Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.914446

55 (2015) 401–409
June

Taylor & Francis
Taylor & Francis Group

Sorption of copper (II) from aqueous solution onto *Arachis hypogaea* husk

Pradnya K. Ingle, Chandrakanth Gadipelly, Virendra K. Rathod*

Department of Chemical Engineering, Institute of Chemical Technology, Matunga (E), Mumbai 400019, India,
Tel. +91 22 33612114; Fax: +91 22 33611020; email: kiranpradnya@gmail.com (P.K. Ingle), Tel. +91 22 33612124;
email: chanduom01@gmail.com (C. Gadipelly), Tel. +91 22 33612020; email: vk.rathod@ictmumbai.edu.in (V.K. Rathod)

Received 21 August 2013; Accepted 4 April 2014

ABSTRACT

Copper (II) is known to be one of heavy metals most toxic to living organisms and more widespread contaminants of the environment. It has a diverse usage in the field of electroplating, alloy making, electrical wiring, etc. Copper has been reported to be a pollutant and its concentration in the range from 1 to 100 mg/L can lead to harmful effects to the ecosystem. This work deals with the application of sorption, as an effective technique for the removal of copper from aqueous waste especially in a continuous manner. The batch experiments were performed to fetch the optimized parameters which were in agreement with the previous results by various researchers. In batch study, at optimum adsorption condition, the highest adsorption capacity of 14.3 mg/g was obtained in absence of metal ions as compared to 9.2 mg/g with real wastewater. Moreover, the effect of competitive ions on copper adsorption was studied. The column studies were carried out with the study of different parameters namely flow rate, bed height, initial concentration of the aqueous copper solution. The performance of column was also studied for copper adsorption in the presence of multi-metal ions. This work provides an insight for the design of a packed bed column for copper removal which includes mass transfer calculation. Desorption studies have also been explored using various solutions like hydrochloric acid, nitric acid, oxalic acid, sodium hydroxide of varying concentrations.

Keywords: Copper (II); Sorption; *Arachis hypogaea*; Packed column; Mass transfer; Desorption

1. Introduction

Heavy metals are on forefront of academics and regulatory body concern since gallons of water containing toxic as well as precious heavy metals are generated annually from various sources like metallurgy industry, metal processing industries, electroplating industry, tannery industries, etc. This has occurred due to rapid population expansion, unplanned urbanization, industrialization which leads to increased disposal of heavy metals into environment there by contributing to pollution [1]. Moreover, heavy metals are not biodegradable and tend to accumulate in living organisms resulting in several diseases and disorders as well as it lead to severe ecological hazards [2,3].

Copper, a heavy metal has diverse use in the field of electroplating, alloy making, electrical wiring, and many such applications. In electronic industry, copper metal is widely used as interconnecting material for the manufacturing of electronic components due to its higher conductivity and greater residence to electromigration [4]. Copper is processed by various ways

---

*Corresponding author.

such as electroplating, etching, rinsing, chemical and mechanical polishing, etc. which lead to accumulation of wastewater contributing heavy metal pollution. Copper is a micronutrient but excessive intake leads to severe kidney failure and liver diseases. Thus, copper (II) is recognized as one of the most widespread heavy metal contaminants in the environment and there is a need to search a cost-effective method for its removal from wastewater [5]. Conventional methods are employed for removal copper from wastewater which include precipitation, coagulation, ion exchange, membrane separation processes (such as ultra filtration, electro dialysis, reverse osmosis, etc.), and last but not least sorption [6]. However, chemical precipitation and electroplating treatment are uncommon as they produce large quantity of sludge, which has to be treated with great effort which is a costly issue. Moreover, when copper ion concentration in aqueous solution is among 1–100 mg/L these methods are ineffective. Ion exchange, membrane processes are extremely expensive and cannot be used for large scale [7].

As an alternative technique, sorption is a cost-effective and so is in huge demand and has capability to overcome the disadvantages of conventional method. In the queue of these techniques, use of biological material including living and non-living micro-organisms as an adsorbent is more popular. This is due to their good performance to remove or recover toxic and precious metals from industrial waste at ease of availability and low cost. This effective technique depends on the parameters like capacity, affinity, specificity of biosorbent, and the conditions in effluents.

Sorption can be used for the treatment of wastewater with low heavy metal concentration as an inexpensive, simple, and effective alternative to conventional methods. Sorption is the capability of active sites on the surface of biomaterials to bind and concentrate heavy metals from even the most dilute aqueous solutions [8]. Biomass is mostly composed of proteins, polysaccharides, and fats, and has many functional groups able to bind heavy metal ions.

