

Effective Activated Carbon as Adsorbent for the Removal of Copper(II) Ions from Wastewater

PATRA VASUNDHARA DEVI¹, M. SUNEETHA² and K. RAVINDHRANATH^{1,*}

¹Department of Chemistry, K L University, Green Fields, Vaddeswaram-522502, India

²Department of Chemistry, IIIT Srikakulam, Etcherla (M), Srikakulam District-532402, India

*Corresponding author: E-mail: ravindhranath.kunta@gmail.com

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Nitric acid activated carbons prepared from the barks of *Limonia acidissima* plant (NALABC) and stems of *Hibiscus cannabinus* plant (NAHCSC) are investigated as adsorbents for the removal of Cu(II) ions from waste water using batch methods of extraction. Various extraction conditions namely, pH, time of equilibration, sorbent concentration, initial concentration of Cu(II) ions and temperature, are optimized for the maximum removal. Substantial amounts of Cu(II) are extracted in the pH range: 3 to 9 and adsorption capacities are 19.6 mg/g for NALABC and 29.4 mg/g for NAHCSC, which are more than many active carbons developed in the previous works. It is interesting to note that the adsorbents are effective in acidic, neutral and also in basic conditions of the water samples and thus paving the way for applying these adsorbents in wide pH ranges of diverse samples. Five-fold excess of common co-ions that are normally present in water, have marginally affected the % removal. Thermodynamic parameters are evaluated for the spontaneity and nature of adsorption processes. The adsorption phenomenon is analyzed using Langmuir and Freundlich isotherm models and noted that Langmuir isotherm model suits better indicating the uniform and mono-layer nature of adsorption. Kinetics of adsorption is analyzed and found that pseudo second-order kinetics preferably explains the adsorption of Cu(II). The spent NALABC and NAHCSC can be regenerated and subsequently used. The adsorbents developed are found to be effective in removing Cu(II) ions from the real water samples collected from polluted lakes and copper based industries.

Keywords: Copper(II), Activated carbon, *Limonia acidissima*, *Hibiscus cannabinus*.

INTRODUCTION

The hazardous effects of copper ions when contaminated in in-taking waters are well known. The ailments such as gastroenterological problems, brain and liver damage, neurological problems *etc.* are resulted [1,2]. The potential sources of contamination of copper are from the sewerages of various industries based on fertilizers, paper, paints, metal plating, *etc.* [3,4]. When the effluents are not properly treated for the removal of Cu(II) ions and let into the environment, the water bodies are polluted and thereby causing high risk to human health [2].

The conventional methods used for the removal of Cu(II) ions based on precipitation, ion-exchange, separations using membranes, reverse osmosis and electro-flotation, have one or the other disadvantage and they involve complicated procedures and non-economical [1,5,6]. Adsorption methods based on sorbents derived from biomaterials are promising and are reported in the literature for the removal of Cu(II) ions. Agric-

ultural by-product such as peanut hull [2], waste sugar beet pulp [3], dehydrated wheat bran [4], coffee waste [7], potato and banana peels [8] are investigated. Further, active carbons derived from green vegetable waste [9], rice husk [10,11], hazelnut husks [12], palm shell [13], rubber wood sawdust [14], Tunisian date stones [15], residue from biomass gasification [16], sewage sludge (treated with H₃PO₄ and ZnCl₂) [17], *Ceiba pentandra* hulls [18], grape seeds [19] and *Eucalyptus camaldulensis* Dehn. Bark [20], are used for the removal of Cu(II) ions from water.

In the present work, active carbons derived from the barks of *Limonia acidissima* plant and stems of *Hibiscus cannabinus* plant are investigated for their sorption nature towards Cu(II) and the conditions for the maximum extractions have been optimized. The surface morphological studies, kinetic of adsorption and thermal studies have been performed. The developed methods are applied to effluent samples from of industries and polluted lakes.

EXPERIMENTAL

Different biomaterials pertaining to various species of plant kingdom have been investigated for their abilities to remove Cu(II) ions from wastewater. Nitric acid activated carbons prepared from the barks of *Limonia acidissima* plant (NALABC) and stems of *Hibiscus cannabinus* plants (NAHCSC) were found to adsorb Cu(II) ions.

Limonia acidissima is commonly called as wood-apple tree and it grows to a height of 9 feet. It is widely grown in South India. It belongs to the Rutaceae family of plant kingdom. *Hibiscus cannabinus*, belongs to Malvaceae family of plant kingdom. Its other trivial names are Java Junta and Deccan hemp and it grows well in South Asian countries.

