

RESEARCH ARTICLE



ISSN: 2321-7758

ADSORPTION MODEL FOR THE REMOVAL OF Cu (II) FROM AQUEOUS SOLUTION USING AGRI-BYPRODUCT ACTIVATED CARBON

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Article Received: 11/07/2014

Article Revised on: 19/08/2014

Article Accepted on:21/08/2014



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International Journal of
Engineering
Research-Online



ABSTRACT

The present investigation deals with the utilization of *Borossus aethiopum* (palmyra) male inflorescence carbon as adsorbents [BAC 1 (raw) & BAC 2 (0.1M NaOH)] for the removal of copper from effluents. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial copper concentration, dose of adsorbents and effect of time were considered. The optimal pH value of copper (II) adsorption onto BAC was found to be pH range 4-3. While the removal efficiency decreased with increasing initial concentration, it increased with increasing adsorbent concentration. For the linear forms of the Langmuir and Freundlich models, the results indicated that the Langmuir adsorption isotherm fitted the data better than the Freundlich adsorption isotherm. Adsorption of these metal ions onto BAC was favorable sorption. Therefore, BAC, the low-cost agricultural waste, is suitable for use as adsorbent for copper ion under this investigation

INTRODUCTION

The progressive increase of industrial technology result in continuous increase of pollution, so that a great effort has been devoted for minimizing these hazardous pollutants and therefore avoiding their dangerous effects on animals, plants and humans. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity. These pollutants are toxic and non-biodegradable and probably have health effects. Conventional processes for heavy metal removal often are neither effective nor economical. Biosorption of heavy metals is one of the most promising technologies involved in removal of toxic metals from industrial waste streams and natural waters. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further research.

Copper is widely distributed in water since it is a naturally occurring element. Copper is an essential trace element, which in small amounts is essential for human health, but, as with many otherwise valuable substances, can be harmful in excess. The U.S. Environmental Protection Agency (EPA) has set a guidance level

for the USA limiting copper in drinking water to 1.3 mg/L (parts per million). The World Health Organization, an organization that many countries of the world rely upon for health guidance, has established a 2 mg/L copper guidance level.

A number of materials exist for the removal of heavy metal pollutant Cu (II) from liquid state when they are present in high concentrations. These include methods such as precipitation, evaporation, electroplating, ion-exchange and membrane processes. These processes are expensive, and also have other shortcomings, such as incomplete removal of metals, limited tolerance to pH change, moderate or no metal selectivity, very high or low working levels of metals, and production of toxic sludge or other waste products that also need disposal(1). From the literature survey it was concluded that removal of copper with activated carbons derived from various sources like, Ceiba pentandra hulls (2), Mn oxide-coated granular activated carbon (3), Pecan shell activated carbon (4), Modified activated carbon are carbonaceous adsorbents which have tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) (5), The macroalgae *Fucus vesiculosus* and peat,(6-7) , Agrobased xanthates, baggase xanthate (IBX) and insoluble wood xanthate (IWX), (8-9), Active carbon, impregnated carbon and bentonite loaded fabric strip, sugar beet pulp and fly ash, (10) Peanut hull carbon, (11) etc

The literature survey indicates that some of the carbons were used for the removal of copper earlier Palmyra male inflorescence carbon (12) was prepared and it was found that the cost is very cheap and was used for the removal of fluoride in potable water. So far no work was done with this carbon for the removal of tracer elements, hence the author chosen to work on the efficacy in the removal of copper from the industrial effluents. The present work is on the removal of copper using the low cost Palmyra inflorescence carbon (KAZA's carbon) in the industrial effluents.

MATERIALS AND METHODS

Bio-Material: *Borassus aethiopum* (Figure 1) is an unbranched palm growing up to 20 m tall, characterized by a crown up to 8 m wide; young palms are covered with dry leaf stalks, showing gradually fading leaf scars; trees over 25 years old have a swelling of the trunk at 12-15 m above the ground (at 2/3 of the height); bark is pale grey in older palms and is more or less smooth.