Biomass includes low-cost agricultural waste, algae, fungi, bacteria, microalgae, marine algae, etc. In spite of availability of numerous techniques for treatment of effluents containing heavy metals, sorption by agricultural waste is highly effective. Recent studies showed that common agricultural waste products can be used as potential biosorbents for the removal of heavy metals. Waste coming as agricultural material particularly which contains cellulose has witnessed sorption for various pollutants. The basic composition of agricultural waste is hemicelluloses, lignin, lipids, proteins, simple sugar, water, hydrocarbons, and starch containing various functional groups. These waste are abundantly available, has low-cost and moreover renewable in nature which make them economical as well as eco-friendly [1]. From decades various agricultural wastes as low-cost adsorbent have been explored [9]. Earlier studies has been carried out with low-cost biomass for removal of copper such as sawdust, rice husk, sago waste, red pepper seeds, barks, teak leaves powder, saltbush leaves, palm kernel fiber, groundnut shells, tree fern, chitosan, etc. [10]. Earlier reports on copper sorption using *Arachis hypogea* husk (AHH) are mainly concentrated on batch sorption studies and thus need to continue this work for continuous sorption and desorption.

The objective of the present work is to study the sorption of copper (II) ions on AHH. Experiments were performed in batch and continuous mode and copper sorption was investigated with respect to initial pH, initial metal ion concentration, and temperature. As per the previous literature much less work has been done on varied concentrations and the desorption studies. Although other types of reactors, e.g. batch or continuous stirred tank reactors and fluidized bed columns can be used, packed bed sorption has a number of advantages. It is simple to operate, attains a high yield, and a scale up can be easily attained [11]. Also, the mass transfer calculation is an important aspect for designing of the packed bed column for such systems [12,13]. Thus, the mass transfer coefficient values for the column under study have also been reported.

2. Materials and method

2.1. Preparation of biosorbent

AHH were washed extensively using tap water for 1–2 h and then washed with distilled and deionized water several times to remove any mud and soil particles adhered to it. The washed husk was dried in oven at 80˚C for 48 h and then grounded, sieved by ASTM standard sieve of 320 μm, and stored for further use.

2.2. Characterization of the biosorbent

The dried biosorbent was characterized by Fourier transform infrared spectrometer (Vacuum FTIR VERTEX 80, Mfg. BRUKER) to better understand the binding mechanism of the metal ion to the biosorbent.

2.3. Preparation of metal solution

A stock solution of 1,000 mg/L of copper (II) was prepared by dissolving appropriate quantity of $CuSO_4 \cdot 5H_2O$ (Mol. Wt. 249.68.) procured from SD Fine Analytical grade in deionized water. Other concentrations were prepared from stock solution by dilution varied between 10 and 300 mg/L, and the pH of the working solutions was adjusted to desired values with 0.1 M HNO_3 or 0.1 M NaOH using a pH meter (Labtronic digital pH meter Model No. LT-10). Fresh dilutions were used for each experiment. All the chemicals used were in analytical grade. The deionized water for the experiments was obtained from Sartorious stedim arium water purifier unit.

2.4. Method of analysis

The metal uptake at equilibrium in batch studies and total metal removal (%) in column studies were evaluated respectively from the given Eqs. (1) and (2).

$$\text{Metal uptake (q)} = \frac{(C_{\mathrm{i}} - C_e)}{M} \times v \tag{1}$$

where C_{i} is the initial metal ion concentration before sorption process in mg/L, C_{e} is the equilibrium metal ion concentration in mg/L, V is the volume of metal ion solution in mL, M is the mass of biosorbent taken in g.

$$\text{Total metal removal (\%)} = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \tag{2}$$

where q_{total} is the total metal ion sorbed in column for a given concentration and flow rate in mg, m_{total} is total metal ion send to column in mg.

q_{total} and m_{total} are determined from flow rate (Q) and total time (t_{total}) using Eqs. (3) and (4).

$$q_{\text{total}} = \frac{Q}{1{,}000} \int_{t=0}^{t=t_{\text{total}}} \mathrm{C}\,\mathrm{d}t \tag{3}$$

$$m_{\text{total}} = \frac{C_i\ Qt_{\text{total}}}{1{,}000} \tag{4}$$

The metal ion concentration was measured by using standard method for copper ion determination with PAN indicator (1-(2-pyridylazo)-2-naphthol) using a UV–vis spectrophotometer.

2.5. Experimental

2.5.1. Batch mode sorption studies

Initially, kinetics experiments were carried out to determine the time required to reach equilibrium. A 250 mL conical flask containing 150 mL metal ion solution of 100 mg/L concentration is equilibrated with 1 g of sorbent. Sorption process is carried out in a conical flask placed in shaker maintained at fixed temperature till equilibrium is attained. About 3 mL of the sample is withdrawn at particular time interval to determine the metal ion concentration. Few batch sorption experiments were performed to identify the pH and temperature dependence and their optimum value. The effect of pH ranging from 3 to 6 on sorption using AHH was carried out at different initial metal ion concentration varying from 10 to 100 mg/L. The pH is maintained by using 0.1 N NaOH and 0.1 N HCl. Similarly, the effect of temperature is carried out in a thermostatic orbital shaker at various temperatures from 20 to 60℃. The effect of competitive ions (cations and anions) on copper adsorption on AHH was also carried out.

