

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

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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 ΔH , ΔS , 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 threat 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 Mining, 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 industries. 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 method

The Chitosan used in the study was purchased from Sigma Aldrich. Epichlorohydrin (ECH) and nitrate purchased from Sd. 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 CuSO₄ is made for stock solution. Working solution was prepared from the stock solution, pH of this solution is adjusted by adding 0.1 mL 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 100°C. 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 and then dried and used for the experiments. 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]

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

C₀ = Initial concentration of Cu(II) ion(ppm), C_e = Final concentration of Cu (II) ion

V= volume of Cu(II) ion solution (mL) and W= weight of the adsorbent SDCCB (g)

3. Result and Discussion

UV-Absorption method

Standard stock solution of copper was prepared in 600 ppm by using CuSO_4 . Different initial concentrations of Cu solution were prepared from stock solution the absorbance of cu solution was taken to prepare standard graph by using UV Spectrophotometric method. 10 mL of the solution was taken and kept in a stirrer for 120 min after adding an 100 mg of adsorbent then 5mL of this solution is taken in a 10 mL SMF 2 mL of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was added and made upto 10 mL. The absorbance of this solution was measured and the concentration of Cu after adsorption was calculated from standard graph [8].

Calorimetric method

Optimum concentration were determined 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 there is no change on the surface of pores shown in Figure 1. The percentage uptake of Cu (II) ion was minimum at low concentration and increase with increasing initial concentration. After saturation level (120 ppm) the uptake of Cu (II) ion will decrease due to lack of availability of adsorption site on SDCCB surface [9].

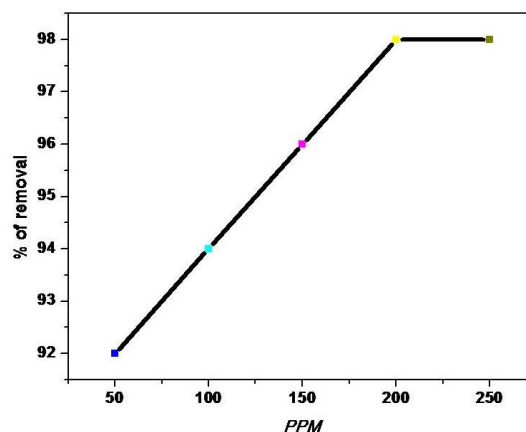


Figure 1. Variation of ppm of the sample and percentage of removal

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 is easily protonized. The maximum adsorption capacity occurs at pH 5 after that the adsorption will decrease as shown in Figure 2, it was concluded optimum pH for removal of Cu was pH 5 [10].

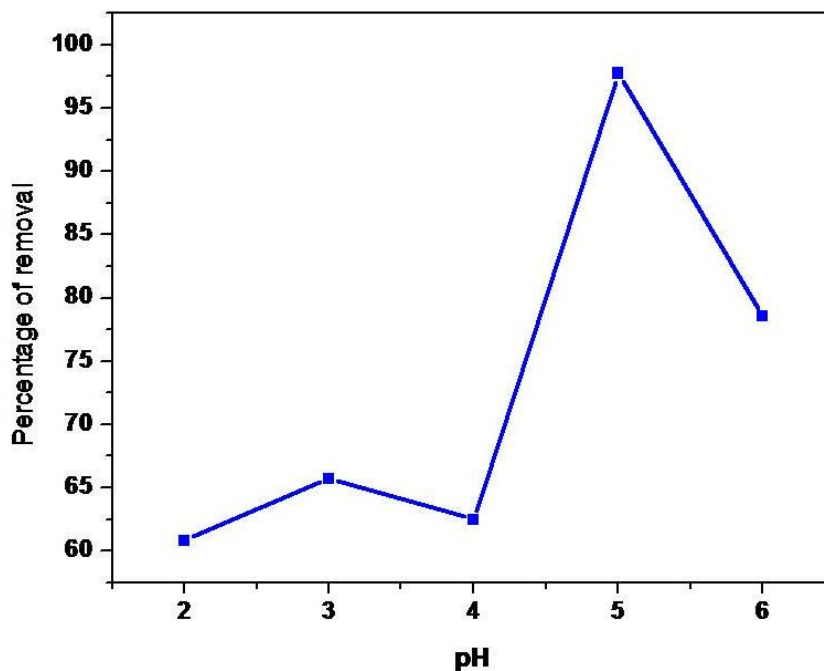


Figure 2. Variation of pH of the sample and percentage of removal

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 3 [11].

