Removal of copper using activated carbon adsorbent and its antibacterial antifungal activity

Abstract

Batch adsorption equilibrium of Cu (II) was studied by using saw dust Chitosan composite beads. Experiments were performed at different pH, various concentrations of adsorbent and adsorbate, agitation speed, contact time for adsorption of Cu (II). Adsorption capacity and percentage removal were calculated. Thermodynamics parameters such as ∆H, ∆S, were calculated. The result shows that Chitosan composite charcoal bead is a good adsorbent for Cu (II) removal. For the activated carbon adsorbent antibacterial and antifungal activity have analyzed and reported.

Keywords; Activated carbon adsorbent, adsorbate, removal of copper and Chitosan

1. Introduction

According to the environmental policy there are several airborne materials that can lead pollution in ground level, this pollutants can cause human health problems and damage to plants animals.In the past decades due to commercialization, urbanization heavy metal pollution was increased. Increasing heavy metal pollution is great thread to living organism. It is great challenge to remove the low level heavy metal from industrial effluent. Industries are the main source of heavy metal (copper) effluent discharge such as Miming, Electroplating, Dying, Pigments, Paper pulp, Fungicides [2]. Copper along with mercury is highest toxic to the mammalian. These are the several methods to remove the heavy metal from effluent they are electro deposition, ion exchange, precipitation, oxidation, reduction, ultra filtration, electro dialysis, coagulation, and adsorption [3]. Among these methods adsorption was recognized as economical and efficient method. Neutralization method is mainly used for the preparation of spherical beads of different size and porosity, obtained by drop wise addition of Chitosan solution to a solution of NaOH, followed by cross-linking. Enzymes may be immobilized on such beads either by adsorption or covalent binding to the matrix. Glutaraldehyde is usually used as a cross-linking and activating agent, due to its bifunctionality, reliability and easy use.

Due to its versatility, eco friendly, effective adsorption charcoal is recognized as an effective adsorbent for removal of heavy metal, dyes and organic matters. It has some disadvantageous, cost, and large scale use. Chitin is a second most abundant natural polymer after cellulose. It is the waste of sea food processing indu stries. Chitosan prepared from deacetylation of chitin. The emerging trend is the adsorption using bio polymer. Bio polymers are excellent adsorbent due to its bio degradability, Bio compatibility, polar poly functional group, less cost, availability. Numerous researches have been done by using charcoal as an adsorbent [4].

Hence in this study Chitosan composite activated charcoal beads are used as an adsorbent. A factorial design was used to evaluate the importance of some experimental factor concerning the adsorption quantities and the thermo dynamical adsorption parameters of copper [5].

2. **Materials and methods.**

The Chitosan used in the study was purchased from Sigma Aldrich. Epichlorohyrdin (ECH) and nitrate purchased from Sd. Fine Mumbai were of analytical grade. Chitosan beads and ECH cross-linked Chitosan. Chitosan was purchased from Aldrich chemicals. Saw dust was collected from local saw mill. Doubly distilled water was used throughout the experiment.0.1 M $CuSO_4$ is made for stock solution. Working solution was prepared form the stock solution, pH of this solution is adjusted by adding 0.1 m HCl. Sawdust was sieved for uniform particle size and it is carbonized with concentrated sulfuric acid in the W/V ratio 1:1. Then it is washed with water until the pH attained neutral, and then it's dried in a hot air oven at 100ºC. 0.2 g of C and 0.2 g of charcoal was dissolved in 2% acetic acid solution was stirred for 3 hours and dropped into a coagulating solution containing 0.5M of NaOH. Then it is dried and used for experiments shown in Figure 1. Batch adsorption study has been done by using this charcoal chitosan composite beads adsorbent [6]. From the stock solution different concentration of copper solution was prepared 0.1g of adsorbent were added and stirred, before and after adsorption the concentration of copper was estimated by using (model) UV-VIS spectrometer. Experiments were done in different concentration of adsorbent adsorbate, time, pH, agitation speed. The adsorption capacity was calculated by using the formula [7]