Carbonization and activation: The waste materials (male inflorescence) were carbonized in the electrical conventional heating reactor by two stages carbonization process known as low temperature carbonization and high temperature carbonization in the range of 250-600 °C and 600-800 °C respectively. The materials were placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out at 400 °C for 30 minutes followed by next stage to develop the pore size structure so that an accessible internal surface could be created. The carbonized product was treated with 0.1M NaOH solution. The base treated product was thoroughly washed with hot distilled water. Indigenously prepared carbon thus produced was thermally activated at 120°C for 1 hr in an air oven. The product was finally dried and sieved to get various particle sizes.

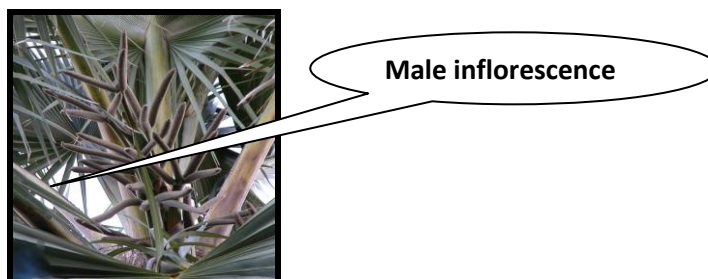


Figure1: *Borassus aethiopum*. Mart

CHEMICALS

Analytical grade (AR) chemicals obtained from RANBAXY and EMERCK chemical laboratories India Ltd., are used in this research programme and all solutions are prepared by double distilled water (pH: 6.88).

EQUIPMENT

AAS (Atomic absorption spectroscopy)-[GBC Avanta double beam, GBC Scientific equipments, Victoria 3175, Australia], FT-IR (Fourier Transfer – Infrared Spectroscopy)-[PERKIN ELMER, Spectrum BX FTIR System], Elico - model pH meter, Elico - model EC meter, Elico - model UV-Vis. Spectrometer, Remi Shaker 2L capacity

COPPER REMOVAL STUDIES

Batch mode analysis : 1 gm of each adsorbent was mixed with 10 mg/L metallic solution in a beaker and agitated for 20 min. on Remi shaker at 200 rpm speed. The resulting mixture was filtered through whatman 42 filter paper and filtrate was estimated for Cu (II) ion by atomic adsorption spectrophotometer.

Solutions preparation

Stock solution: Dissolve 1.000 g of copper metal in a minimum volume of (1+1) HNO₃. Dilute to 1 liter with 1% (v/v) HNO₃ to make 1000 mg/L Cu (II) solution.

Standard Flame Emission Conditions for Cu (II) ion

Wavelength (nm)	Slit (nm)	Flame
327.4	0.2	Air-acetylene

1. Recommended Flame: air-acetylene, oxidizing (lean, blue), 2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 \times sensitivity improvement. 3. Characteristic Concentration with Air - C₂H₂ flame at 327.4 nm: 0.45 mg/L.

Light source: With multi element lamps containing nickel or iron, a 0.2 nm spectral slit width should be used with the copper 324.8 nm line.

The amount of metal adsorbed by AC's was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_i - C_e) \times V / M$$

Where Q is the metal uptake (mg/g); C_i and C_e are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biosorbents (g).

The percentage of removed of Cu (II) ions (Rem %) in solution was calculated using the following equation

$$\text{Rem (\%)} = (C_i - C_e) / C_i \times 100$$

Adsorption experiments have been carried out to determine the effect of particle size, initial pH, contact time, dose and initial concentration of Cu (II) was investigated by varying any one of the process parameters and keeping the other parameters constant. pH of the solution was adjusted by 0.01N solutions of HCl and NaOH.