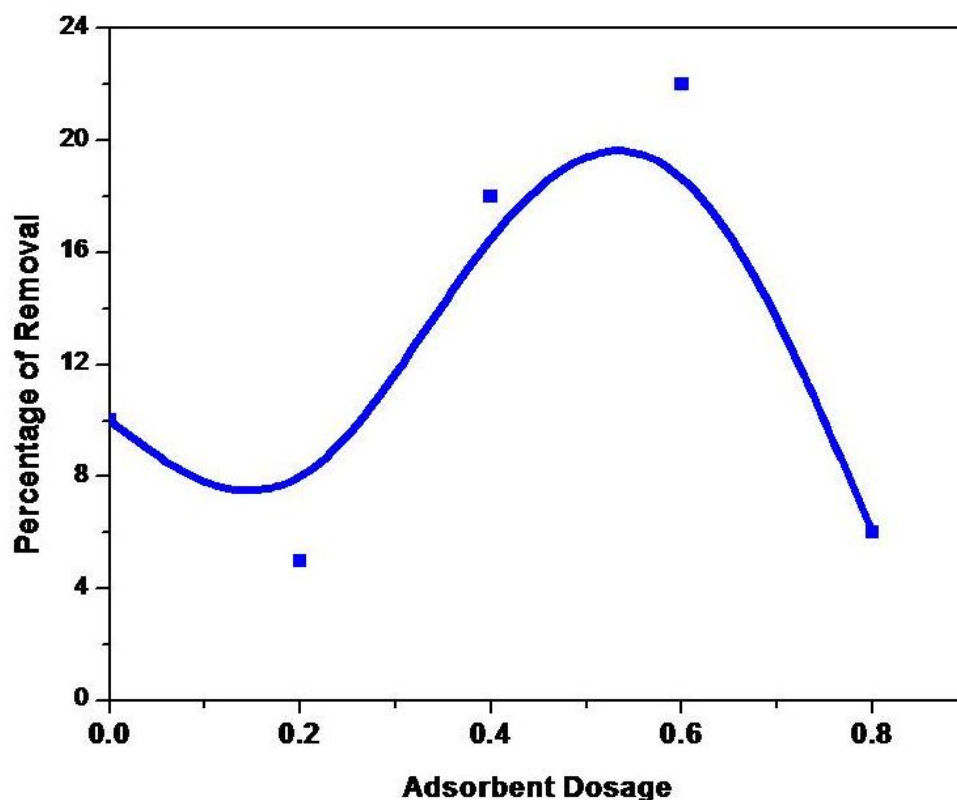


Figure 3 Variation of adsorbent dosage of the sample and percentage of removal

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 [12]. It does not seem to be that from stirring there was no change in their equilibrium time which is shown Figure 4.

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.