$$Q_e = \left[\frac{(C_o - C_e)}{W} V \right] \text{--------(1)}$$

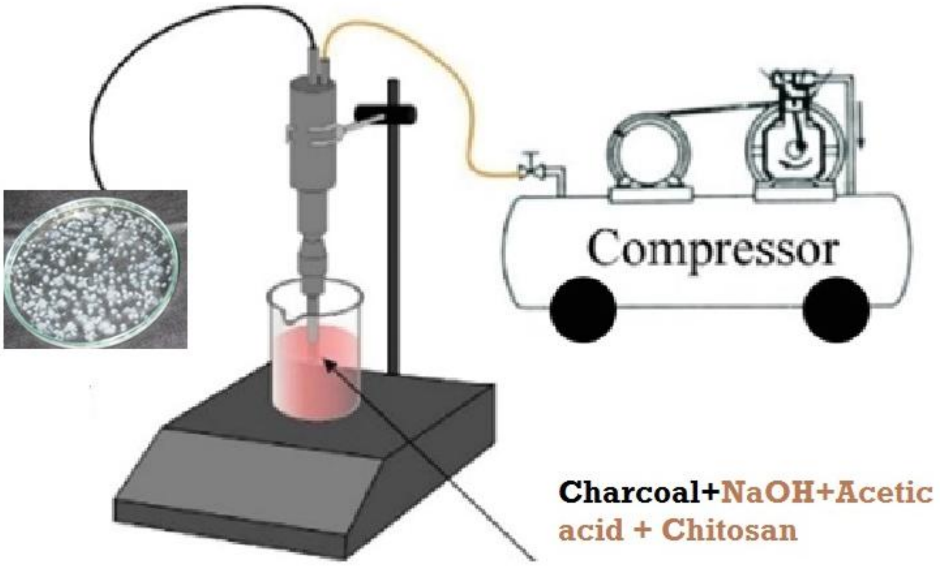

Figure 1 Preparation of Chitosan beads

3. Result and Discussion

Optimum concentration were determine after the experimental studies at various initial metal ion concentration between 30 *ppm* and 120 *ppm*, adsorption capacity increased by increasing the initial metal ion concentration at certain level. After the saturation the metal ion can't adsorbed by the adsorbent because of the saturation of the surface pores shown in Figure 2

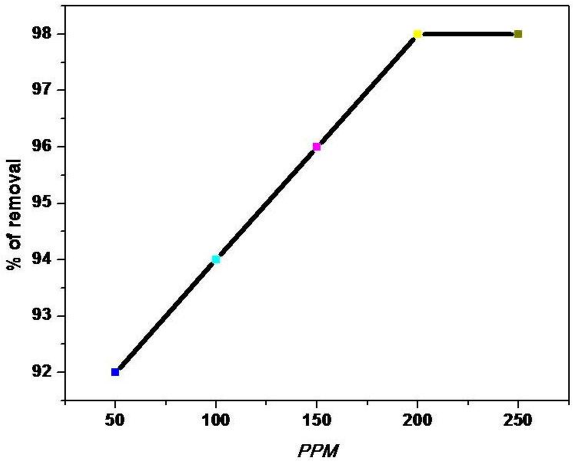

Figure 2. Variation of ppm of the sample and percentage of removal

3.1 Effect of pH

pH of the solution is the important parameter for controlling the adsorption process.

In order to investigate the effect of pH of copper adsorption onto the surface of the SDCCB the experiment were carried out from pH 2 to pH 6.The results have been showed in the graph. Adsorption of the copper increases when the pH of the solution increased from 2 to 5, it may be that at a lower pH, the amine group on SDCCB surfaces are easily protonized. The maximum adsorption capacity occurs at pH 5 after that the adsorption will decrease as shown in Figure 3.

