



## Removal of Copper(II) Using Bio-adsorbents from Prepared Aqueous Solution

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### ABSTRACT

The effect of pH, dose of adsorbent, concentration of Cu(II), and contact time has been studied well on adsorption rate of Cu(II) from aqueous solution using commercially available activated carbon (CAC), prepared activated carbon from cotton stem (PACC) and prepared activated carbon from bagasse (PACB). Increased adsorption of Cu(II) by CAC, PACC and PACB was found at pH 6. The adsorption of Cu(II) was observed to be highest at 4g, 5g and 6g dose of CAC, PACC and PACB respectively. Adsorption was observed maximum at PACC (90.5%)>PACB (87.5 %)>CAC (85.5%) in a solution containing 25 mg/L concentration of Cu(II) for all PACs. Comparable adsorption was observed at contact time for CAC (30 min), PACC (60 min) and PACB (90 min). The results revealed that all the adsorbents have ability to adsorb Cu(II) significantly at particular pH, dose, concentration and time.

### INTRODUCTION

It has been pointed out by several scholars that presence of heavy metal traces in ecosystems is hazardous to health of animals and human beings (Gupta & Diwan 2017, Sankhla et al. 2016, Dash et al. 2015). Heavy metal pollution has been observed to be most dangerous threat to environment. The main sources of heavy metals are the waste disposal from different industries viz., mining, surface finishing, energy and fuel production, fertilizers and pesticides, electroplating, nuclear energy power stations, tannery, electrolysis and photography industries which leads to environmental pollution (Al-Homaidan et al. 2014, Kanyal & Bhatt 2015). Moreover, rapid increase in modern technologies in industrial sector has been responsible for adverse consequences of water, soil and air pollution. Hence, heavy metal contaminants are considered to be serious due to harmful impact on human health and ecological diversity (Alluri et al. 2007, Kamble et al. 2010).

The mitigation of heavy metal pollution is an important concern to evade health hazards and toxic impacts of it. A number of advanced techniques have been developed to minimize or remove heavy metals from wastewater generating from industries before discharge into natural water bodies. The techniques include reverse osmosis,

electrophoresis, ion-exchange, chemical coagulation, chemical precipitation, bioremediation and phytoremediation etc. which are used for heavy metal removal from effluents (Kanyal & Bhatt 2015).

However, complete removal and cost effectiveness, make these methods as limiting factor. Further, cautious disposal of effluents without heavy metals in environment is the need of time (Ahalya et al. 2003). To tackle with this problem, alternative use of microbial biomass, microorganisms like *Aspergillus*, *Pseudomonas*, *Sporophyticus*, *Bacillus*, *Phanerochaete*, etc. and activated carbon prepared by using woody biomass have been applied in industrial and wastewater treatment processes (Congeevaram et al. 2007, Al-Homaidan 2014, Yan & Viraraghavan 2003, Gopalan & Veeramani 1994).

Copper, a toxic heavy metal in environment gets accumulated easily in biological food chains due to contaminated food, water and air. Copper toxicity causes acute impact on human beings mainly anaemia, intravascular haemolytic, acute liver and renal failure with tubular damage, shock, coma and death. Even lower concentrations may lead to vomiting, nausea and diarrhoea (Salvadori et al. 2014, Wylie 1957, Spitalny et al. 1984, Knobloch et al. 1994). It is not easily digested or metabolized and can be harmful to

human health (Dermentzis et al. 2009). At least five transition metals or metalloids in one form or the other, are accepted as human carcinogens by International Agency for Research on Cancer (Farajzadeh & Monji 2004). Continued inhalation of copper containing spray is linked with an increase in lung cancer among exposed workers (Nwabanne & Igbokwe 2012). There are several studies attempting removal of copper using biomass or microorganisms (Gupta & Diwan 2017).

The present paper documents, how to remove Cu(II) by prepared activated carbon using cotton stem and bagasse at various pH, adsorbent dose, concentration and contact time through aqueous medium. The results were compared with commercially available activated carbon.