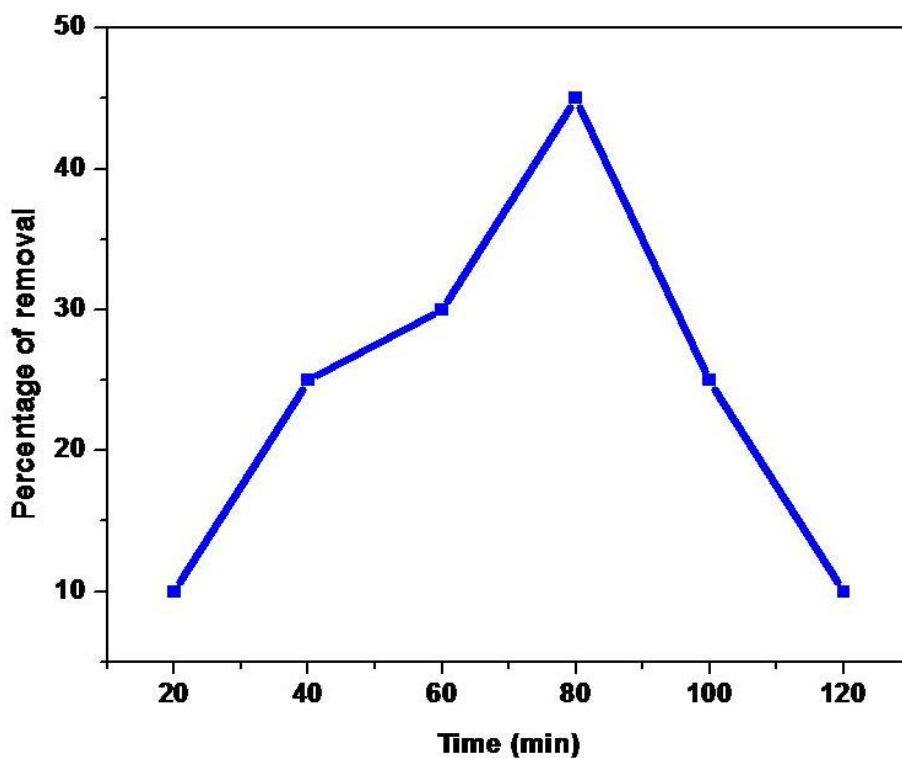


Figure 4. Variation of **time(min)** and percentage of removal

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 [13].

3.5 Thermodynamic parameters.

Adsorption is an exothermic spontaneous process. From the following formulas change in **free energy ΔG , Enthalpy ΔH , and Entropy ΔS were calculated by using the formula**

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

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 [14].

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 [15].