2.5.2. Continuous column sorption studies

Column experiments were performed in a glass column with inner diameter ID = 1 cm and length L = 10 cm, packed with sorbent AHH. The density of AHH was found to be 2.204 g/cm^3. A known quantity of sorbent AHH was placed in the column and the copper solution of known concentration was pumped downward through the column at a rate of 0.75 mL/min with the help of a peristaltic pump. The flow rate was frequently measured during the experiment. The column effluent samples were collected at regular intervals and were analyzed by UV spectrophotometer. The effect of various parameters such as flow rate, column height, type of flow, initial metal ion concentration, and multi-metal ions concentration on performance of the column was studied.

2.5.3. Desorption of copper

To explore the reusability of the biosorbent material and to recover the metal ions so that the process becomes economical, desorption experiments were performed using different solvents with varying concentrations. The desorption solvents used for recovery of copper from AHH were screened from strong acid, strong base, and weak acid namely nitric acid, hydrochloric acid, sodium hydroxide, oxalic acid. The concentration of solvents was varied from 0.1 to 1 M. The percentage desorption is calculated based on total of metal desorbed using particular solvent.

3. Results and discussion

3.1. FTIR analysis of biosorbent

The FTIR spectrum of groundnut husk shows broad peak at 3435.98 –OH stretch is the indicator of –OH and –NH groups. The stretching of the -OH groups bound to methyl radicals presented a signal between 2923.51

and 2852.58 cm^{-1}. The peaks located at 1638.43 cm^{-1} are characteristics of carbonyl group stretching from aldehydes and ketones. The peaks at 1465.48 cm^{-1} are due to N–H bending vibrations. The presence of -OH group, along with carbonyl group, confirms the presence of carboxylic acid groups in the biosorbent. The peaks at 1638.43 cm^{-1} are associated with the amide stretching as well as aromatic ring stretch at 1560.45 cm^{-1}.The peaks observed at 1035.15 and 1261.97 cm^{-1} are due to C–H and C–O bonds. The –OH, –NH, carbonyl, and carboxylic groups are important sorption sites [14,15]. The FTIR spectrum of groundnut husk before and after sorption is shown in Fig. 1 which reveals that after sorption of copper ions there is a shift in intensity of –OH and carbonyl bands.

3.2. Batch mode sorption studies

The sorption of copper using AHH was optimized for various parameters. Fig. 2 depicts the variation of copper sorption with time and it was observed that the sorption increases with time due to higher mass transfer rate at start because of higher concentration difference on surface and solvent. However, after 50 min, there was no change in copper sorption as equilibrium is reached. The maximum sorption capacity for 1,000 mg/L Cu (II) initial concentration was found to be 19.96 mg/g. Thus, in order to determine the effect of pH and temperature, all batch experiments were further performed till 1 h and results are shown in Figs. 3 and 4, respectively. From the Fig. 3 it can be seen that as the pH increases higher removal of copper is obtained for pH 3–5 while sorption is found to be less at pH 6. Further the data obtained were fitted to different isotherm and found that Freundlich isotherm gave best fit. Table 1 shows values of Freundlich constant which indicates that adsorption is higher at pH 5. At higher pH the copper precipitates forming the visible flocks and the low removal of copper at low pH may be due to competency of Cu (II) with H$^+$ ions. Hence, the optimum pH was found to be 5 and further used for continuous study. Similarly, it is observed from Fig. 4 and Table 2 that the copper uptake at equilibrium increases with temperature till 50 ˚C. But as temperature is increased further, at 60 ˚C the equilibrium metal ion uptake decreased which reveals predominance of physical sorption over chemisorption in this temperature region. The optimum parameters obtained were contact time 60 min, pH 5, and temperature 50 ˚C which were matched with earlier reports [16,17]. The Freundlich isotherm fits the experimental data which implies that there is strong bonding between AHH and copper.

The effect of competitive ions (Ca^{2+}, Mg^{2+}, CO_3^{2-}, SO_4^{2-}, Cl^-) was studied by adding respective cations and anions to the stimulated wastewater. Both the cations and anions concentration were studied at equimolar as well as excess concentrations. In the study it was found that in the presence of cations the copper adsorption is reduced. The copper adsorption in the absence of cations was found to be 13.95 mg/g whereas in the presence of cations was 9.93 mg/g. However, the effect of anions on copper adsorption was witnessed to be slightly reducing. The copper