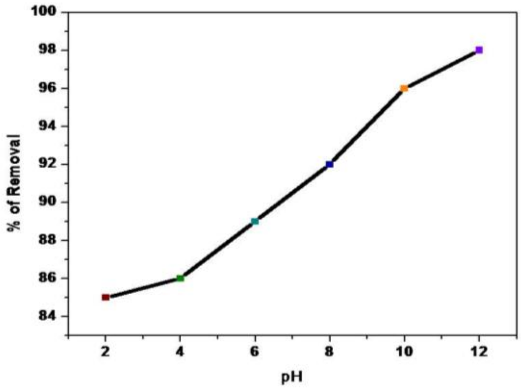

Figure 3. Variation of pH of the sample and percentage of removal

3.2 Effect of adsorbent dosage

In order to investigate the optimum dosage of adsorbent the experiments were carried out from 0.05 gm to 0.5 gm. The figure shows the effect of adsorbent dosage. It shows that rapid increase in adsorption till 0. 2 gm it may be the increases in surface area. A further increase in adsorbent dosage doesn't increase the adsorption, as shown Figure 4.

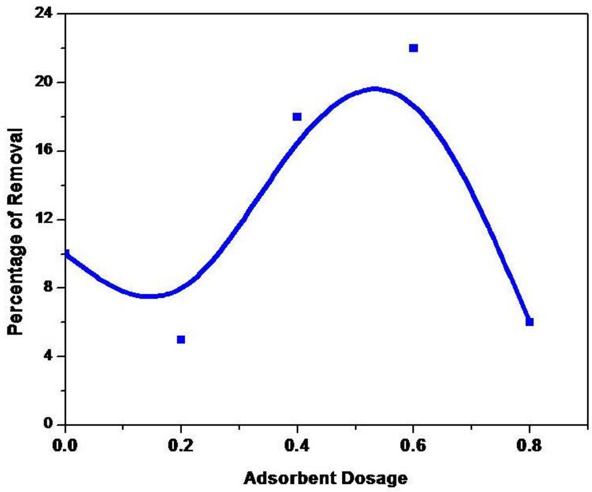

Figure 4. Variation of adsorbent dosage of the sample and percentage of removal

3.3 Effect of contact time.

To establish the appropriate equilibrium time for a copper adsorption on SDCCB adsorption capacities were measured as a function of time. It reveals that the adsorption is increased at initially, after the equilibrium there is no notable change. This may due to the surface area of adsorbent is occupied, vacant sites for further adsorption is a few. It does not seem to be much benefit from stirring time longer than its equilibrium time is shown Figure 5.

3.5 Effect of agitation speed.

Agitation speed on Cu (II) was studied by varying the agitation speed from 100 to 300 for 25 ml of initial concentration 30 *ppm* solution at pH5 solution. The optimum agitation speed was calculated from the graph. The adsorption capacity was increased by increasing the agitation speed this may due to the diffusion of copper on the solution.