3.7 FWSEM Analysis

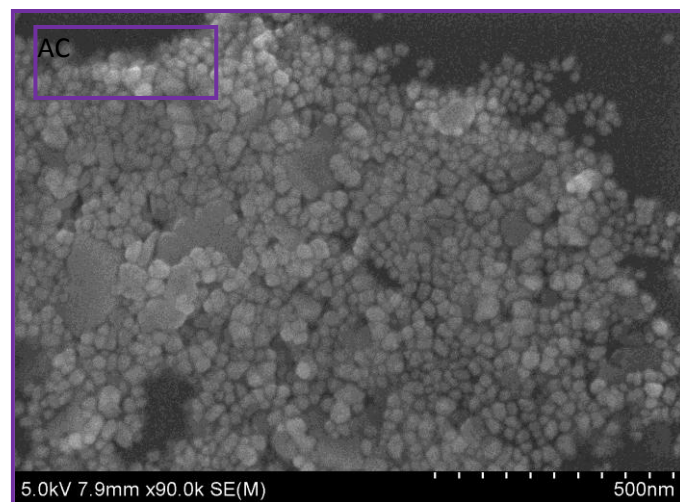


Figure 5. SEM Analysis of adsorption of copper on SDCCB

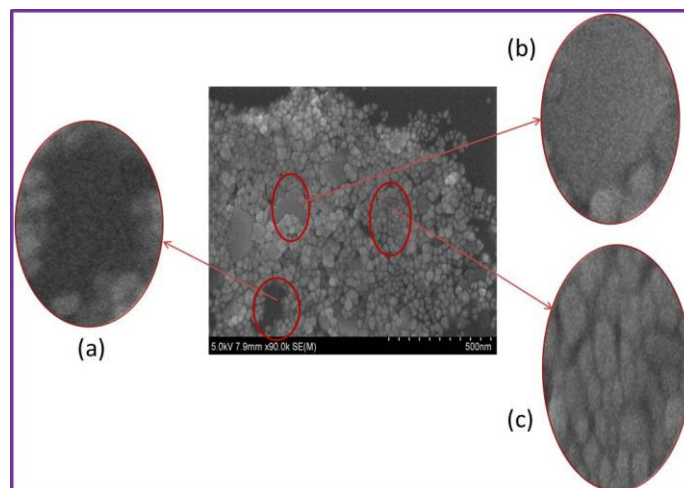


Figure 6(a-c). Described SEM image of activated Carbon (a) Super Activated carbon nanoparticles ~ 10 nm (b) Activated Carbon nanoparticles ~ 100 nm (c) Activated Carbon nanoparticles ~ 250 nm decorated on chitosan beads.

SEM analysis explains, a novel composite was synthesized by impregnating copper (Cu), on powdered activated carbon (AC) for effective copper adsorption and the synthesis was made using chemical method. FESEM was employed for the surface morphology, comparison of various zones present in it and its grain size. The image of SEM is shown in the Figure 5. As can be seen in the Figure 6(a-c), separate grain domains are applicable for metal adsorbent as well as microbial strain resistance applications. From observed SEM image, there are three described regions are separately isolated to infer the natural morphology of activated carbon nanoparticles as shown in the separate described inset [16]. As for as this concerns, region with high surface to volume ratio of powerful surface having the grain size of around 10 nm known as Super Activated Carbon (SAC) nanoparticles but dispersion on beads have uniform distribution and large particle size 250 nm and also agglomerated particle size is 100 nm. This allowed the impact that increasing surface area of the SCA has on the capture of the copper contaminant. Hence, as a SAC's previous studies, the prepared samples region (a) having very high porosity, negative ions concentration, better discoloring, adsorption and dispersion invariably [17]. Moreover, as can be observed morphology, the porous concentration increases on nano size, comparatively three different regions in the SEM image of synthesized powder having better porosity. These composite beads powders with large rough and non-uniform surface provide negative ions transfer rate and an appropriate zone for better removal of metal nanoparticles and less efficiency in anti-microbial activity. However from the image, we can observe that concentration of chitosan beads is high and highly responsible for antibacterial activity in an effective manner since them itself having dense amines positive charged ions. But also it has been depicted that negative ions group provide better interaction among activated charcoal, super activated charcoal as called as SCA and beads and also this interaction stabilize the nanoparticles. By increasing the SCA composition in

the sample, they will remove the copper nanoparticles effectively. So this negatively charged sample is electro statically capture and removes the copper [18].

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 $37\pm 2^{\circ}\text{C}$ for 48 hours for fungal activity and for 24 hours for bacterial activity. The plates were observed for the zone formation around the wells [19].

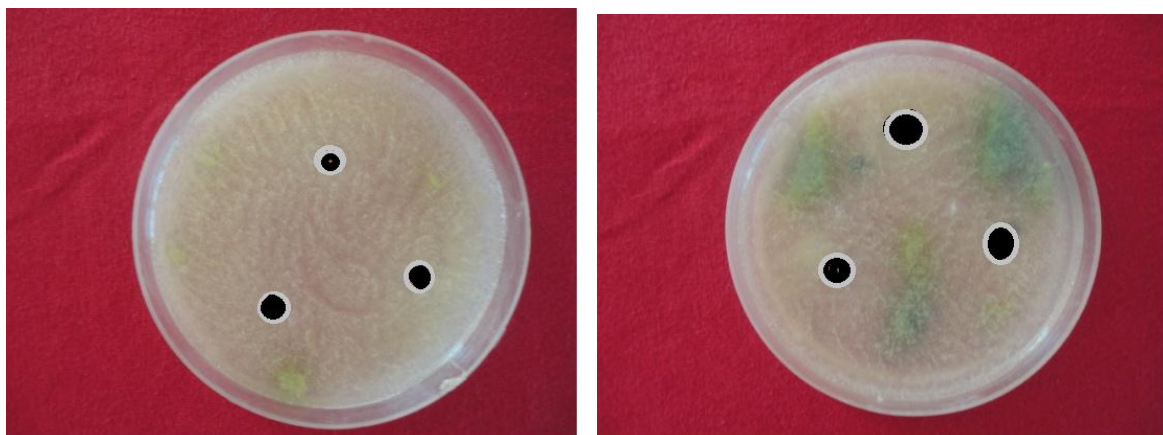


Figure 7(a-b). Antibacterial activity activated Carbon adsorbent for 3 different dosages of Pathogens *Escherichia coli* (1576) and *Pseudomonas aeruginosa* (MTCC-3542)