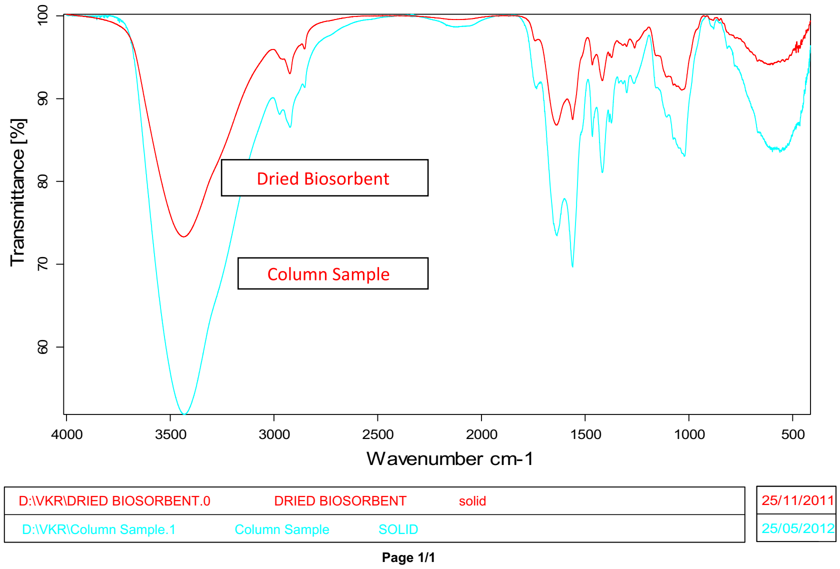

Fig. 1. FTIR for peanut husk.

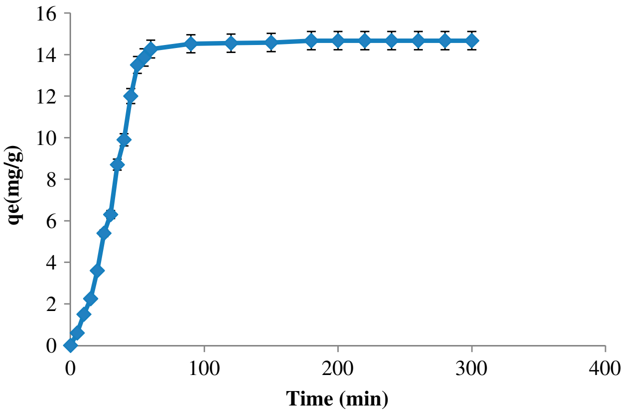

Fig. 2. Effect of time on Cu adsorption.

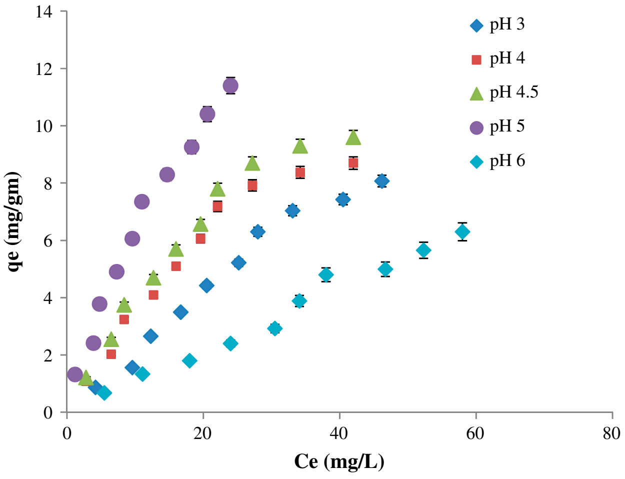

Fig. 3. Effect of pH on Cu adsorption.

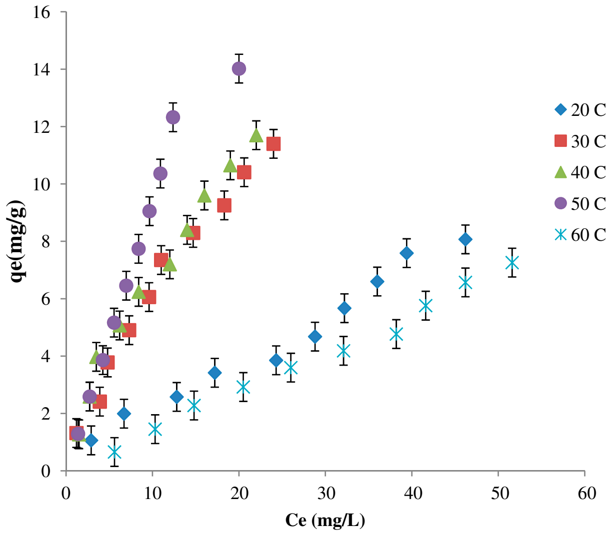

Fig. 4. Effect of temperature on Cu adsorption.