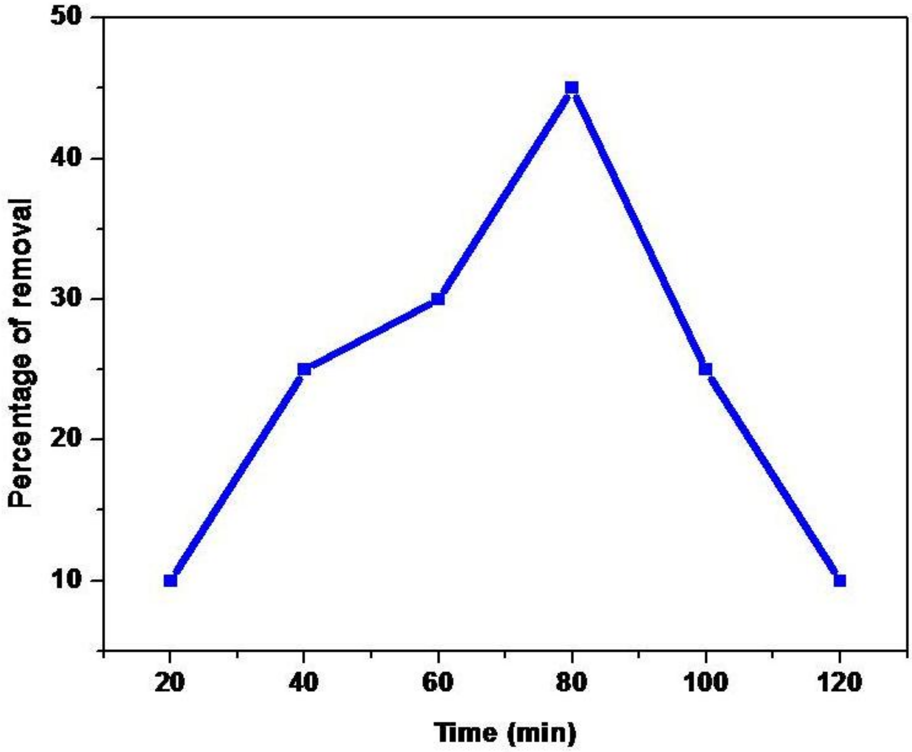

Figure 5. Variation of adsorbent dosage of the sample and percentage of removal

3.4 Effect of temperature.

Temperature is an important parameter for controlling the adsorption. To study the effect of temperature of adsorption on SDCCB adsorption capacity was measured as a function of temperature. The figure shows that the adsorption increases with increasing temperature this may mobility of the metal ion increased.

3.5 Thermodynamic parameters.

Adsorption is an exothermic spontaneous process. From the following formulas ΔG, ΔH were calculated by using the formula

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The positive ΔH° value shows that adsorption of copper on SDCCB is an endothermic process, and the negative ΔG° value shows that the adsorption is spontaneous process. Increases of ΔS value shows that randomness increases the reaction is spontaneous.

3.6 Antibacterial activity & Antifungal activity

36g of Muller Hindon Media (Hi-Media) was mixed with distilled water and then sterilized in autoclave at 15 lb pressure for 15 minutes. The sterilized media were poured into petridishes. The solidified plates were pored with 5 mm dia cork porer. The plates with wells were used for the antibacterial studies.

Bacterial strains

The bacterial and fungal pathogenic strains were obtained from the Microbial Type Culture Collection (MTCC), The Institute of microbial technology. Sector 39-4 Chandigarh, India. Bacterial strains were *Pseudomonas aeruginosa* (MTCC-3542) and *Escherichia coli* (1576).

Antibacterial and antifungal activity of the plant extract was tested using well diffusion method. The prepared culture plates were inoculated with different selected strains of bacteria and fungi using streak plate method. Wells were made on the agar surface with 5mm cork borer. The extracts were poured into the well using sterile syringe. The plates were incubated at 37±2^{o}C for 48 hours for fungal activity and for 24 hours for bacterial activity. The plates were observed for the zone formation around the wells

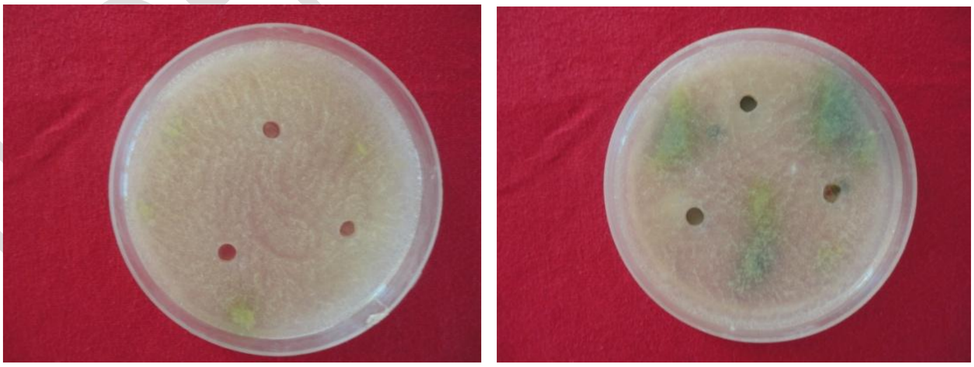

Figure 6(a-b). Antibacterial activity activated Carbon adsorbent for 3 different dosages of Pathogens *Escherichia coli* (1576) and *Pseudomonas aeruginosa* (MTCC-3542)

The extract of the antibacterial activity activated Carbon adsorbent *was* used throughout the study. The extract was dissolved in sterile distilled water to form dilution such as 5, 10 and 25 mg. Each concentrations of the drug were tested against different bacterial pathogens.