RESULTS AND DISCUSSION

FTIR Analysis: In this investigation, the interpretation of the FTIR is based on the chemical structure of agricultural byproducts and on the various stages of the chemical and/or thermal treatments for carbon materials. The identification of all the chemical species on the surface of a modified activated carbon is not an easy task; however, important information about the chemical nature of the carbon surfaces may be obtained by using FTIR spectroscopy. Figure 2 shows the spectra of raw and base treated activated carbon samples. The FTIR spectrums of BAC₁ and BAC₂ shows strong broad band at 3429.99 and 3436.95 cm⁻¹ involving single broad band, it was ascribed to OH stretching vibration in hydroxyl groups and appears in this lower region where these groups are involved in hydrogen bonds. So, water still remained in adsorbent samples. Water still remaining in all carbon materials after the oven-drying treatment of the material could take part in the formation of hydrogen bonds. The same observation was also given by Zawadzki, when investigating the mechanism of HCl, oxidation of carbonaceous materials prepared from poly furfuryl alcohol and cellulose, a broad band in the range of frequencies below 3700 cm⁻¹ was associated with hydrogen bonds of type(H₂O...H...OH₂)⁺, which were formed between water and protons of acidic groups (13-14).

In FTIR spectrum of both samples, two strong bands were existed at 1639.46 to 1577.15 cm^{-1} , it was connected with C=C stretching band of aromatic vibration bands or may expect to the C=C stretching in olefinic double bonds. The band located around 1600 cm^{-1} has been often observed for carbons or carbonaceous materials (15). The band around 1580 cm^{-1} that appears in the original and base treated samples has been observed by many authors and has not been interpreted unequivocally. This has been assigned to aromatic ring stretching coupled to highly conjugated carbonyl groups (C=O) (16). Peak around 1420 cm^{-1} can be attributed either to an O-H deformation vibration in carboxyl groups or C-H bending vibrations (17-18), and appears in both samples. The bands in the region of 1400–1380 cm^{-1} that also appear in carbon samples, can be ascribed either to carboxyl-carbonate structures (19) or to aromatic C=C bond and various substitution modes of the aromatic ring (20). The band at around 1019.66 cm^{-1} in two carbon samples is ascribable to O-H bending and to C=O stretching vibrations (21). Bands below 950 cm^{-1} are characteristic of out-of-plane deformation vibrations of C-H groups in aromatic structures (22).

It was conclude that the organic matter present on the surface of the two carbonaceous materials was paraffin type, moisture content and carbonyl functional groups.

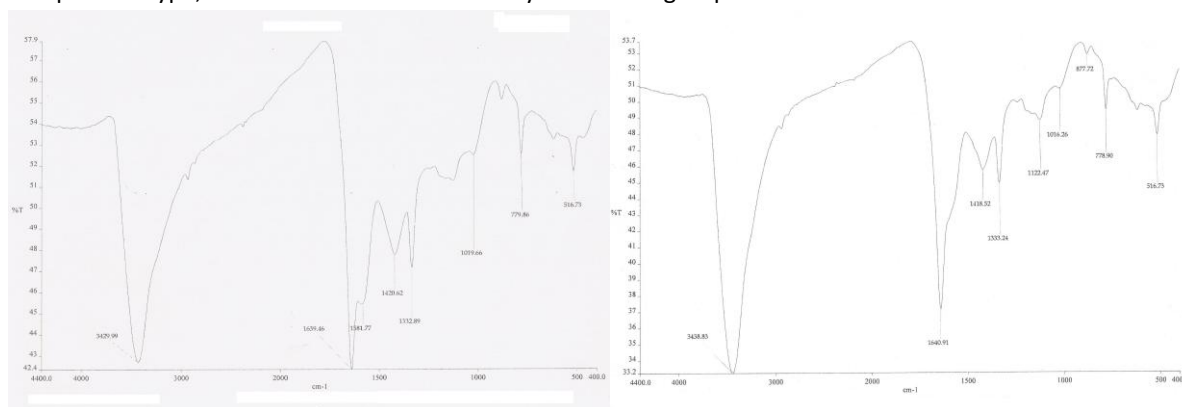


Figure 2: FT-IR Spectrum before (Left) and after adsorption

BATCH ADSORPTION STUDIES OF COPPER REMOVAL

Effect of adsorbent dose: The loading capacity of the material decreases with the increase in the adsorbent dose from 1.0 to 3.0 g/L at a fixed adsorbate concentration (10 mg/L), pH 3.0, temperature $30 \pm 1^\circ\text{C}$ (Figure 3). This is consistent with the argument that surface sites of oxide systems are heterogeneous. According to the surface site heterogeneity model, the surface is composed of sites with a spectrum of binding energies. Figure 3. Various reasons have been suggested to explain the decreased biosorption capacity at increasing biosorbent concentration including availability of solute, electrostatic interactions and interference between binding sites (161). With an increase in biosorbent concentration, from 1.0 to 5.0 g/L, the percentage of Cu^{+2} ion removal increased from 98.12 to 99.00 % when BAC1 and 98.68 to 99.75 % when BAC2 is used as adsorbent.

