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# Radiation-Induced Graft Copolymerization of Monomer Mixture onto Sugarcane Bagasse for Removal of Cu(II) Ions: A Comparative Study†

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Removal of copper(II) ions from aqueous solution was carried out using acid treated sugarcane bagasse (ATSB), irradiated sugarcane bagasse (ISB), irradiated acid treated sugarcane bagasse (IATSB) and radiation induced graft copolymerized sugarcane bagasse (RIGCSB). For this purpose sugarcane bagasse was irradiated in Co-60 γ-chamber 900A with a dose rate of 3.7 Gy/min. The radiation induced graft polymerization was carried out using $CH_3CN$/DMF at a dose of 6 kGy. Copper(II) ions were removed by batch adsorption process at determined optimized parameters *viz.* pH 3, dosage 2 g of 250 µm of adsorbent and contact time 120 min. The percentage removal of the modified adsorbent was found to be significant and in the order RIGCSB (82.9 %) > ATSB (72 %)> IATSB (81.9 %), while ISB did not adsorb Cu(II) ions. Thus, the modified adsorbents proved to be promising material for removal of Cu(II) ions.

**Key Words: Graft copolymerization, Copper, Sugarcane bagasse, Radiation, Adsorption.**

## INTRODUCTION

Large amount of toxic metals are being released from industrial wastewaters such as textile, paint formulation and electroplating industries. These metals end up in natural bodies and affect living organisms. Copper is one of these metals, which are known to be significantly toxic. This raises the need for efficient method for removal of Cu(II) ions from wastewater. In the last few years, adsorption has been proved to be an economically feasible alternative method for removal of heavy metals. Consequently many researchers have studied the feasibility of low-cost adsorbents such as corn cubs[1], pecan nutshell[2], palm kernel husk[3], onion skins[4] and pinus bark[5].

In this work, we reported the use of sugarcane bagasse, which is modified by chemical reaction. Sugarcane industries produce a large amount of bagasse, which is considered as waste. However, with little processing we can use it as cost effective adsorbent. Sugarcane bagasse, as a raw adsorbent, has been reported in literature[6], which owes low adsorption capacity. The present work demonstrates a chemical and radiation method to increase the adsorption capacity of sugarcane bagasse.

## EXPERIMENTAL

AR Grade copper sulphate was used to prepare adsorbate solution. The concentration chosen was 0.01 M. pH adjustments of solutions were made using low concentrations of NaOH and $H_2SO_4$. Orthophosphoric acid of AR grade supplied by SD-fine chemicals limited was used for modification of the adsorbents. *N,N*-dimethylformamide (DMF) of GR was purchased from Merck, India. For further modification of the adsorbents, acrylamide extra pure was purchased from Sisco Research Laboratories Pvt. Ltd., India.

### Preparation of adsorbents

**Acid treated sugarcane bagasse (ATSB):** Sugarcane bagasse was collected from a local juice centre. Sugarcane bagasse was dried under sunlight for about 15 days and was ground to fine powder in mill. The bagasse powder was three times washed with distilled water. 100 g of washed bagasse powder was treated with 660 mL of 1.0 M orthophosphoric acid for 30 mins by continuous stirring. The treated bagasse was then washed several times with distilled water to remove excess acid for which the process given by Vaughan[7] was followed and it was dried for 24 h at 50 ºC in vacuum. Acid treated sugarcane bagasse obtained was then further modified.

**Irradiated acid treated sugarcane bagasse (IATSB):** Acid treated sugarcane bagasse was further modified by irradiating it. It was gamma irradiated with a dose of 20 kGy using a Co-60 γ-chamber 900A with a dose rate of 3.7 Gy/min.

**Radiation induced graft copolymerized sugarcane bagasse (RIGCSB):** Radiation induced graft copolymerized

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sugarcane bagasse was prepared by irradiating acid treated sugarcane bagasse with a gamma dose of 6 kGy and by copolymerizing it with 40 % acryilonitrile/DMF monomer mixture.