By using the obtained activated Carbon adsorbent content from the *Escherichia coli* and *Pseudomonas aeruginosa* of three concentrations of 5 mg, 10 mg and 25 mg of drug was tested. The zone of inhibition was calculated by measuring the diameter of the inhibition zone around the well (in mm) including the well diameter. The readings were taken in three different fixed directions in all 3 replicates and the average values were tabulated in Table 1.

Table-1 Antibacterial activity of activated carbon adsorbent for 3 different dosages

S. No	**Bacteria**	**Zone of Inhibition (mm)**		
		Copper adsorption Carbon activated sample		
		5 mg	**10 mg**	**25 mg**
1	*Escherichia coli*	**9**	**14**	**16**
2	*Pseudomonas aeruginosa*	**7**	**9**	**11**

Fungal strains

Fungal strains were *Aspergillus niger* (MTCC-1344) and *Aspergillus flavus* (MTCC-1973) *were estimated.* The methanolic and aqueous extract of 100, 200 & 500 mg were tested against two different fungal pathogens

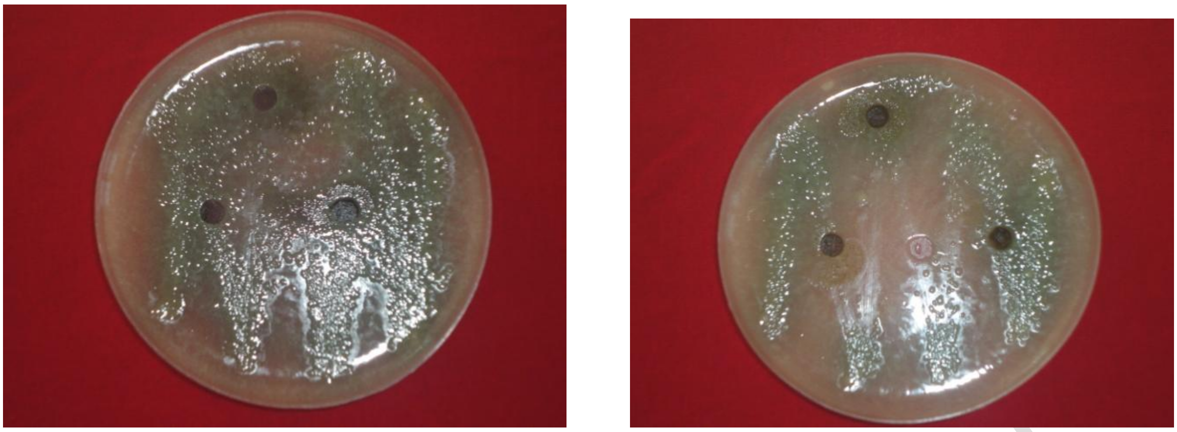

Figure 6. Antifungal activity activated Carbon adsorbent for 3 different dosages 100,200 & 500 mg

In the present antimicrobial investigation, the antibacterial effect of the activated carbon adsorbent sample is mainly due to the generation of different factors such as ROS and the release of C. Then dissolved oxygen molecules are transformed to superoxide radical anions ($^{\bullet}O^{2-}$), which in turn react with H^{+} to generate ($HO_2^{\bullet}$) radicals, which upon subsequent collision with electrons produce hydrogen peroxide anions (HO_2^{-}). Therefore they reacted with hydrogen ions to produce molecules of H_2O_2. Finally the generated H_2O_2 can penetrate into the cell membrane by collapsing inter cell system bacteria will be inhibited [17]. When the crystallite size is small the antibacterial effects are larger Cu^{4+} has higher ionic radius than that of the host ion Carbon [18].

Conclusion

The mishandling of hazardous waste materials poses immediate and long-term risks to plants animals, humans and the environment. If heavy metals are in any liquid and solid that contains carcinogenic or teratogenic compounds including pesticides, paint strippers solvents paint gasoline bleach ammonia industry cleaning agents and drain cleaners we can prefer carbon activated adsorbent in the field of heavy metal removal.

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