Table 1
Constants and regression coefficients for different adsorption isotherm at different pH

Isotherm	Parameters	pH 3	pH 4	pH 5	pH 6
Freundlich	n	1.18	1.50	1.32	1.24
	K_F (L/g)	0.33	0.80	1.08	0.24
	R^2	0.97	0.95	0.98	0.95

Table 2
Constants and regression coefficients for different adsorption isotherm at different temperature

Isotherm	Parameters	293 K	303 K	313 K	323 K	333 K
Freundlich	n	1.11	1.32	1.46	1.27	1.0
	K_F (L/g)	0.26	1.08	1.39	1.46	0.14
	R^2	0.90	0.98	0.98	0.98	0.97

uptake capacity was obtained as 12.9 and 13.95 mg/g in the presence and absence of the anions.

Further, batch study of real wastewater sample was carried out. The wastewater was obtained from a copper plating industry in Bhiwandi Mumbai. The known amounts of wastewater and adsorbent were taken in the conical flask and placed in the shaker under optimum conditions. The adsorption mixture is allowed to attain equilibrium and sample was withdrawn for copper content analysis. The copper uptake capacity of real waste was found to be 9.2 mg/g which showed comparable drop in adsorption of copper without ions. This may be due to presence of excess other cations in the real wastewater as observed in the case of effect of competitive ions. On the other hand, adsorption capacity of copper using AHH has been further compared with the earlier reports in Table 3. The copper uptake capacity is highest for AHH in comparison with other adsorbents like wheat shells, banana peel, hazel nut and cashew nut husk, moss, tobacco fibers. Moreover, the adsorption of metal ions can be further increased by adopting appropriate activation technique for AHH.

3.3. *Column sorption studies*

3.3.1. *Effect of flow rate*

The study of effect of flow rate is considered as an important parameter since on industrial scale the removal of heavy metal from waste stream will be carried out as a continuous operation. Fig. 5 shows the ratio of effluent copper concentration to initial con-

Table 3
Copper uptake for different agricultural waste

S. no.	Agricultural waste	Copper uptake (mg/g)	References
1	Wheat shells	8.26	[18]
2	Banana peel	1.439	[19]
3	Hazelnut husk	0.0635	[20]
4	Cashew nut husk	20	[21]
5	Rice husk modified by NaOH	10.9	[22]
6	Barley straw	4.64	[23]
7	Peanut hull pellets	12	[24]
8	Moss	11.8	[25]
9	*Arachis hypogea* husk	14.3	Present study
10	Tobacco fiber	10.5	[26]

centration of copper against time for the flow rate varied from 0.5 to 2 mL/min. It is found that the amount of copper uptake reduces with an increase in flow rate. The breakthrough occurs early for 2 mL/min flow rate. For varied flow rates i.e. 0.5, 0.75, 1, and 2 mL/min, the total removal of copper was obtained as 50, 79, 60, and 59%, respectively. The lowering of the copper adsorbed at higher flow rate of 2 mL/min maybe due to unavailability of sufficient retention time for the metal ion with the biosorbent which results in limited diffusion of metal ions in the adsorptive sites or pores available for sorption. As the flow rate is increased, the breakthrough curve becomes steeper. Therefore, at high flow rates the copper solution is eluted without attaining equilibrium and the contact time between copper solution and adsorbent is minimized, leading to early breakthrough [27].

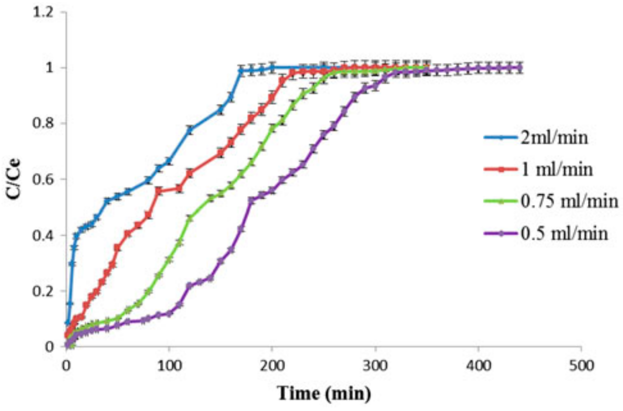

Fig. 5. Effect of flow rate on Cu adsorption.

3.3.2. Effect of bed height

The sorption of metal in a packed bed is highly influenced by bed height i.e. the amount of biomass used. Experiments were conducted in a column of 1 cm diameter for three column heights 2, 3, and 5 cm using 1, 1.8, and 2 gm of biosorbent, respectively. The feed with an initial copper concentration of 100 mg/L was passed though column at a flow rate of 0.75 mL/min. Fig. 6 represents the breakthrough curves for AHH for column height 2 cm, 3 cm, and 5 cm which clearly shows that breakthrough time has increased with increasing bed height. The total copper removal achieved at different heights 2, 3, and 5 cm was 50, 79, and 65%, respectively. It is also seen from Fig. 6 that the slope of breakthrough curve decreased with increasing bed height. This can be attributed to the fact that copper ions get maximum residence time within the column resulting in lower effluent concentration in the eluted stream. Besides, at higher bed heights the availability of the effective surface area of adsorbent is more which offers more active sites to sorption and it also broadens the mass transfer zone length [28].

