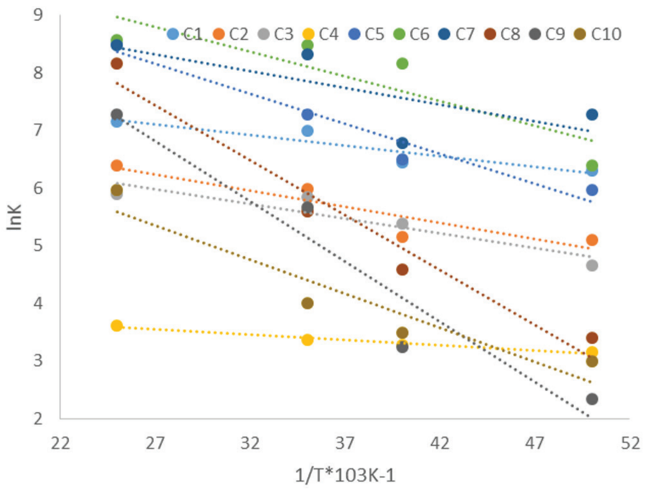


Fig. 10. Van't Hoff plots for copper adsorption on prepared adsorbents.

acid activation (N_2 atmosphere) methods were used to prepare oxidized and un-oxidized activated carbons. Oxidized carbons showed high copper ion uptake as compared with un-oxidized carbons. The adsorption isotherms data fitted well to Langmuir model while kinetic data was well explained by pseudo-second order kinetics model. The values of $\Delta G°$ and $\Delta H°$ were negative while that of $\Delta S°$ were positive which indicates that the adsorption of copper onto these adsorbents was exothermic one and also there was an increase of adsorption with increase in temperature. It was concluded that adsorbents prepared from biomass will be a good alternative for commercially available activated carbons and processes such as oxidation used for activation of adsorbents will further render it well suited for metal adsorption as they have positive charges while oxidation rendering the surfaces of activated carbons more negative.

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