**Irradiated sugarcane bagasse (ISB):** Irradiated sugarcane bagasse was used as a control in this study. Irradiated sugarcane bagasse was prepared by irradiating untreated sugarcane bagasse with a gamma dose of 20 kGy.

**Batch adsorption experiment:** Batch adsorption studies were carried out at room temperature. In this process, aliquots of 25 mL of 0.01 M of Cu(II) ions were placed in round bottom flasks and the desired pH of the metal solution was adjusted. As an initial dosage 0.5 g of acid treated sugarcane bagasse with 420 μm particle size was added to flask and was stirred on magnetic stirrer for 1 h to reach equilibrium at room temperature. After stirring, solution was centrifuged and the supernatant was collected for analysis. The pH of solution was varied between 2 to 5 and was optimized. Similarly, contact time, adsorbent dosage and particle size of the acid treated sugarcane bagasse were varied in order to optimize the conditions for maximum adsorption.

The experiments were carried out with all the modified sugarcane bagasse adsorbents at the same optimized conditions.

The percentage removal of metal ions by the different adsorbents is calculated by the equation:

$$R(\%) = \frac{C_0 - C}{C_0} \times 100$$

where, $C_0$ is the initial metallic ion concentration (mg/L), C is the final metallic ion concentration in aqueous solution (mg/L) after batch adsorption.

A Shimadzu FTIR 8400 spectrophotometer was used to characterize the sorbent. Analysis of the metal ion concentration, after adsorption, was carried out using a UV-spectrophotometer (Shimadzu 1650PC) at 810 nm.

## RESULTS AND DISCUSSION

**Characterization of the adsorbents:** The FTIR spectrum of the adsorbents before and after adsorption was recorded using FTIR spectrophotometer (Shimadzu 8400) in the range of 4000-400 $cm^{-1}$ using KBr disk for reference. The spectra of the virgin adsorbents and loaded with Cu(II) ions are shown in Figs. 1-4. Sharp peaks at 3553 $cm^{-1}$ indicate the presence of O-H bond, which confirms with the additional intense bands in the ranges 1600-1300, 1200-1000 and 800-600 $cm^{-1}$ [8] Fig. 1 shows change in intensities of the peaks in case of adsorbed Cu(II), which indicates the binding of the metal ions to the adsorbent by adsorption process. A further change in intensities is observed in Figs. 2 and 3 in the spectra of loaded irradiated acid treated sugarcane bagasse and radiation induced graft copolymerized sugarcane bagasse with Cu(II) ions, which indicate a higher percentage removal of the metal ions. From Fig. 4, it can be seen that better removal is achieved by using radiation induced graft copolymerized sugarcane bagasse as an adsorbent.

**Effect of initial pH:** The pH of the adsorbate solution was varied from 2 to 5. As pH was increased from 2 to 3, the removal of Cu(II) ions increased. Further increase in pH,

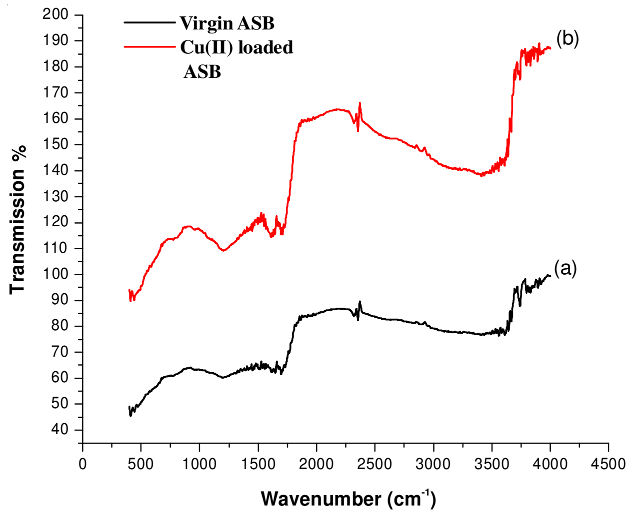


Fig. 1. FTIR spectra of (a) virgin acid treated sugarcane bagasse and (b) Cu(II) ions loaded acid treated sugarcane bagasse.