## MATERIALS AND METHODS

**Collection of raw material for preparation of activated carbon:** Preparation of activated carbon was carried out by Nwabanne and Igbokwe method (Nwabanne & Igbokwe 2012). Cotton stem and bagasse were collected from local market and sugar industrial plant of Pravaranagar respectively. Materials were cut in to small pieces of 2-3 cm size and dried in sunlight. The dried material was soaked in a boiling solution of 10% phosphoric acid for an hour and dried at room temperature for 24 h. The contents were then carbonized in muffle furnace at 400°C for 1 h and washed with distilled water. The residual char was also ground using mortar and pestle to make powder. At last powdered contents were again heated at 600°C for 10 min. The sieves size of the carbon powder was then determined by using various micron sieves using sieve shaker. In the present study less than 106 µm size prepared carbon powder was used.

**Ash content:** Ash percentage was determined by heating 1 g of finely powdered char at 500°C for 1 h in Muffle furnace (Nwabanne & Igbokwe 2012).

**Moisture content:** It was determined by heating 1 g of air-dried charcoal powder for about 1 h at 105°C in oven (Nwabanne & Igbokwe 2012).

**Surface area and iodine number:** The surface area of adsorbent was measured using oxalic acid solution, 0.1 N NaOH and phenolphthalein indicator. Larger the surface area more is the adsorption, using sear method. The specific surface area of the activated carbon was measured using Sear's method (Al-Qodah & Shawabkah 2009, Al-Najar 2009). The iodine number was determined by using sodium thiosulphate volumetric method (ASTM 2006).

**Sieve size:** The sieve size was determined by using various microns with the help of sieve shaker. The collected powdered material was retained by each sieve and size was recorded (ASTM 2006).

## Experimental Setup

**Stock solution:** The stock solution of Cu(II) (100 mg/L) was prepared in laboratory by dissolving 0.392 mg of cupric sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , Merck) in 1000 mL distilled water. The stock solution was stored in Borosil glass bottle at room temperature.

**Batch study:** Batch adsorption studies were conducted for the experiments. The activated carbon obtained from locally available agricultural materials cotton plant stem (PACC) and bagasse (PACB) and commercially available activated carbon (CAC, Merck) were used as adsorbents in order to study removal of copper (II) from aqueous solution.

Sieve size less than 106 µm was selected for experimental purpose. Batch adsorption studies were conducted at various pH (2, 4, 6, 8), dose (1, 2, 3, 4, 5, 6 g), concentration (25, 50, 75, 100 mg/L) and contact time (30, 60, 90, 120 min). The contents were kept in separate conical flasks of 50 mL capacity. Contents of the flasks were well mixed by using controlled shaking for 1 h and subsequently filtered through Whatman 41 and finally taken for analysis of Cu(II) using atomic absorption spectrometer (AAS).

**Effect of pH on adsorption:** 50 mL of solution of Cu(II) of 100 mg/L concentration was kept in 5 different conical flasks. pH was adjusted to 2, 4, 6 and 8 by adding 0.1 N HCL and 0.1 N NaOH. At the constant amount of adsorbent dose (1 g) activated carbon treatment was given for time of 2 h. All treatments were given in duplicates.

**Effect of doses on adsorption:** Various doses of the adsorbent activated carbon 1g, 2g, 3g, 4g, 5g and 6g were added to each conical flask and kept on shaker for 2 h. Cu(II) solution of 100 mg/L was used in the flasks.

**Effect of Cu(II) concentration on adsorption:** 50 mL each of different concentrations of 25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L of Cu(II) solution was taken in 5 different flasks in duplicate. pH was adjusted to 6 by using 0.1 N HCL and 0.1 N NaOH. The adsorbent dose of activated carbon 4g, 5g, 6g of CAC, PACC and PACB respectively was added as optimum dose to each conical flask containing solution and treated for 2 h.

**Effect of contact time on adsorption:** The adsorbent dose of activated carbon 4g, 5g and 6g of CAC, PACC and PACB respectively was added in duplicate to the solutions and kept for various contact time interval of 30, 60, 90 and 120 min. 50 mL of 75 mg/L Cu(II) solution was treated for this purpose.

**Statistical analysis:** The average values and standard errors have been calculated using statistical formula. Graphs were plotted using KaleidaGraph Synergy software 4.5.3.