Effect of pH: The removal of metal ions from aqueous solution by adsorption is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate (23) (Figure 3). Results shows the effect of pH on the removal of Cu (II) by AC's. The Cu (II) removal by AC's decreased with increasing pH and attained percent removal values of 97.90 to 98.94% for BAC1 and 98.87 to 99.86% for BAC2 of Cu (II) respectively, at an initial pH of 9.0 to 3.0. It is evident that the carbon is effective for the maximum removal of Cu (II) over the pH range 4-3. The increase in metal ion removal as pH decreases can be explained on the basis of increase in H^+ on the surface sites and by a increase in positive surface charge, which results in less repulsion of adsorbing metal ions (24).

Effect of Initial concentration: At different copper ion concentrations for a fixed adsorbent dose. the surface sites are fully exposed. With increased concentration there is an increase in % removal up to a certain value, which may be due to a high intramolecular competitiveness to occupy the lower energetic surface sites left

behind. After saturation point the process becomes purely reversible and there will be no adsorption (25). The effect of concentration (1 to 100 mg/L) of copper ions on the uptake behavior of AC's have been studied and shown in Figure. 3. The results are plotted for amount adsorbed (mg/g) versus initial concentration (mg/L). It is found from the Figure 3, that the adsorption density increases with increased adsorbate concentration from 1.0–80.0 mg/L, but thereafter remains constant, suggesting that the surface of ACs is heterogeneous (26).

Effect of agitation time: Equilibrium time is one of the important parameters for economical wastewater treatment applications. The removal curves were single, smooth and continuous indicating mono-layer coverage of Cu (II) on the surface of the adsorbent (27-28). Figure.3 shows the effect of agitation time and percent removal on adsorption of copper ion removal by carbon adsorbents. The removal of Cu (II) was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium. The curves were shown in Figure 4, present a double nature; the initial portion of the curve rises linearly and is change into a curve and levels of 70 and 90 min of contact time. The plateau portion of the curve corresponds to pore diffusion and linear portion of the cure reflects surface layer diffusion (29-30). The equilibrium time is the time taken for the maximum adsorption of Cu (II) onto the adsorbent surface, above which the adsorption remains constant. The adsorption capacity of carbon samples increased with increasing agitation time, with equilibrium being attained at 50 to 60 min. for initial Cu (II) ion. The adsorption equilibrium value (Q_e) increased with increasing agitation, 2.714 to 3.123 & 3.123 to 3.263 and also the percentage of Cu (II) ions removal increased from 81.41 to 93.68, 93.70 to 97.90 for BAC1 and BAC2 respectively. The curves were smooth, simple and continuous, suggesting monolayer coverage of Cu (II) ions on the surface of the adsorbent.