3.3.3. Effect of initial concentration

In order to evaluate the effect of Cu^{2+} concentrations on the removal efficiency, the sorption process was carried out with initial Cu^{2+} concentrations between 25 and 300 mg/L at constant bed height and flow rate of 3 cm and 0.75 mL/min, respectively. Cu^{2+} uptake decreased by increasing the initial Cu^{2+} concentration, where as breakthrough in column is

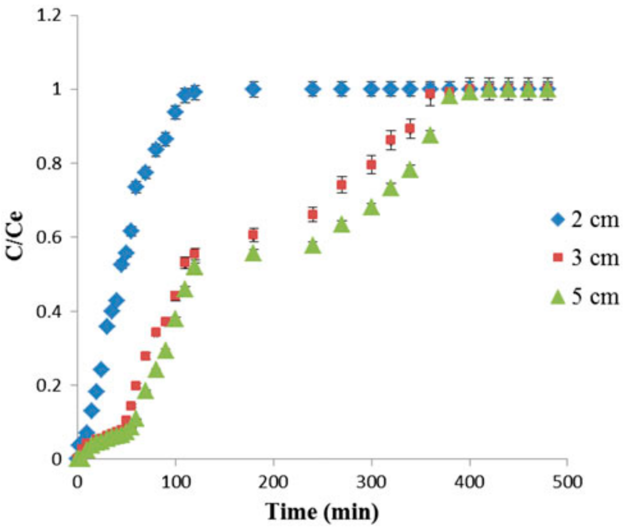

Fig. 6. Effect of bed height on Cu adsorption.

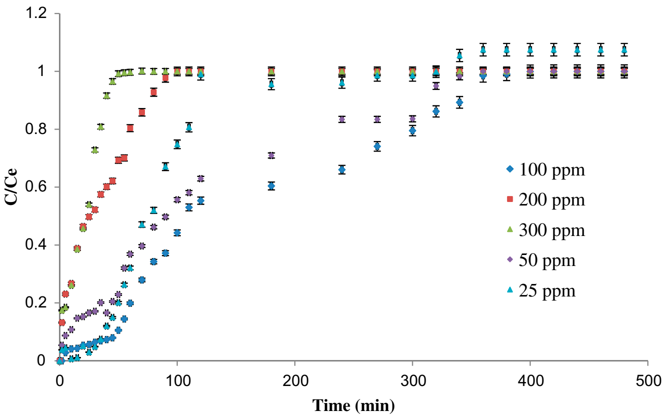

Fig. 7. Effect of initial concentration on Cu adsorption.

accelerated with an increase in the Cu^{2+} concentration. The removal of copper for concentration of 25 mg/L was 66%, whereas for 50, 100, 200, and 300 mg/L the removal was 70, 79, 51, and 50%, respectively. Fig. 7 gives the break through curve for different concentration. It indicates that the column exhausted very fast for initial higher concentration and takes very long time for lower concentration i.e. 25 and 50 mg/L. The initial metal ion concentration acts as a driving force to overcome mass transfer resistance for metal ion transport between the solution and the surface of the adsorbent. But as the concentration rises the active sites get occupied by copper ions and further removal is not possible. Although, the rate of uptake is very fast at higher concentration, it also saturates the available active sites on the surface of functional groups, preventing further metal ion uptake [29].

3.3.4. Effect of multi-metal ions

The presence of anions showed negligible effect on the copper adsorption in the batch mode, whereas in the presence of cations the reduction was evident. Hence, the column study for effect of ions was done in the presence of cations. The equimolar concentration of Ca^{2+}, Mg^{2+}, and copper was introduced as a feed to the column and under optimum conditions the column performance was studied. The result showed that column has exhausted early in comparison with the absence of cations. Moreover, the column efficiency has reduced from 79 to 56.7% in the absence and presence of multi-metal ions, respectively.

Table 4
Variation of mass transfer coefficient with flow rate, bed height, and initial concentration

Parameters		Mass transfer coefficient $K_{La} \times 10^2$ (s^{-1})
Flow rate (mL/min)	0.50	2.4
	0.75	3.1
	1.00	3.3
	2.00	2.8
Height (cm)	2.00	3.3
	3.00	3.1
	5.00	2.9
Concentration (mg/L)	25	2.2
	50	2.6
	100	3.1
	200	2.3
	300	2.1
Multi-metal ions	Ca^{2+} Mg^{2+}	2.4

3.3.5. Mass transfer coefficient

The uptake of Cu^{2+} species from the solution to the adsorbent is carried out by transfer of mass from the former to the latter. The overall sorption process is assumed to occur in three steps [12]:

(1) Mass transfer of copper ions from the aqueous phase onto the solid surface.
(2) Sorption of copper ions on to the surface sites.
(3) Internal diffusion of copper ions via either a pore diffusion or homogeneous solid-phase diffusion.