## RESULTS AND DISCUSSION

The moisture content of CAC, PACC and PACB was observed to be 4%, 8% and 6% respectively. Ash percentage of available activated carbon was 3.3% while of prepared activated carbon from cotton plant material and bagasse were 14% and 15% respectively. The iodine number of available commercially activated carbon was 700.52, prepared activated carbon from cotton plant material was 530.91 while for bagasse it was 479.30 (Table 1). The surface area ( $\text{m}^2/\text{g}$ ) of CAC was  $6.1 \times 10^8$  and PACC and PACB was  $2.496 \times 10^7$  and  $1.2134 \times 10^7$  respectively.

The residual concentration ( $\text{mg/L}$ ) of Cu(II) after treatment at various pH and time is reported in Table 2, while after treatment at various concentrations and at different dosages of activated charcoal is presented in Table 3. In case of pH treatment, concentration of Cu(II) with CAC at pH of 2, 4, 6 and 8 was 56.5 ( $\pm 1.5$ ), 49.5 ( $\pm 1.5$ ), 24.5 ( $\pm 0.5$ ) and 30.5 ( $\pm 0.05$ )  $\text{mg/L}$  respectively. However, in case of PACC it was 57.5 ( $\pm 1.5$ ), 59.5 ( $\pm 1.5$ ), 44.5 ( $\pm 0.5$ ) and 50.5 ( $\pm 1.5$ )  $\text{mg/L}$  respectively at pH 2, 4, 6 and 8, while by using PACB it was 55.5 ( $\pm 1.5$ ), 50.0 ( $\pm 1.0$ ), 46.5 ( $\pm 0.5$ ) and 52.5 ( $\pm 1.0$ )  $\text{mg/L}$  respectively. Initial concentration of Cu(II) was 100  $\text{mg/L}$  for treatment at various pH (Table 2). In case of different time intervals of treatment, concentration of Cu(II) with CAC at 30, 60, 90 and 120 min was 6.4 ( $\pm 1.6$ ), 11.3 ( $\pm 1.1$ ), 11.3 ( $\pm 1.1$ ) and 10.9 ( $\pm 0.5$ )  $\text{mg/L}$  respectively at the initial concentration of 75  $\text{mg/L}$  (Table 2). However, in case of PACC it was 14.6 ( $\pm 0.4$ ), 8.6 ( $\pm 0.4$ ), 13.9 ( $\pm 0.4$ ) and 14.3 ( $\pm 0.8$ )  $\text{mg/L}$ , while with PACB it was 18.8 ( $\pm 0.8$ ), 17.6 ( $\pm 1.9$ ), 11.3 ( $\pm 0.0$ ) and 12.4 ( $\pm 0.4$ )  $\text{mg/L}$  respectively at the same time intervals.

In case of different concentrations of Cu(II) at 25, 50, 75 and 100  $\text{mg/L}$ , after treatment concentration of Cu(II) with CAC was 3.6 ( $\pm 1.2$ ), 4.1 ( $\pm 1.0$ ), 3.4 ( $\pm 0.8$ ) and 5.4 ( $\pm 0.4$ )  $\text{mg/L}$  respectively. However, in case of PACC it was 2.4 ( $\pm 0.3$ ), 4.1 ( $\pm 0.4$ ), 4.8 ( $\pm 1.3$ ) and 5.8 ( $\pm 0.9$ )  $\text{mg/L}$ , while in case of PACB it was 3.1 ( $\pm 1.1$ ), 5.1 ( $\pm 0.9$ ), 6.1 ( $\pm 1.7$ ) and 6.9 ( $\pm 1.9$ )  $\text{mg/L}$  respectively (Table 3). In case of different dosage, after treatment concentration of Cu(II) with CAC at 1, 2, 3, 4, 5 and 6g/100 mL was 26 ( $\pm 1.0$ ), 34 ( $\pm 1.0$ ), 32 ( $\pm 2.0$ ) and 19 ( $\pm 1.0$ ), 25 ( $\pm 1.0$ ) and 24.5 ( $\pm 0.5$ )  $\text{mg/L}$  respectively. However, in case of PACC it was 47 ( $\pm 2.0$ ), 55 ( $\pm 3.0$ ), 43 ( $\pm 1.0$ ), 38.5 ( $\pm 2.5$ ), 21.5 ( $\pm 0.5$ ) and 37 ( $\pm 1.0$ )  $\text{mg/L}$ , while in case of PACB it was 49.5 ( $\pm 2.5$ ), 50.5 ( $\pm 0.5$ ), 45 ( $\pm 1.0$ ), 34.5 ( $\pm 0.5$ ), 28.5 ( $\pm 0.5$ ) and 25 ( $\pm 1.0$ )  $\text{mg/L}$  respectively at the same doses of the adsorbent. For this treatment initial concentration of 75  $\text{mg/L}$  of Cu(II) was used (Table 3).