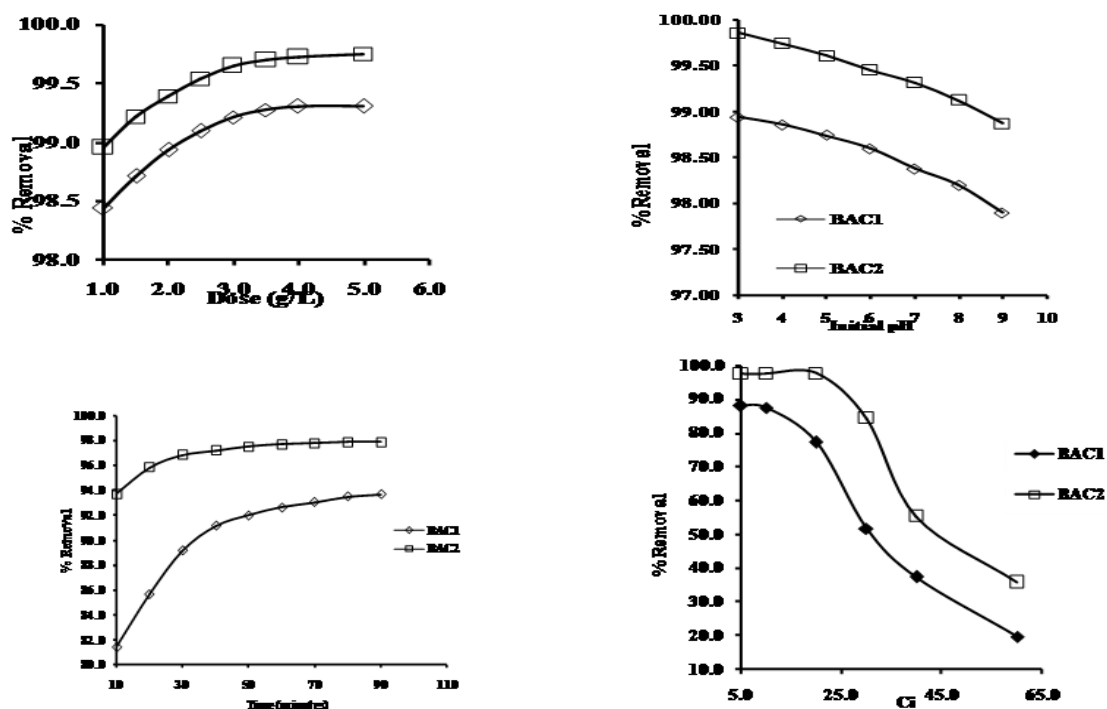


Figure 3: Effect of various parameters from left top (Effect of Dose, Effect of pH, Effect of time, Effect of Initial concentration)

ADSORPTION ISOTHERMS

Langmuir isotherm : When $1/q_e$ is plotted against $1/C_e$, a straight line with slope is obtained which shows that the adsorption follows the Langmuir isotherm as shown in Figure 4.6. The Langmuir constants 'b' and 'a' are calculated from the slope and intercept with Y-axis. The observed linear relationships as evidenced by R-values close to unity (0.9) confirm that these two adsorption isotherms are applicable.

In the present study the values of R_L being 0.4031, 0.315, respectively for the adsorbents BAC1 and BAC2 indicating that the adsorption process is favorable for all these low-cost adsorbents. Where b and C_i are terms appearing in Langmuir isotherm. From Figures 4, it is found that the R^2 value for Langmuir model is near to unity (0.99) and hence the process of copper ion removal using treated biosorbents follows the Langmuir isotherm well.

In all these cases, the correlation coefficient (R^2) was 0.9703 (Average) indicating a very good mathematical fit. The Langmuir equation involves the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate on the outer surface of the adsorbent. It also assumes that adsorption occurs at specific homogeneous sites within the adsorbent and once a metal ion occupies a given site, no further adsorption can occur at that site. It also assumes that all sorption sites are identical and energetically equivalent.

Freundlich isotherm: The linear plots of $\log C_e$, versus $\log Q_e$ ($R^2 = 0.98$) obtained when the experimental data were plotted in accordance to the Freundlich isotherm equation indicate that the Freundlich isotherm model also applied in the present studies (Figure 4). The magnitudes of KF and n were calculated from the intercept and slope of the plots and were found to be 0.1011, 0.2000, and 0.4883, 0.4739, respectively for BAC1 and BAC2. Such values of 'n' which lie between 0 and 10 support the favourability towards the adsorption of Cu (II) ions onto AC's.