Preparation of activated carbon: The barks of *Limonia acidissima* plant and stems of *Hibiscus cannabinus* plant were collected, cut to pieces, washed with tap-water followed by distilled water and then air dried under sunlight for 2 days. Then by using muffle furnace, bio-substances were carbonized at 550 °C in the absence of air. Thus obtained carbons were cooled to room temperature and crushed to a mesh size of 75 µm (ASTM). Then both sample of carbons were washed with distilled water and dried at 110 °C in hot air oven. Then the two carbons were activated (liquid oxidation) by mixing with 1.0 N HNO₃ in the ratio 1:10 (w/v) and refluxing for 1 h. Thus activated carbons were washed thoroughly with distilled water until the washings were neutral to litmus. After that the carbons were dried at 150 °C for 24 h. Thus prepared active carbons from the barks of *Limonia acidissima* plant and stems of *Hibiscus cannabinus* plant were named as NALABC and NAHCSC respectively.

Adsorption studies: Batch extraction systems were adopted in this study [21-23]. Stock solution of simulated Cu(II) ions of 100 mg/L concentration was prepared and the solution was suitably diluted as per requirement. Double-distilled water was used for the preparing the solutions. The chemicals used were of A.R. grades.

Known concentrations of simulated Cu(II) solutions were taken into 250 mL stoppered conical flasks. To each conical flask, desired amounts of NALABC and NAHCSC were added. The pHs of the solutions were adjusted to the requisite values using dil. HCl and dil. NaOH. The temperature was maintained at 303 K. Then the conical flasks were agitated at 300 rpm using orbital shaker. After equilibrating the solution with the adsorbents for the desired time, the agitation was stopped and the solutions were filtered through Whatman No. 1 filter paper. The filtrates were analysed for the residual Cu(II) by atomic adsorption spectroscopic method using AA 500 instrument having the features: flame absorption; fuel flow rate: 1200 (mL/min); slit: 0.4; lamp current: 5.0 amp; wavelength: 217.00 nm and high voltage: 416.25 V as described in the literature [24].

By adopting the above procedure, the effect of pH, time of equilibration, sorbent concentration, initial Cu(II) ions, temperature and co-ions were investigated for both the adsorbents: NALABC and NAHCSC. The efficiencies of NALABC and NAHCSC in removing Cu(II) ions were investigated using water samples procured from polluted lakes in Guntur District of India and the effluents of copper based industries in Hyderabad, India.

RESULTS AND DISCUSSION

Effect of pH: The influence of initial pH of solution has been investigated by varying the initial pH of the solution while keeping the other extraction conditions constant at optimum levels as has been shown in Fig. 1. It can be inferred that both the adsorbents are successful in removing substantial amounts of Cu(II) throughout the pH range from 3 to 9. The percentage removal has not comes down below 90 % at optimum conditions of extraction. In case of NALABC, the percentage removal is found to be 99.3 % at pH 3; 99.0 % at pH 4; 98.1 % at pH 5; 97.4 % at pH 6; 96.5 % at pH 7; 95.2 % at pH 8; and 94.2 % at pH 9. With NAHCSC, percentage removal of Cu(II) is found to be 98.5 % at pH 3; 98.0 % at pH 4; 97.2 % at pH 5; 96.0 % at pH 6; 94.0 % at pH 7; 92.0 % at pH 8; and 90.0 % at pH 9. It is interesting to note that both the adsorbents are effectively removing Cu(II) ions from acid, neutral and basic solutions.