The garden grass was firstly used by Hossain et al. (2012) to remove copper (II) from water as bioadsorbent where they observed higher adsorption and desorption capacities by

Table 1: Physical and chemical characteristics of CAC, PACC and PACB.

Parameter	CAC	PACC	PACB
Ash (%)	3.3	14	15
Moisture (%)	4	8	6
Iodine Number	700.52	530.91	479.30
Surface Area ( $\text{m}^2/\text{g}$ )	$6.1 \times 10^8$	$2.496 \times 10^7$	$1.2134 \times 10^7$
Sieve Size ( $\mu\text{m}$ )	106	106	106

58.34 and 319.03  $\text{mg/L}$  respectively. They also observed that actual amount of copper adsorbed per unit mass of garden grass increased from 14.06 to 137.12  $\text{mg/g}$  with increase in copper concentration from 10 to 100  $\text{mg/L}$  in test water. The biosorption studies on lead, copper and cadmium using different cortex fruit wastes including banana (*Musa paradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peel have been evaluated by Kelly Vargas et al. (2012) where they found that banana peel was capable of adsorbing around 65  $\text{mg}$  of Pb and Cd per gram but only 36  $\text{mg}$  of Cu per gram.

The potential of NPN (Nipa Palm Nut), PPN (Palmyra Palm Nut), EFB (Oil Palm Empty Fruit Brunch), OPF (Oil Palm Fibre) and OPS (Oil Palm Shell) as low cost adsorbents for the removal of Cu from aqueous solution was studied well. The study reported that NPN and PPN were very efficient adsorbents for removing Cu from aqueous solution. They also reported ranking of adsorbents for the removal of Cu and showed following order as NPN > PPN > EFB > OPE > OPS. Cu(II) adsorption was found to be dependent with adsorption dose, pH, initial ion concentration, particle size, and content time (Nwabanna & Igbokwe 2012). The percentage of copper (II) adsorption decreased from 86.03% to 76.17% with the increase of initial copper (II) concentration while studying biosorption of copper onto cashew nut shell from 10 to 50  $\text{mg/L}$  (Senthilkumar et al. 2011).

Nakbanpote et al. (2007) studied copper (II) ions adsorption on rice husk (RH), cellulose extracted from rice husk (RH-cellulose), rice husk heated to 300°C (RHA 300) and rice husk heated to 500°C (RHA 500) to understand sites of adsorption.

Najim et al. (2009) observed copper ion removal by pine fruit as adsorbent by 94.1- 96% along the whole range of initial concentrations. Larous et al. (2005) have studied the sawdust as adsorbent and mechanism of copper (II) adsorption at solid-solution interface for effective removal from river water samples. Ahmad et al. (2008) investigated that about to 95% copper (II) removal is possible in concentration below  $4 \times 10^{-4}$  M (68.216  $\text{mg/L}$ ) and about 85% removal was achieved in the concentration range between  $4 \times 10^{-4}$  M and  $1 \times 10^{-3}$  M by activated carbon.

**Effect of pH on adsorption of Cu(II):** pH is an important factor for adsorption of metal ions and directly influence metal solubility or the dissociation degree of functional groups situated on surface of adsorbent (Al-Homaidan 2014). Fig. 1 (A) illustrates effect of pH change on adsorption in CAC. This dependence is closely related to the acid-base properties of various functional groups on adsorbent surface (de Godoi Pereira & Arruda 2003). At lower pH, due to protonation of the binding sites resulting from high concentration of protons, the negative charge intensity on the sites is reduced, resulting in reduction or even inhibition of binding of metal ions (Kanyal & Bhatt 2015, Mohammad et al. 2013, Yusoff et al. 2014). It is fact that, as pH of the solution increased, OH ions also increase and form complexes with metal ions and precipitate as metal hydroxides (Al-Najar 2009).

Adsorption percentage of Cu(II) was moderately increased at pH 2, pH 4 and pH 6 up to 43.5 % ( $\pm 1.5$ ), 50.5% ( $\pm 1.5$ ) and 75.50% ( $\pm 0.5$ ) respectively, and then decreased to 69.5 % ( $\pm 0.5$ ) at pH 8. It was observed that, optimum pH for the adsorption of Cu(II) by CAC was attained at pH 6.