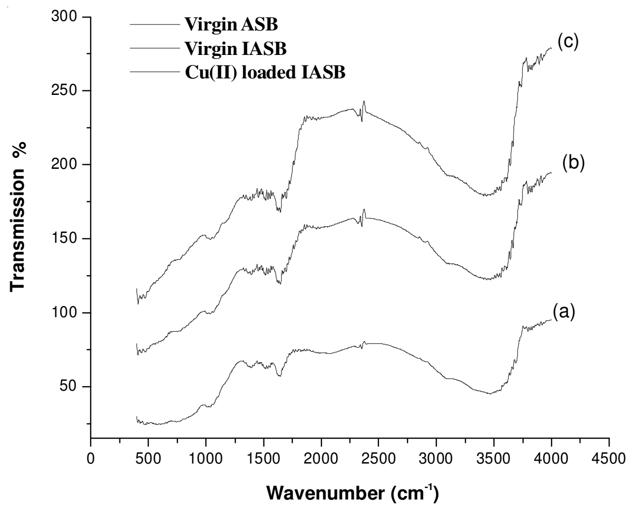


Fig. 2. FTIR spectra of (a) virgin acid treated sugarcane bagasse (b) virgin irradiated acid treated sugarcane bagasse and (c) Cu(II) ions loaded irradiated acid treated sugarcane bagasse

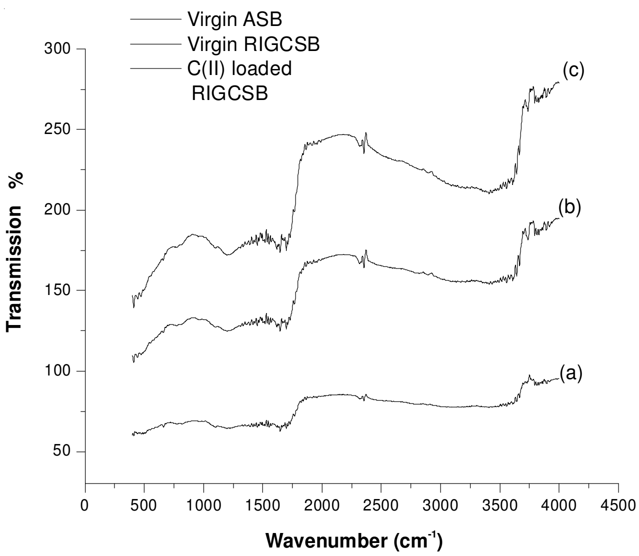


Fig. 3. FTIR spectra of (a) virgin acid treated sugarcane bagasse (b) virgin radiation induced graft copolymerized sugarcane bagasse and (c) Cu(II) ions loaded radiation induced graft copolymerized sugarcane bagasse

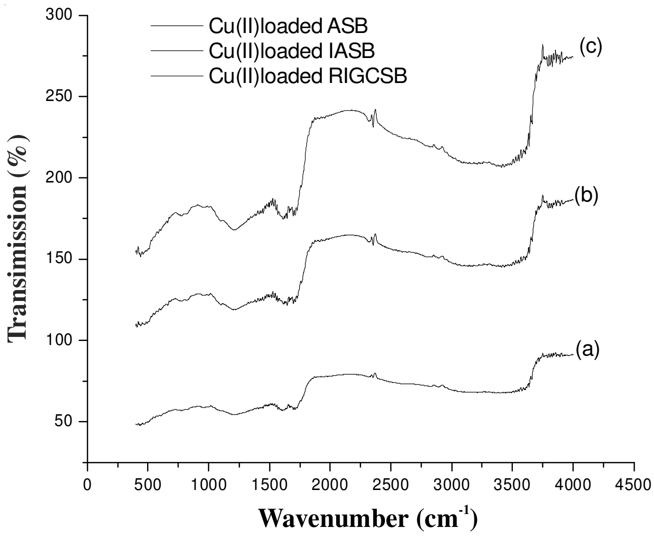


Fig. 4. FTIR spectra of Cu(II) ions loaded (a) acid treated sugarcane bagasse (b) Irradiated acid treated sugarcane bagasse and (c) Radiation induced graft copolymerized sugarcane bagasse