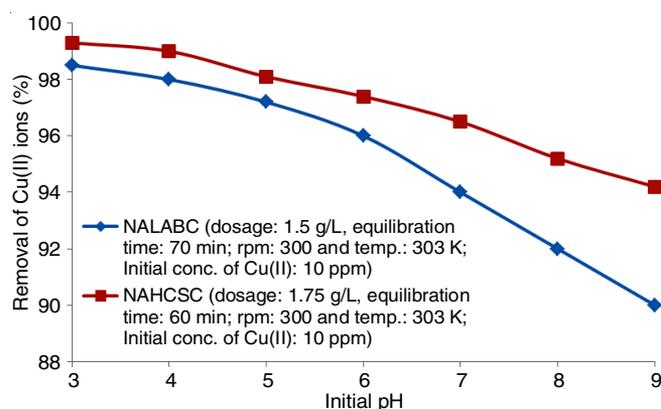


Fig. 1. pH vs. % removal of Cu(II) ions

Fig. 2a-b showed that pHz_{PC} for NALABC and NAHCSC are found to be 6.7 and 6.2, respectively. Thus, NALABC and NAHCSC surfaces acquires surface negative charge above pHs 6.7 and 6.2 due to the dissociation of surface functional groups such as -OH, -COOH, etc. Below this pH, the surface functional groups are undissociated and at sufficiently low pHs, they may also acquire positive charge due to protonation. For the Cu(II) ions at low pHs, it exists as Cu²⁺ and as the pH is increased, Cu²⁺ undergoes hydrolysis to different extents to yield species Cu(OH)⁺, Cu(OH)₂, [Cu(OH)₃]⁻ and [Cu(OH)₄]²⁻.

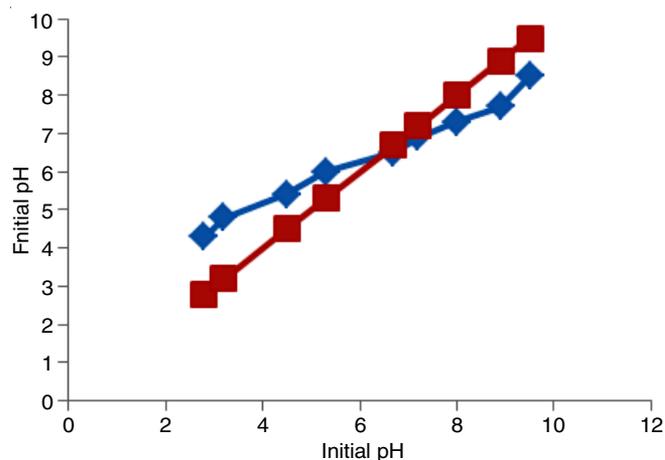


Fig. 2a. pHzPC of NALABC

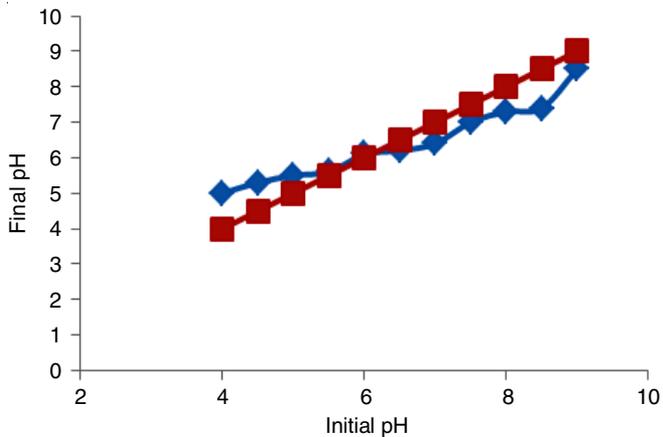


Fig. 2b. pHZPC of NAHCSC

It is observed that at low, neutral and also in basic pHs, substantial amount of Cu^{2+} is removed. The removal at low pHs is due to the exchange Cu^{2+} to H^+ of functional groups of the active carbons. As the pH is increased above pH_{zpc} of the adsorbents, the removal is mainly attributed to physical adsorption of hydrolyzed species besides the insolubility of the species in aqueous solution. As the pH increases, there is marginal loss of adsorption capacity of the sorbents towards $\text{Cu}(\text{II})$. This is due to the fact that at low pHs, the removal of Cu^{2+} is due to cation-exchange while at high pHs, it is a cumulative affect resulting on one hand, from the attraction between hydrolyzed species (due to the presence of $-\text{OH}$ groups) and the functional groups of the adsorbent and on the other hand, the repulsion caused between the negatively charged surface of the adsorbent and negatively charged hydrolyzed species, $[\text{Cu}(\text{OH})_3]^-$ and $[\text{Cu}(\text{OH})_4]^{2-}$, besides the insolubility of $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ species.

Contact time: At constant pH 4, rpm 300 and temperature 303 K, the effect of equilibration time on the percentage of extractions has been studied using 10 mg/L Cu^{2+} simulated solutions with the adsorbents: NAHCSC (1.75g/L) and NALABC (1.5g/L). It can be inferred from Fig. 3 that the removal of $\text{Cu}(\text{II})$ ions is more for NAHCSC as adsorbent than NALABC at a given time. For example, after 10 min of equilibration, the % removal is found to be 81.41 % with NALABC while it is 93.7 % with NAHCSC.