In case of PACC, adsorption percentage was increased at pH 2, pH 4 and pH 6 and was 42.5 % ( $\pm 1.5$ ), 40.5 % ( $\pm 1.5$ ) and 55.5 ( $\pm 0.5$ ) respectively, then it showed decline to 49.5% ( $\pm 1.5$ ) at pH 8. Here also, optimum pH was 6 for adsorption of Cu(II) by PACC Fig. 1 (A).

In case of PACB, Cu removal at pH 2, pH 4 and pH 6 was 44.5 % ( $\pm 1.5$ ), 50 ( $\pm 1.0$ ) and 53.5% ( $\pm 0.5$ ) respectively, and then decreased to 48% ( $\pm 1.0$ ) at pH 8. The pH 6 was optimum pH for the adsorption of Cu(II) for all the three activated carbons (Fig. 1A). The Cu(II) adsorption was affected

in CAC, PACC and PACB by acidic pH (2 and 4) and also by slightly alkaline pH (7 and 8). Moreover, our results are in accordance with other studies (Al-Homaidan et al. 2014, Vannela & Verma 2006). Kaewsarn (2002) has argued that increased pH resulted in decreased protons because of which the competition between proton and heavy metal significantly decreases. At higher pH concentration of protons decreases and the surface of the adsorbent became negative which increases the adsorption of metal ions. The solubility of metal ions also decreases at higher pH facilitating the adsorption. The further increase of pH results in precipitation of metal ions as hydroxides (Shrestha et al. 2013). At higher pH, that is, above optimum pH of 6, increase in OH<sup>-</sup> ions cause a decrease in adsorption of metal ions at adsorbent-adsorbate interface (Namasivayam & Periasamy 1993). An increase in metal adsorption with increasing pH values can be explained on the basis of competition between the proton and metal ions for the same functional groups, and a decrease in the positive surface charge, which results in a higher electrostatic attraction between the biosorbent surface and the metal (Senthilkumar et al. 2000). Thus the increase in pH helps to increase adsorption of Cu(II) while at the edge of alkaline pH resulted into the decrease in adsorption (Kanyal & Bhatt 2015, Al-Homaidan 2014). At increased pH value biomass surface was observed to be more negatively charged while biosorption of metal ions with positive charge Cd(II) and Cu(II) reached maximum around pH 5 (El Hassouni et al. 2014). Meena et al. (2005) found maximum removal of Cu(II), Zn(II) and Ni(II) at pH 6, which was nearly 88.8, 93.3 and 69%, respectively.

**Effect of adsorbent dose on adsorption of Cu(II) from aqueous solution:** In case of CAC (Fig. 1 B) removal efficiency of

Table 2: Residual concentration of Cu(II) in mg/L after treatment with different pH and time.

Name of Adsorbent	Initial concentration 100 mg/L				Initial concentration 75 mg/L			
	pH 2	pH 4	pH 6	pH 8	30 min	60 min	90 min	120 min
CAC	56.5( $\pm 1.5$ )	49.5( $\pm 1.5$ )	24.5( $\pm 0.5$ )	30.5( $\pm 0.5$ )	6.4( $\pm 1.1$ )	11.3( $\pm 0.8$ )	11.3( $\pm 0.8$ )	10.9( $\pm 0.4$ )
PACC	57.5( $\pm 1.5$ )	59.5( $\pm 1.5$ )	44.5( $\pm 0.5$ )	50.5( $\pm 1.5$ )	14.6( $\pm 0.4$ )	8.6( $\pm 0.4$ )	13.9( $\pm 0.4$ )	14.3( $\pm 0.8$ )
PACB	55.5( $\pm 1.5$ )	50.0( $\pm 1.0$ )	46.5( $\pm 0.5$ )	52.0( $\pm 1.0$ )	18.8( $\pm 0.8$ )	17.6( $\pm 1.9$ )	11.3( $\pm 0.0$ )	12.4( $\pm 0.4$ )

Table 3: Residual concentration of Cu(II) in mg/L after treatment with increasing concentrations of Cu(II) and at different doses of activated charcoal.