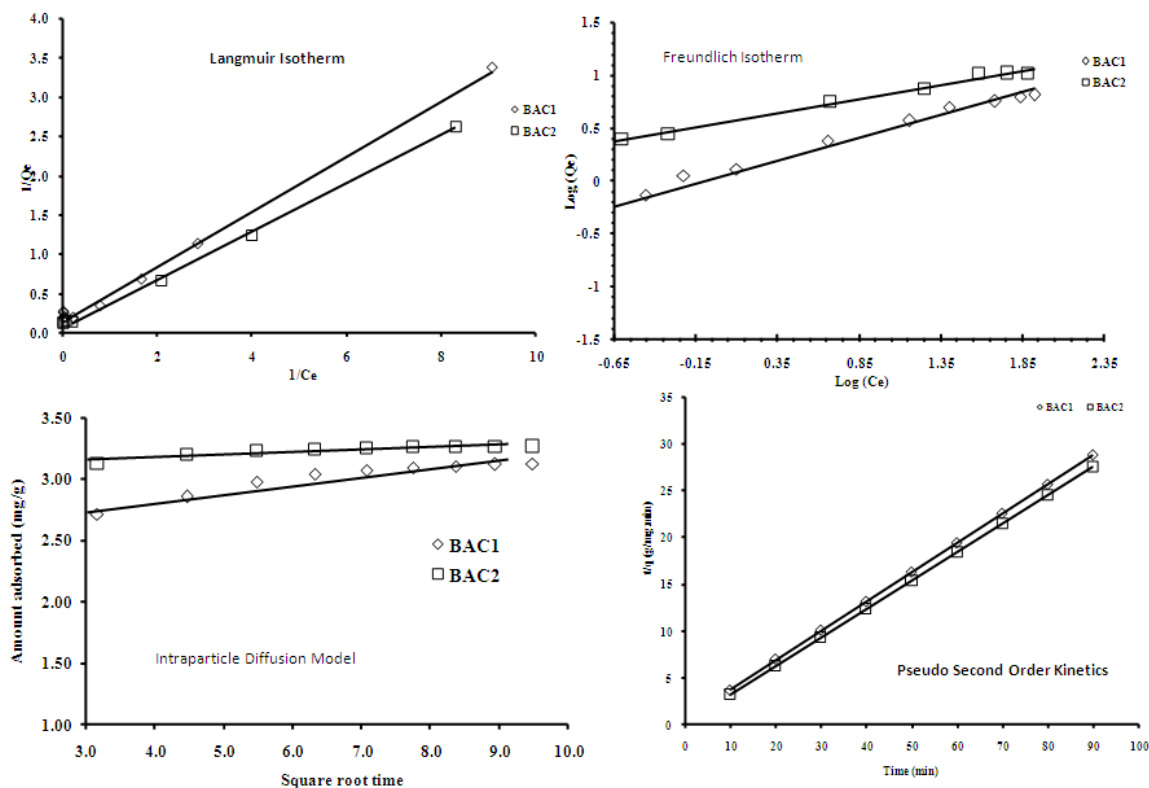


Figure 4: Adsorption Isotherm and Kinetic study

Intraparticle diffusion: The values of intraparticle diffusion rate constant (k_p) calculated for various adsorbents are also reported in Figure 4.8. The calculated maximum value of k_p for BAC2 (0.078) & minimum for BAC1 is (0.0207), which indicate that the intraparticle diffusion process is more significant in BAC system than in BAC1 system. The values of intercept (C) give an idea of boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect (29). The values of intercept decrease in the order BAC2 > BAC1.

ADSORPTION KINETICS

To analyze the mechanism of adsorption, the data were fitted to various kinetic models such as the first-order and pseudo-second-order rate expressions. A linear plot of $\log(q_e - q_t)$ versus t for the metal ion studied at different initial concentrations would indicate the applicability of the Lagergren equation. In the present studies, the plots show that the adsorption of Cu (II) ions onto the adsorbent (Figure 4) did not precede via a first-order reaction values (from R^2).

If pseudo second-order kinetics is applicable, a plot of t/q versus t should be linear, with the values of K_2 and q_e being calculated from the intercept and slope of the plot. Figure 4 shows such a plot for the data obtained in the present study, indicating that the experimental data were well represented by the second-order kinetic model (R^2 values). The correlation coefficients for second-order kinetics were greater than 0.90 for all the concentrations studied. A similar phenomenon has been observed for the adsorption of various dyes (30).

Field application: The various industrial effluents containing copper were collected (Table 1). The amount of copper present in the samples and after treatment with adsorbent were presented in the Table (2)

Industrial effluent collected from various locations.