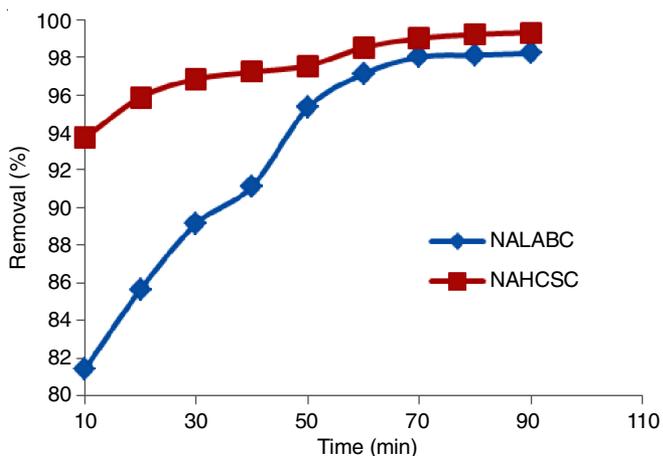
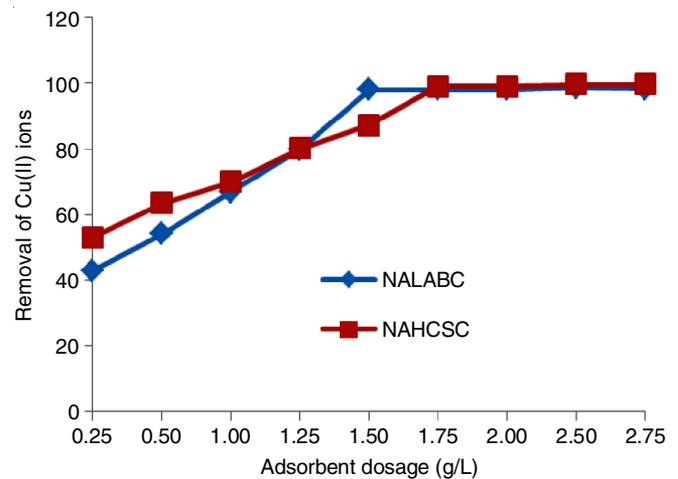


Fig. 3. Effect of time on the % removal of copper ion

The percentage removal at 10, 20, 30, 40, 50, 60, 70, 80 and 90 min of agitation is found to be 81.41, 85.66, 89.15, 91.13, 95.3, 97.1, 98.0, 98.1 and 98.2 % respectively for NALABC; and 93.7, 95.86, 96.84, 97.2, 97.54, 98.5, 99.0, 99.2 and 99.3 % for NAHCSC. Initially, extraction percentage is more and it slow down with time and after certain duration, an equilibrium state is reached. In fact, in case of NAHCSC, 93.7 % is observed even at 10 min of agitation while the maximum possible removal is 99.2 % after 90 min. With NALABC as adsorbent, 81.41 % removal is observed even at 10 min of agitation while the maximum removal is 98.1 % at 90 min of agitation. These observations are agreeable to the fact that initially more adsorption sites are available on the adsorbents for the adsorbate ions (Cu^{2+}) and so, the % removal is more. But with the time, the sites are exhausted and hence lower are the extractions.

Dosage of sorbents: By varying the sorbent concentrations from 0.25 g to 2.75 g/L, the changes in the percentage of extraction is investigated. The other optimum extractions conditions *viz.* pH: 4.0; time of equilibration: 70 min; rpm: 300; initial $\text{Cu}(\text{II})$ solution concentration: 10 mg/L; and temp.: 303 K are maintained constant. With increase of dosage of adsorbents, the extraction percentage also increases but after certain dosage, the % removal almost remains constant (Fig. 4). The optimum sorbent dosages are found to be 1.5 g/L for NALABC and 1.75 g/L for NAHCSC.