Name of Adsorbent	Concentration of Cu(II)				Initial Concentration of Cu 100 mg/L					
	25 mg/L	50 mg/L	75 mg/L	100 mg/L	1 g	2 g	3 g	4 g	5 g	6 g
CAC	3.6( $\pm 1.2$ )	4.1( $\pm 1.0$ )	3.4( $\pm 0.8$ )	5.4( $\pm 0.4$ )	26( $\pm 1.4$ )	34( $\pm 1.4$ )	32( $\pm 2.8$ )	19( $\pm 1.4$ )	25( $\pm 1.4$ )	24.5( $\pm 0.7$ )
PACC	2.4( $\pm 0.3$ )	4.1( $\pm 0.4$ )	4.8( $\pm 1.3$ )	5.8( $\pm 0.9$ )	47( $\pm 2.8$ )	55( $\pm 4.2$ )	43( $\pm 1.4$ )	38.5( $\pm 3.5$ )	21.5( $\pm 0.7$ )	37( $\pm 1.4$ )
PACB	3.1( $\pm 1.1$ )	5.1( $\pm 0.9$ )	6.1( $\pm 1.7$ )	6.9( $\pm 1.9$ )	49.5( $\pm 3.5$ )	50.5( $\pm 0.7$ )	45( $\pm 1.4$ )	34.5( $\pm 0.7$ )	28.5( $\pm 0.7$ )	25( $\pm 1.4$ )

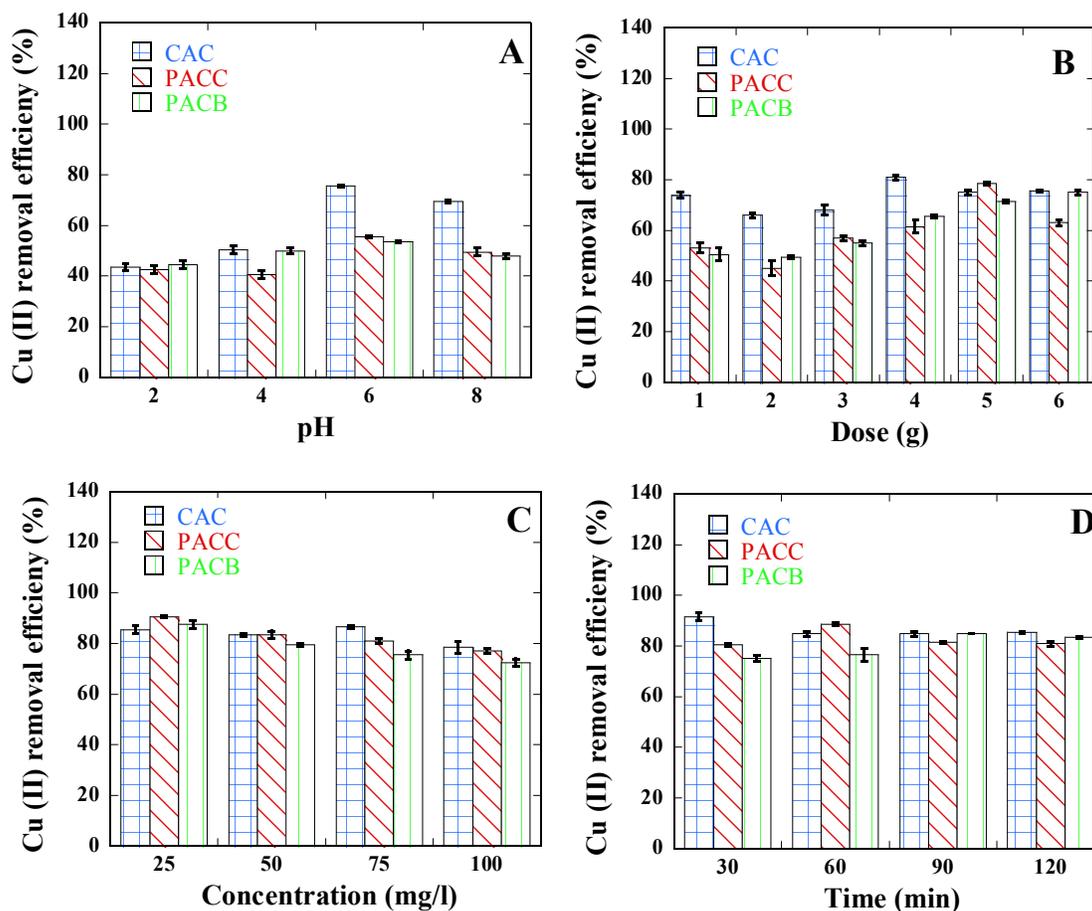


Fig. 1: (A) Effect of change in pH on Cu(II) removal on adsorbent, (B) Effect of adsorbents dose on Cu(II) removal on adsorbent, (C) Effect of concentration on Cu(II) removal on adsorbent, (D) Effect of contact time on removal of Cu(II) on adsorbent.