An increase in the initial concentration of Cu^{2+} makes the breakthrough curves much steeper. It is evident from the Table 4, an increase in the mass transfer coefficient with an increase in initial concentration of copper. As the concentration of copper in the feed increases from 25 to 100 mg/L, the mass transfer coefficient increases from 2.2×10^{-2} to $3.1 \times 10^{-2}\,s^{-1}$.

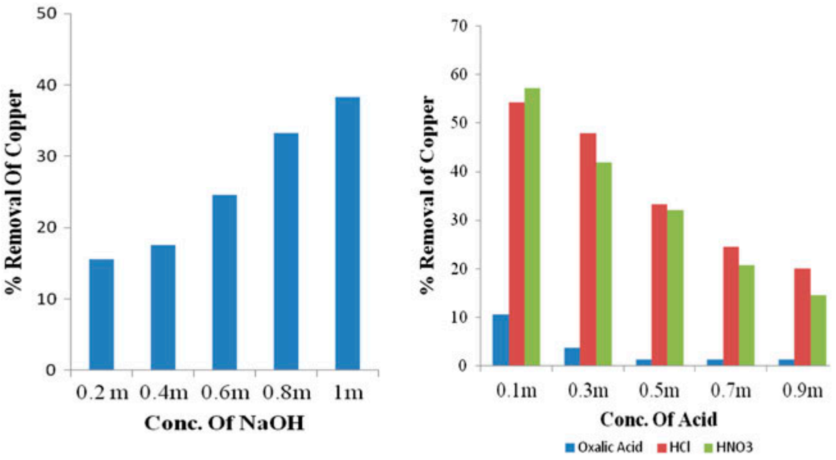

Fig. 8. Desorption of copper using different solvents.

Further as the concentration of copper is increased to 300 mg/L mass transfer coefficient values drop down to $2.1 \times 10^{-2}\,s^{-1}$ This can be anticipated on the basis that the driving force for mass transfer increases with an increase of concentration of adsorbates in the solution and thus increasing the mass transfer coefficient, but eventually further increase in concentration saturates the active sites thereby preventing the removal of copper ions. Table 4 also shows the effect of flow rate on mass transfer coefficient whereby increasing the flow rate may be expected to make reduction of the liquid film thickness. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate as well as there is not enough time for sorption equilibrium to be reached. This phenomenon is in agreement as observed by Ravikumar et al. [30]. The optimum flow rate for the experiments was found to 0.75 mL/min based on the breakthrough which is significant from the K_{La} value of $3.1 \times 10^{-2}\,s^{-1}$. Concerning the bed height generally indicates that the longer the bed, the better the process performance. The value of K_{La} values of mass transfer coefficient is almost similar for all the heights. The mass transfer coefficient was evaluated for copper adsorption in the presence of multi-metal ions and was $2.4 \times 10^{-2}\,s^{-1}$.

3.4. Desorption

To study the reusability of the biosorbent material and to recover the metal ions so that the process becomes economical and the wastewater treatment cost-effective, desorption was carried out by using different solvents with varying concentrations. Fig. 8 depicts the desorption capacity of different sorbents. The desorption solvents screened were varied concentrations of NaOH, HCl, HNO_3, and Oxalic acid. Desorption studies by NaOH showed the least recovery as compared to other adsorbents. For different concentrations of NaOH, the maximum recovery obtained was 38% by 1 M NaOH. HCl showed satisfactory removal efficiency but being a weak organic acid, oxalic acid showed poor results. It can be seen from Fig. 8 that the maximum desorption of 59% occurs at lower concentration of HNO_3 i.e. 0.1 M which indicates desorption is favorable in acidic pH as the Cu^{2+} ion is replaced by the acidic H^+ ion.

4. Conclusions

AHH has a significant potential as a sorbent for application as remedy for copper effluent. In the present study, the optimum conditions for sorption mechanism are contact time 60 min, pH 5, and temperature 50˚C. The isotherm study indicates that the sorption data fits Freundlich isotherm with high correlation factor. The mechanism of copper removal on AHH occurred through ion-exchange and physical sorption. The copper uptake for real wastewater was obtained to be 9.2 mg/g which is comparable with the adsorption capacity of copper in the presence of multi-metal ions (cations). The decline in copper ion capacity may be due to presence of excess cations in the real wastewater. From the desorption study, HNO_3 proves to be an efficient desorption solvent and thus making the process feasible. The values of mass transfer coefficient shows a significant effect on the breakthrough curve and indicated that at lower bed height and flow rate efficient sorption of copper can be achieved. This data can be used further for the design of a packed column for the removal of copper from aqueous stream using AHH.

References

[1] A. Bhatnagar, A.K. Minocha, Biosorption optimization of nickel removal from water using *Punica granatum* peel waste, Colloids Surf. B. 76(2) (2010) 544–548.