Fig. 4. Effect of adsorbent dosage vs. % removal of $\text{Cu}(\text{II})$ ions

Initial concentration: The effect of initial $\text{Cu}(\text{II})$ ion concentration on the percentage of extraction of $\text{Cu}(\text{II})$ is investigated by varying the initial concentration of $\text{Cu}(\text{II})$ ions from 5 mg/L to 60 mg/L while maintaining the other extraction conditions at optimum levels: pH: 4; time of agitation: 70 min; sorbent concentration: 1.5 g/L for NALABC and 1.75 g/L for NAHCSC; 300 rpm and 303 K temperature. At low initial concentrations of $\text{Cu}(\text{II})$, the extraction percentage is more while at high concentrations, it is less (Fig. 5a). As the initial concentration of $\text{Cu}(\text{II})$ ions varied, there is a steep fall in the curve after 20 mg/L for NALABC and 30 mg/L for NAHCSC. The amount adsorbed, Q_e , is increasing (though irregularly) as the initial concentration of $\text{Cu}(\text{II})$ is increased (Fig. 5b). Steep rise in Q_e values are noticed when the concentration of $\text{Cu}(\text{II})$ is less than 20 mg/L in the case of NALABC and 30 mg/L with NAHCSC as adsorbents (Fig. 5b).

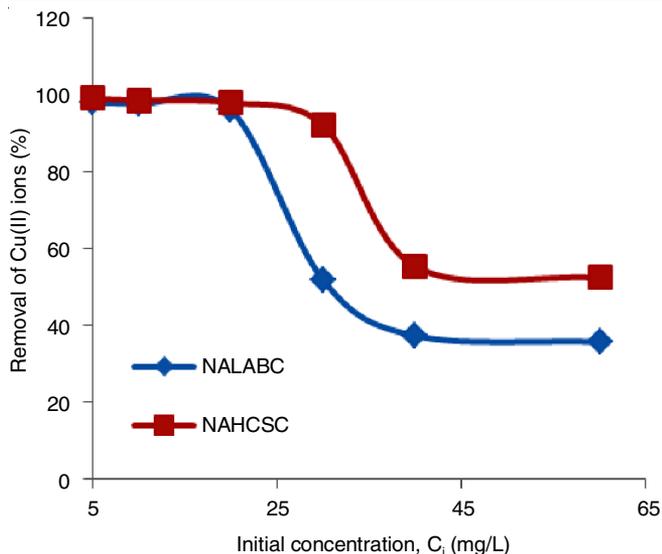


Fig. 5a. Effect of initial conc. of Cu(II) ions on % removal

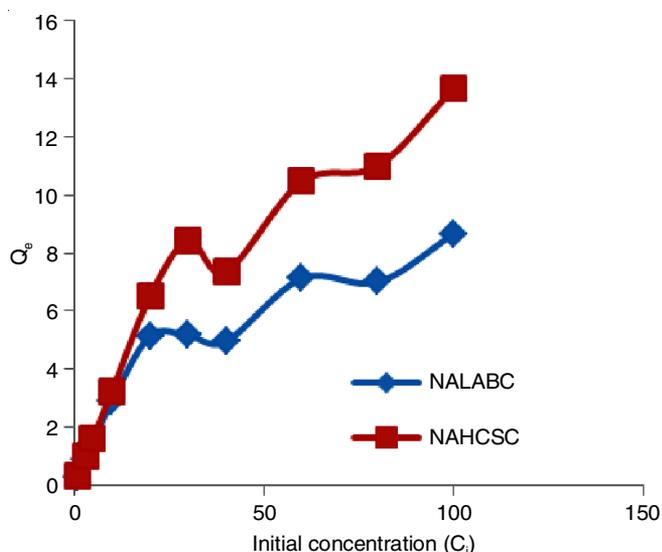


Fig. 5b. Amount adsorbed by activated carbons at various concentrations

At low concentrations of Cu(II) ions, the needed active sites on the fixed amounts of adsorbents are available and hence the adsorption is more. But at high concentrations of Cu(II) ion, sufficient number of active sites on the adsorbent are not available as the amount of the adsorbent is fixed and it results in decrease in the percentage removal of Cu(II) ions.

Effect of co-ions: The effect of the presence of five-fold excess co-ions that are commonly found in water on the adsorption of Cu(II) ions onto to the surface of adsorbents has been investigated. The anions have marginally affected the adsorption on both the adsorbents, NALABC and NAHCSC (Fig. 6). The interference of the cations is also less and their relative interference follow the order: $Al^{3+} > Fe^{2+} > Zn^{2+} > Mg^{2+} > Ca^{2+}$