Cu(II) at adsorbent dose of 1 g/100 mL, 2 g/100 mL, 3 g/100 mL, 4 g/100 mL, 5 g/100 mL, 6 g/100 mL was 74% ( $\pm 1.0$ ), 66% ( $\pm 1.0$ ), 68% ( $\pm 2.0$ ), 81% ( $\pm 1.0$ ), 75% ( $\pm 1.0$ ) and 75.5% ( $\pm 0.5$ ) respectively. The optimum dose for adsorbent was 4 g which showed higher percentage of adsorption (81%).

In case of PACC (Fig. 1 B) removal of Cu(II) at adsorbent dose of 1 g/100 mL, 2 g/100 mL, 3 g/100 mL, 4 g/100 mL, 5 g/100 mL and 6 g/100 mL was 23% ( $\pm 2.0$ ), 45% ( $\pm 3.0$ ), 57% ( $\pm 1.0$ ), 61.5% ( $\pm 2.5$ ), 78.5% ( $\pm 0.5$ ) and 63% ( $\pm 1.0$ ) respectively. However the optimum dose was 5 g for adsorption of Cu(II) in PACB, while the adsorbent doses 1, 2, 3, 4, 5, 6 g were 50.5% ( $\pm 2.5$ ), 49.5% ( $\pm 0.5$ ), 55% ( $\pm 1.0$ ), 65.5% ( $\pm 0.5$ ), 71.5% ( $\pm 0.5$ ) and 75% ( $\pm 1.0$ ) respectively, and optimum dose was 6 g.

The removal efficiency of metals is predominantly dependent on quantity of the biosorbent. Several researchers have reported that increase in percentage removal with increase in sorbent dosage is due to greater availability of the exchangeable sites or surface area at higher

concentration of the biosorbent (Bermúdez et al. 2012, Rao Popuri et al. 2007). Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites (Mall et al. 2006, Abdel Wahab 2007, Vijayaraghavan et al. 2009, Esposito 2001). The decrease in biosorption efficiency with further increase in biomass dose above 1 g could be explained as a consequence of a partial aggregation of biomass, which results in decrease in effective surface area for the biosorption process (Karthikeyan et al. 2007). Moreover, Bansal & Goyal (2005) have explicitly argued that the adsorption performance may depend on analytical method used for decontamination test like batch method, column, reactors, etc. (Bansal & Goyal 2005).

More specifically, the rates of these parameters are high for lower adsorbent doses and low for the higher ones, due to the progressive partial saturation of the active sites in the solution (Aydin et al. 2008, El-Ashtouky et al. 2008).

However, several workers also showed that bioabsorbants were better for removal of heavy metals from wastewaters. Chromium and nickel resistant microorganisms were isolated from wastewater and contaminated environments. The organisms were used to remove heavy metals from industrial wastes (Congeevaram et al. 2007). Al-Homaidan et al. (2014) revealed that microbes act as absorbent of Cu. They used micro-alga, *Spirulina platensis* as bioabsorbent of Cu from aqueous solution. They exposed various concentrations of Cu and various different conditions of absorbents and reported best eco-remedial techniques for heavy metal removal from aqueous medium.

**Effect of concentration on adsorption of Cu(II):** In case CAC the removal efficiency of Cu(II) at the concentration of Cu(II) 25, 50, 75 and 100 mg/L was 85.5% ( $\pm 1.5$ ), 83.5% ( $\pm 0.5$ ), 86.5% ( $\pm 0.5$ ) and 78.5% ( $\pm 2.5$ ) respectively (Fig. 1C). It was revealed that the removal efficiency was higher at 25 mg/L concentration. Thus the optimum concentration for removal of Cu(II) was 25 mg/L.