Sample No	Sample Type	Location	Area
1	Klin slag	Hindustan Zinc Limited	Vishakapatnam
2	ETPS (Effluent Treated Plant sludge)	Samkarg Pistons	Srikakulam
3	Waste sludge	Revathi Zinc Products	Vishakapatnam
4	Waste sludge	Radhika Vegetable Oils	Vijayanagaram
5	Sludge	Jankapur Metal Industries	Vishakapatnam
6	Klin sludge	Hindustan Zinc	Vishakapatnam
7	Ferro carbon dust	Andhra Ferro Alloys	Vishakapatnam
8	Incinerators ash	EVB Technologies	East Godavary dist.
9	Incinerators ash	Maridi Eco Industries	Vishakapatnam
10	Incinerators ash	ASRAM	Eluru

Table 1: Copper removal studies in industrial effluents before and after treatment with carbon samples

S.No	Element	C_i	C_f	% Removal
1	Cu^{2+}	8.23	2.356	71.37
2	Cu^{2+}	3.74	1.025	72.59
3	Cu^{2+}	12.64	3.59	71.60
4	Cu^{2+}	0.05	0.0092	81.60
5	Cu^{2+}	0.24	0.045	81.25
6	Cu^{2+}	77.75	22.15	71.51
7	Cu^{2+}	4.5	1.25	72.22
8	Cu^{2+}	7.77	2.236	71.22
9	Cu^{2+}	4.2	1.123	73.26
10	Cu^{2+}	5.75	1.625	71.74

* C_i , C_f : initial and final concentration (mg/g)

From the above analytical studies it was inferred that both slag and sludge samples were mixed with various heavy metal ions along with copper ion. It was inferred that copper ion was present in considerable amounts. These samples were treated with base activated carbon sample (BAC2) at optimum conditions. After treating with carbon sample copper ion was successfully reduced to around 72%. It was concluded that carbon sample was very effective in the removal of Cu (II) ion. It was also concluded that BAC2 was also useful to remove various heavy metal ion. Because BAC2 was also adsorb Pb^{2+} , Cr^{3+} , Mn^{2+} , Zn^{2+} and Fe^{3+} ions along with Cu^{2+} ion.

CONCLUSION

Copper ion in small quantities no doubt is essential as a nutrient for prevention of hard tissues in the human body. On the contrary excess of copper beyond the permissible limit in drinking water is highly harmful to health and causes variety of diseases. Several methods have been developed for removal of Cu (II) ion from drinking water. These methods are based on the principles of adsorption, ion-exchange, precipitation, electrochemical deposition and reverse osmosis. Most of the methods have several drawbacks, the important being (1) high capital investment and operating costs, (2) complexity of operation and regeneration process, and undesirable changes in physico-chemical characteristics of water. Criteria for application of technology in rural areas involve (1) simplicity, (2) low cost and (3) user-friendly. With this aim the author has taken up the work "removal of copper ion from potable water with low cost adsorbents". The raw material of the adsorbent samples BAC1 and BAC2 are available in plenty as wastes in agricultural lands. The preparation of adsorbents from the raw materials is easy. Hence this bio-adsorbent can be considered as low cost adsorbents. The physical properties of these adsorbents samples are determined and each property is compared with that of raw carbon (BAC1). All the determined parameters of NaOH treated carbons are better than raw carbon. The determination of these physical properties may be helpful to know the character of the adsorbents in general and their use in particular.

The FT-IR analysis indicates the exact nature of the adsorbent surface purity of prepared material and also confirm prepared materials are capable to remove various impurities like fluoride, Cu^{2+} , Mn^{2+} , Pb^{2+} , and color materials etc,. The present study has demonstrated that plant by products acts as a cost-effective adsorbent for the removal of Cu (II) ions from aqueous solutions. Adsorption increased with increasing contact time and attained an equilibrium value after 30 min. The adsorption of Cu (II) ions onto carbon samples followed second-order kinetics. The adsorption data were analyzed using the Langmuir, Freundlich isotherms. Regeneration of the adsorbent was only favourable at acidic pH values. As an application to test the bio adsorbent effectively reduces the copper ion concentration in industrial effluents, and also concluded that prepared carbon sample BAC2 was showing better adsorption properties when compared with BAC1.

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