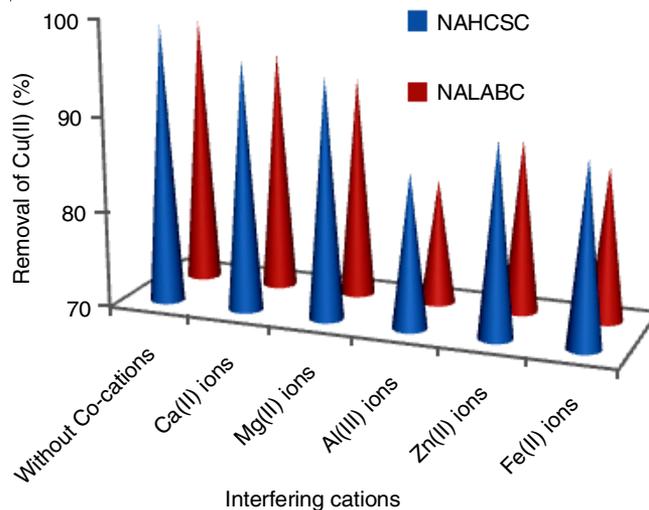


Fig. 6a. Effect of co-cations on the extraction of Cu(II)

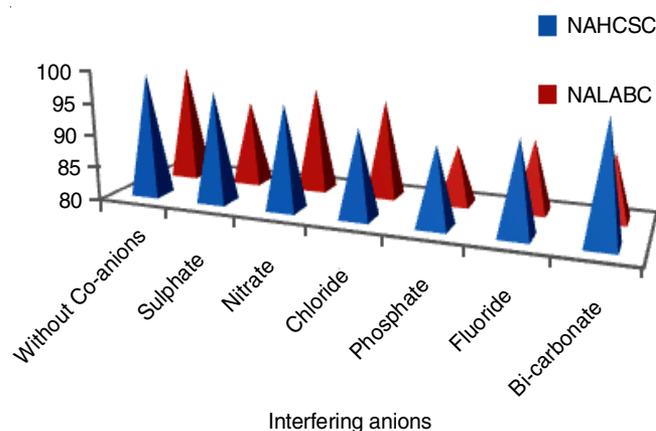


Fig. 6b. Effect of co-anions on the extraction of Cu(II)

and the extraction has not come down below 83.0 % with NALABC and 86.0 % with NAHCSC.

Thermodynamic studies: The effect of solution temperature on the adsorption of Cu(II) ions has been investigated at different temperatures *viz.*, 303, 313, 323 and 333 K. For this, using NALABC (1.5 g/L) and NAHCSC (1.75 g/L) as adsorbents, the extraction studies have been made with 30 mg/L Cu(II) ion solutions at optimum pH: 4; time of agitation: 70 min; and rpm: 300. With NAHCSC, the extraction percentage is progressively increased from 84.3 to 94.2 % as the temperature increases from 303 to 333 K. But in case of NALABC, the extraction percentage is increased from 51.7 % at 303 K to 56.2 % at 313 K and there is a sharp jump to 67.5 % at 323 K and further increased to 70.4 % at 333 K. The thermodynamic parameters are shown in Table-1.

ΔH values are positive for both the adsorbents NALABC and NAHCSC. This reflects the endothermic nature of adsorption. ΔS values are positive for both the adsorbents and this

TABLE-1
THERMODYNAMIC PARAMETERS: ADSORPTION OF Cu(II) ONTO NALABC AND NAHCSC

Adsorbent	ΔH (KJ/mol)	ΔS (J/mol)	ΔG (KJ/mol)				R^2
			303 K	313 K	323 K	333 K	
NALABC	23.91	75.93	0.905	0.145	-0.613	-1.373	0.9508
NAHCSC	29.43	105.94	-2.661	-3.721	-4.782	-5.841	0.9421

indicates the increase in randomness at the solid/solution interface. As the solution temperature increases, the thickness of outer surface of the adsorbent decreases with the simultaneous increase in the kinetic energy of Cu(II) ions and hence, rate of diffusion of Cu(II) ions crossing over into the surface layers or pores of the adsorbent increases. The negative values of ΔG for NAHCSC indicate that the adsorption is spontaneous. In the case of NALABC, positive values are observed at 303 and 313 K while negative values are observed at 323 and 333 K. The positive values indicate the non-spontaneous nature while negative values indicate spontaneous nature. So, in the case of NALABC, the adsorption is spontaneous at 323 and 333 K while at low temperatures, the process is non-spontaneous. This is reflected in the sudden jump in removal percentage by a value 11.3 % as the solution temperature is increased from 313 K (56.2 %) to 323 K (67.4 %).