In case of PACC the removal efficiency of Cu(II) at concentration 25, 50, 75 and 100 mg/L was 90.5% ( $\pm 0.5$ ), 83.5% ( $\pm 1.5$ ), 81% ( $\pm 1.0$ ) and 77% ( $\pm 0.1$ ), respectively. It was observed that the removal efficiency was 91% at concentration 25 mg/L. So the optimum concentration was 25 mg/L (Fig. 1C).

In case of PACB the removal efficiency of Cu(II) at concentration of Cu(II) 25, 50, 75 and 100 mg/L was 87.5% ( $\pm 1.5$ ), 79.5% ( $\pm 0.5$ ), 75.5% ( $\pm 1.5$ ) and 72.5% ( $\pm 1.5$ ) respectively for PACB. It was observed that the removal efficiency was higher at concentration 25 mg/L which was optimum concentration for removal of Cu(II) (Fig. 1C). As the concentration is increased, more metal ions are available in the solution for the adsorption process (Okure et al. 2010). It may be explained on the basis that at lower concentration of metal ions more adsorption sites are available on adsorbent but at higher concentration competing metal ions are increased for the available adsorption sites (Bhatti et al. 2007).

**Effect of contact time on adsorption of Cu(II) from aqueous solution:** In case of CAC, it was observed that removal efficiency of Cu(II) at contact time 30, 60, 90 and 120 min was 91.5% ( $\pm 1.5$ ), 85% ( $\pm 1.0$ ), 85% ( $\pm 1.0$ ) and 85.5% ( $\pm 0.5$ ) respectively. The optimum contact time for removal of Cu(II) was 30 min (Fig. 1D).

In case of PACC the removal efficiency of Cu(II) at contact time 30, 60, 90 and 120 min was 80.5% ( $\pm 0.5$ ), 88.5% ( $\pm 0.5$ ), 81.5% ( $\pm 0.5$ ) and 81% ( $\pm 1.0$ ) respectively. Thus, the optimum contact time for removal of Cu(II) was 60 min (Fig. 1D).

It was observed that removal efficiency of Cu(II) at

contact time 30, 60, 90 and 120 min was 75% ( $\pm 1.0$ ), 76.5% ( $\pm 2.5$ ), 85% ( $\pm 0.0$ ) and 83.5% ( $\pm 0.5$ ) respectively with PACB. Thus optimum contact time for removal of Cu(II) was 90 min (Fig. 1D).

The rapid stage may be due to abundantly available sites on the biomass and in the slower stage the occupancy of these sites becomes less efficient (Sengil & Ozacar 2008). Similar results were reported by Hizal et al. (2013) on biosorption of copper, cobalt and nickel by marine brown alga *Sargassum* in fixed-bed column. The initial high rate of adsorption of metal ions is due to free active binding sites available on the surface of the adsorbent, and as the number of available sites decreases the rate of adsorption of metal ions also decreases (Shrestha et al. 2013). This could also be due to the migration of higher fraction of the metal ions from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent as time progresses. This enhanced sorption of the metal ion with increase in agitation time, which may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in kinetic energy of the hydrated metal ions (Okuo et al. 2008). Equilibrium attained in relatively short contact time indicates that the adsorption of copper is a chemical-reaction controlled, rather than diffusion controlled process (Wahab et al. 2017, McKay 1995). Thus, the adsorption of Cu(II) ions took place in two distinct steps: a relatively fast one followed by a slower one (El-Ashtoukhy et al. 2008).

## CONCLUSION

Although many techniques can be employed for the treatment of wastewater and removal of copper, it is important to choose most appropriate treatment for metal which is based on basic factors such as pH, initial metal concentration, contact time and amount of adsorbent. There is a strong need of such treatment methods to reduce harmful environmental impacts. The best optimum conditions for the copper removal were pH 6, contact time of 30 min (CAC), 60 min (PACC) and 90 min (PACB), 25 mg/L of the metal concentration and 4g (CAC), 5g (PACC) and 6g (PACB) of dose of activated carbon.

The preparation of activated carbon and its use in treatment is indeed an eco-friendly and financially feasible for removal of Cu(II) and other heavy metals. It may, therefore, be concluded that cotton stem, bagasse and commercially available activated carbon could serve as cheap, readily available effective adsorbents for the removal of Cu(II).

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