decreases the removal of Cu(II) ions. This is because the pH (acidity or alkalinity) of medium affects the metal uptake on an adsorbent because $H^+$ ions can compete with metallic ions for active sites on the adsorbent surface[9]. The percentage removal of Cu(II) ions was observed to vary from 34.15 to 40.65 % (Fig. 5).

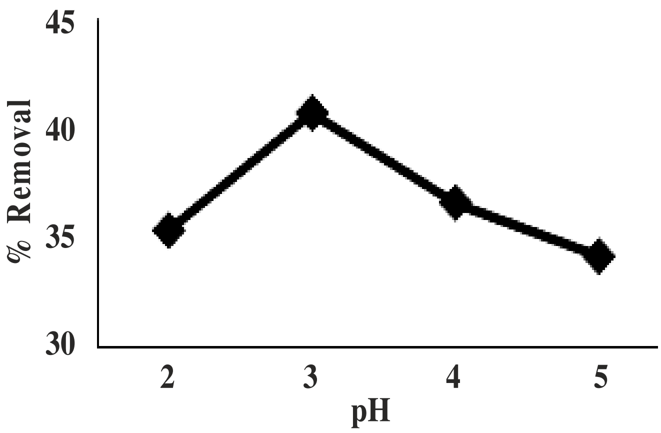


Fig. 5. Effect of pH on adsorption of Cu(II) ions on acid treated sugarcane bagasse

**Effect of contact time:** The effect of contact time on removal of Cu(II) ions is shown in Fig. 6. As it can be seen, percentage removal increases with time and attains saturation in 120 min. This shows that the sorption of copper ions is rapid but gradually decreases with time until reaches equilibrium. Fig. 6 reveals that maximum percent removal of Cu(II) ions is 44.26 % at 120 min and the rate of adsorption becomes almost insignificant after 120 min due to quick exhaustion of the adsorption sites on acid treated sugarcane bagasse. In the beginning, the rate of adsorption is higher which is due to larger surface area of the adsorbent being available. After the adsorbed material forms a molecule (ion) of thick layer, the capacity of the adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the metal ion is transported from the exterior to the interior sites of the adsorbent particles.

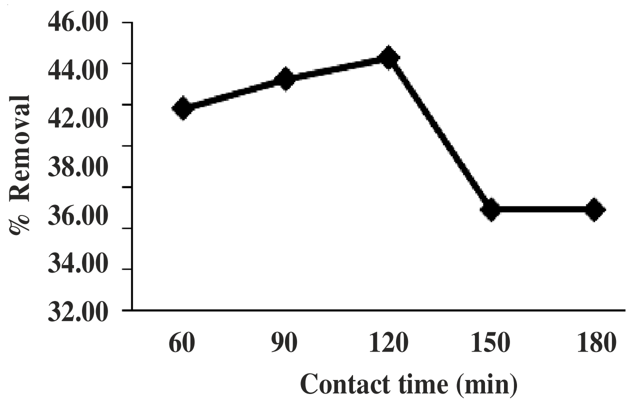


Fig. 6. Effect of contact time on adsorption of Cu(II) ion on acid treated sugarcane bagasse

**Effect of adsorbent dosage:** The effect of adsorbent dosage on removal of Cu(II) ions is shown in Fig. 7. It is observed that that the highest removal was found to be 72.13 % using 2 g of acid treated sugarcane bagasse. There is a slight increase in Cu(II) ions removal using 0.5 to 1.5 g of acid treated sugarcane bagasse. A sudden increase is noticed using 2 g of adsorbent. However, a dose of 3 g of ASB lowers the percentage removal of metal ions. Such results are not uncommon, *e.g.* Cu(II) on sawdust[10], Ni(II) ions and Cu(II) ions on natural and acid treated algae[11] showed similar results.