Adsorption isotherms: Adsorption mechanism is analyzed using Langmuir and Freundlich isotherm models as described in literature [25-27]. In case of Langmuir isotherm model, the R^2 values are 0.9987 for NALABC and 0.9693 for NAHCSC. With Freundlich isotherm model, the R^2 values are respectively 0.885 and 0.8921 for NALABC and NAHCSC. Langmuir isotherm models are much near to unity than Freundlich isotherm models (Table-2). Hence, it is inferred that Langmuir isotherm model suits better than the Freundlich model in explaining the adsorption phenomenon. Langmuir isotherm model suggests the uniform and mono-layer nature of adsorption. Further, $R_L = 0.0342$ for NALABC and $R_L = 0.1264$ for NAHCSC suggest the favourableness of adsorption process.

Adsorption kinetics: The adsorption kinetics are studied using pseudo-first and second-order models, intraparticle diffusion model and Elovich equations [28,29]. As per R^2 values, adsorption kinetics follows the order: pseudo second-order (0.9994) > pseudo first-order (0.9967) > interparticle diffusion model (0.9683) > Elovich model (0.922) in the case of NAHCSC; and pseudo second-order (0.9998) > pseudo first-order (0.9843) > Elovich (0.9694) > intraparticle diffusion model (0.9358)

in the case of NALABC (Table-2). Pseudo second-order kinetics preferably explains the adsorption of Cu(II) onto the surface of NAHCSC and NALABC adsorbents.

Applications: The effectiveness of adsorbents developed in this work were tested with the real water samples collected in polluted lakes in Guntur district of India and the effluents of copper based industries in Hyderabad, India. The samples were analyzed for the actual content of Cu(II) ions and fed with further known amounts of Cu(II) (if sufficient Cu^{2+} ions were not available). These samples were subjected to the extraction using two adsorbents (NAHCSC and NALABC) at the optimum conditions of extraction. The results are shown in Table-3.

Regeneration and reuse: The regeneration of spent adsorbents was investigated using various extracting solutions and it was found that 0.1N HCl was successful in regenerating both the adsorbents. At each cycle of adsorption experiment, the spent adsorbent was collected, regenerated with 1.0 N HCl and thus regenerated adsorbent was again used for the removal of Cu(II). The loss of removal ability of each regenerated adsorbent is depicted in Fig. 7. It can be seen that there is marginal loss of adsorption ability until 4 regenerations in the case of NALABC and 5 regenerations in the case of NAHCSC. Thus these two adsorbents are cost effective.

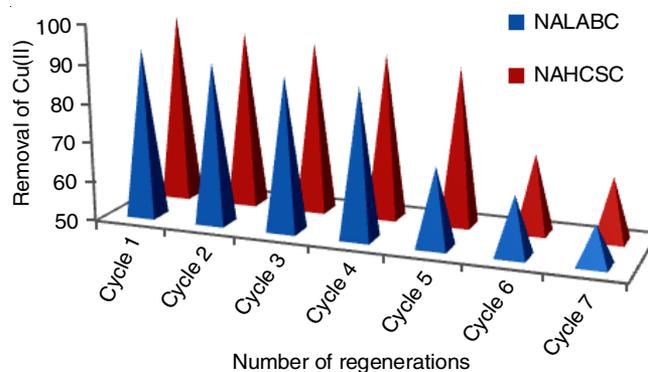


Fig. 7. Repetitive use of spent adsorbents after regenerating with 0.1 N HCl

TABLE-2
ADSORPTION ISOTHERMS AND KINETIC MODELS; VARIOUS PARAMETERS-
ADSORPTION OF Cu(II) ONTO NALABC AND NAHCSC

Models	NALABC			NAHCSC		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Langmuir isotherm model	0.3553	0.126	0.9987	-	0.0874	0.9693
Freundlich isotherm model	0.4401	0.1764	0.885	0.2795	0.6323	0.8921
Intra particle diffusion model	0.0784	2.3911	0.9358	0.0491	2.9691	0.9683
Pseudo first model kinetics	-0.0163	-0.0671	0.9843	-0.0275	-0.65	0.9967
Pseudo second order kinetics	0.339	0.9278	0.9998	0.3372	-0.0694	0.9994
Elovich model	0.3816	4.5945	0.9694	0.1052	5.1474	0.922

TABLE-3
APPLICATION OF THE DEVELOPED METHODS FOR REAL WATER SAMPLES
COLLECTED FROM POLLUTED LAKES AND EFFLUENTS OF Cu-BASED INDUSTRIES