[2] S. Loutseti, D.B. Danielidis, A. Economou-Amilli, C. Katsaros, R. Santas, P. Santas, The application of a micro-algal/bacterial biofilter for the detoxification of copper and cadmium metal waste, Biores. Technol. 100(20) (2009) 99–105.

[3] G.E. Batley, S.C. Apte, J.L. Stauber, Speciation and bioavailability of trace metals in water: Progress since 1982, Aust. J. Chem. 57 (2004) 903–919.

[4] S. Rengaraj, J. Yeon, Y. Kim, Y. Jung, K. Ha, W.H. Kim, Adsorption characteristics of Cu(II) onto ion exchange resins 252H and 1500H: kinetics, isotherms and error analysis, J. Hazard. Mater. 143 (2007) 469–477.

[5] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, Process Biochem. 38(7) (2000) 1047–1061.

[6] I. Bakkaloglu, T.J. Butter, L.M. Evison, F.S. Holland, I.C. Hancock, Screening of various types of biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedimentation and desorption, in: IAWQ 19th Biennial International Conference: Vancouver, Canada (1998).

[7] B. Volesky, Detoxification of metal-bearing effluents: Biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.

[8] W. Jianlong, C. Can, Biosorbents for heavy metals removal and their future, Biotech Adv. 27 (2009) 195–226.

[9] W.S. Wan Ngah, M. A. K. M. Hanafiah, Adsorption of copper on rubber (Hevea brasiliensis) leaf powder: Kinetic, equilibrium and thermodynamic studies, Biochem. Eng. J. 39 (2008) 521–530.

[10] F. Umar, A. Janusz, M.A.K. Kozinski, A. Makshoof, Biosorption of heavy metal ions using wheat based biosorbents—A review of the recent literature, Biores. Technol. 101 (2010) 5043–5053.

[11] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: A review, J. Hazard. Mater. 157 (2008) 220–229.

[12] E. Valdman, L. Erijman, F.L.P. Pessoa, S.G.F. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum* sp., Process Biochem. 36 (2001) 869–873.

[13] R.W. Gaikwad, Mass transfer studies on the removal of copper from wastewater using activated carbon derived from coconut shell, J. Univ. Chem. Technol. Metallurgy 46(1) (2011) 53–56.

[14] B.V. Babu, S. Gupta, Modeling and simulation for dynamics of packed bed adsorption, Chem. Conf, Mumbai, 2004.

[15] S.G. Susmita, G. Krishna, G. Bhattacharyya, Adsorption of Ni(II) on clays, J. Colloid Interface Sci. 295 (2006) 21–32.

[16] A. Ozcan, A. Safa, S. Ozcan, T. Tunali, I.K. Akar, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of, J. Hazard. Mater. B124 (2005) 200–208.

[17] A. Witek-Krowiak, R.G. Szafran, S.S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination 265 (2011) 126–134.

[18] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of copper (II) from aqueous solutions by wheat shell, Desalination 164 (2004) 135–140.

[19] K. Banerjee, S.T. Ramesh, R. Gandhimathi, P.V. Nidheesh, K.S. Bharathi, A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions, Iran. J. Eng. Environ. 3(2) (2012) 143–156.

[20] Ö. Demirbaş, A.M. Karadağ, M.D. Alkan, Removal of copper ions from aqueous solutions by hazelnut shell, J. Hazard. Mater. 153 (2008) 677–684.

[21] P. SenthilKumar, S. Ramalingam, V.S. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell, Desalination 266 (2011) 63–71.

[22] K.K. Krishnani, X. Meng, C.V. Christodoulatos, M. Boddu, Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk, J. Hazard. Mater. 153 (2008) 1222–1234.

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

[24] P.D. Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, Waste Manage. 22 (2002) 471–480.

[25] A. Grimm, R. Zanzi, E. Björnbom, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, Bioresour. Technol. 99 (2008) 2559–2565.

[26] C. Zhu, L. Wang, W. Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull, J. Hazard. Mater. 168 (2009) 739–746.

[27] P. Sivakumar, P.N. Palanisamy, Adsorption studies of basic Red 29 by a non-conventional activated carbon prepared from Euphorbia antiquorum L., Int. J. Chem. Tec. Res. 1(3) (2009) 502–510.

[28] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column, J. Hazard. Mater. 113(1–3) (2004) 223–230.

[29] P. Puranik, R.K. Paknikar, Biosorption of lead and zinc from solutions using Streptoverticillium cinnamoneum waste biomass, J. Biotechnol. 55(2) (1997) 113–124.

[30] K. Ravikumar, S. Krishnan, S. Ramalingam, K. Balu, Optimization of process variables by the application of response surface methodology for dye removal using a novel adsorbent, Dyes Pigm. 72(1) (2007) 66–74.