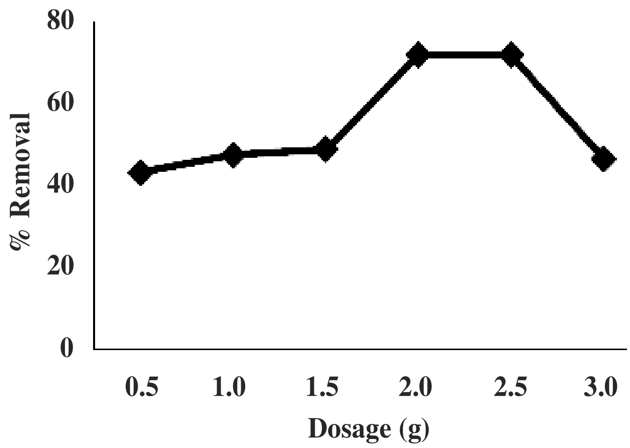


Fig. 7. Effect of acid treated sugarcane bagasse dosage on adsorption of Cu(II) ions

**Effect of particle size:** Particle size of acid treated sugarcane bagasse was chosen to be 125 μm, 250 μm and 420 μm. Fig. 8 shows the percentage removal of Cu(II) ions at the these particle sizes. As can be seen from this figure smaller particle size gave higher percentage removal. This is due to the fact that smaller particle size gives rise to large surface area and hence more adsorption capacity.

These optimized parameters were used to study removal of Cu(II) ions using modified sugarcane bagasse adsorbents. The obtained results are shown in Table-1. It is to be noted that irradiated sugarcane bagasse did not adsorb Cu(II) ions.

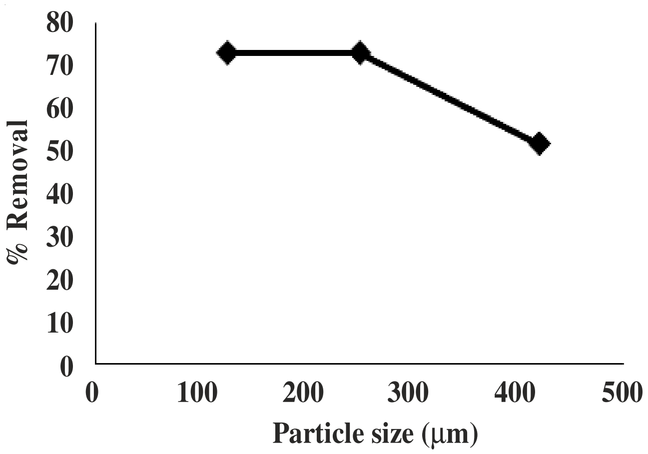


Fig. 8. Effect of particle size on adsorption of Cu(II) ion on acid treated sugarcane bagasse

TABLE-1
PERCENTAGE REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTION USING MODIFIED SUGARCANE BAGASSE ADSORBENTS

| Adsorbent | Initial conc. (mg/L) | Concentration after adsorption (mg/L) | Removal (%) |
|---|---|---|---|
| ASB | 630 | 165 | 72.0 |
| IASB | 630 | 110 | 81.9 |
| RIGCSB | 630 | 105 | 82.9 |

## Conclusion

Modified sugarcane bagasse adsorbents exhibit promising potential for removal of Cu(II) ions. Sugarcane bagasse does not adsorb Cu(II) ions unless it is treated. It was found that percentage removal was highest at pH 3, agitated for 120 min using 2 g of 250 μm acid treated sugarcane bagasse. The percentage removal of the modified adsorbent was found to be significant and in the order RIGCSB (82.9 %) > ASB (72 %) > IASB (81.9 %), while irradiated sugarcane bagasse did not adsorb Cu(II) ions. The developed method can be effectively applied for removal of Cu(II) ions from actual industrial wastewater samples.

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