Water samples	NALABC®			NAHCSC®		
	Before (mg/g)	After (mg/g)	Removal (%)	Before (mg/g)	After (mg/g)	Removal (%)
Sample 1	7.70	0.75	90.2	7.70	0.3	96.1
Sample 2	9.20	1.0	89.1	9.20	0.5	94.6
Sample 3	11.0	1.3	88.2	11.0	0.7	93.6
Sample 4	12.5	1.8	85.6	12.5	0.9	92.8
Sample 5	14.5	2.0	86.2	14.5	1.0	93.1

TABLE-4
COMPARISON OF Cu(II) UPTAKE CAPACITY OF NALABC AND NAHCSC
WITH THE ACTIVE CARBONS DEVELOPED IN PREVIOUS WORKS

Adsorbent	pH	Adsorption capacity (mg/g)	Ref.
Rice hulls activated carbon	5.3	3.92	[11]
Hazelnut husks active carbon	6.7	6.645	[12]
Palm shell active carbon	3.0	18.60	[13]
Phosphoric acid activated rubber wood sawdust	5.7	5.72	[14]
Tunisian date stones active carbon	5.0	31.25	[15]
Activated carbon residue from biomass gasification	5.0	23.00	[16]
Phosphoric acid activated sewage sludge	5.0	7.73	[17]
Zinc chloride activated sewage sludge	5.0	10.56	[17]
<i>Ceiba pentandra</i> hulls activated carbon	6.0	20.80	[18]
Chestnut shell	3.3	38.75	[19]
Grape seed activated carbon	3.0	31.84	[19]
Active carbon of <i>Eucalyptus camaldulensis</i> Dehn. bark	5.0	53.98	[20]
HNO ₃ activated carbon of barks of <i>Limonia acidissima</i> plant NALABC	3-9	19.6	Present work
HNO ₃ activated carbon of stems of <i>Hibiscus cannabinus</i> plant (NAHCSC)	3-9	29.4	Present work

Comparative study: The efficiencies of NALABC and NAHCSC for the removal of Cu(II) ions are compared with the active carbons developed in the previous works with respect to the optimum pH and adsorption capacity and presented in Table-4.

It can be inferred from Table-4 that the present developed activated carbons NALABC and NAHCSC have substantial adsorption capacity of 19.6 and 29.4 mg/g, respectively and they are more than many active carbons developed in previous works. Further, the novelty of these adsorbents lies in wide range of effective pH 3 to 9 and this permits the application of the said adsorbents to diverse samples, acidic, neutral and basic.

Conclusion

Nitric acid treated active carbons prepared from the barks of *Limonia acidissima* plant (NALABC) and stems of *Hibiscus cannabinus* plant (NAHCSC) are investigated for their adsorption abilities towards Cu(II) ions from wastewater using batch methods of extraction. Both the adsorbents are effective in removing Cu(II) ions in the pH range 2 to 9. This observation is significant as the removal of Cu(II) is effected in acidic, neutral and basic conditions. At pH 4 and at other optimum conditions of extraction namely, equilibration time: 70 min; sorbent dosage: 1.5 g/L for NALABC and 1.75 g/L for NAHCSC; rpm: 300 and temperature: 303 K, the removal percentage is found to be 98.0 % for NALABC and 99.0 % for NAHCSC when the initial concentration of Cu(II) is 10 mg/L. The percentage removal is marginally affected by co-anions that are normally present in water while the co-cations affect the percentage removal in the order: Al³⁺ > Fe²⁺ > Zn²⁺ > Mg²⁺ > Ca²⁺, though to a less extent both for NALABC and NAHCSC. The thermodynamic parameters were also evaluated for both adsorbents. The adsorption is spontaneous for NAHCSC at all temperatures while for NALABC, the adsorption is spontaneous only at 323 and 333 K. Similarly, it is noted that the Langmuir isotherm model suits better than the Freundlich model in explaining the adsorption phenomenon. It suggests the uniform and monolayer nature of adsorption. Overall on the basis of the various kinetic models studied, pseudo second-order kinetics preferably explains the adsorption of Cu(II) onto the surface of NAHCSC and NALABC. The adsorption kinetics follows the order: pseudo

second-order (0.9994) > pseudo first-order > interparticle diffusion model > Elovich model in the case of NAHCSC; and pseudo second-order > pseudo first-order > Elovich > intraparticle diffusion model in the case of NALABC.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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