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 [20].

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 [21]. 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	<i>Escherichia coli</i>	9	14	16
2	<i>Pseudomonas aeruginosa</i>	7	9	11

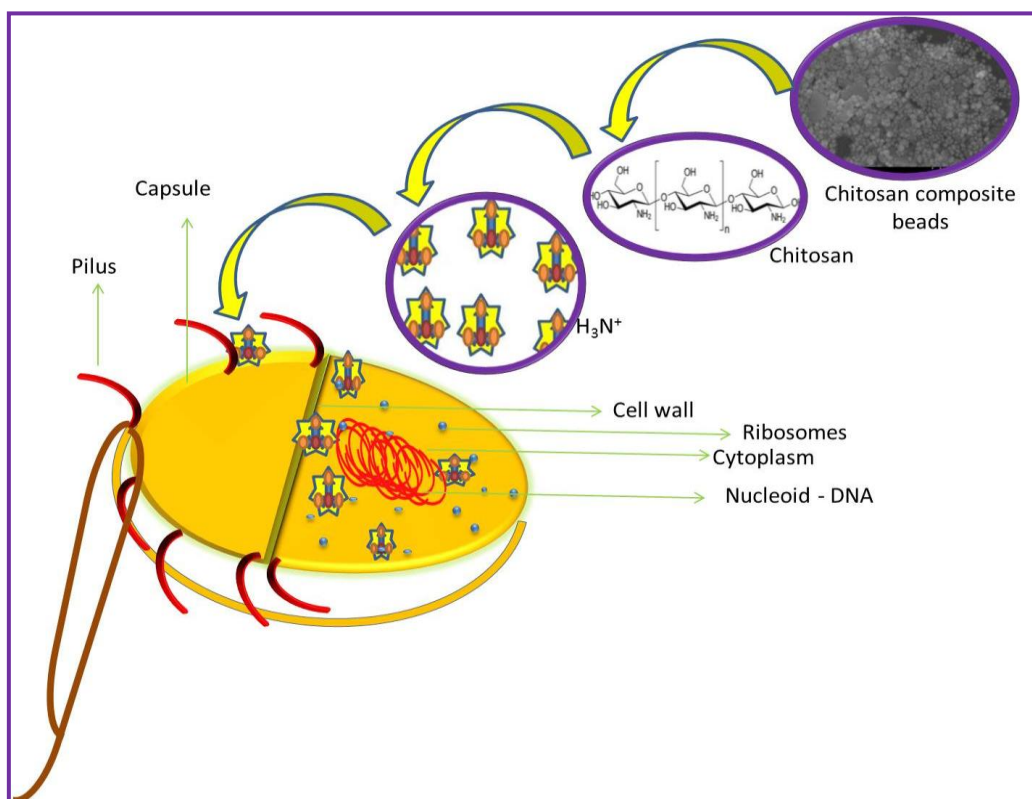


Figure 7c. Described mechanism for the enhanced antibacterial activity of activated Carbon adsorbent for 3 different dosages of Pathogens *Escherichia coli* (1576) and *Pseudomonas aeruginosa* (MTCC-3542)

This technique of inducing charge on the surface of the beads has employed in the present research to generate positive charge ions with higher antimicrobial efficacy. However, to the best of our knowledge, the application of SCA coated chitosan beads for the preparation of positively charged nanoparticles has not been previously investigated by other researchers [22]. Electrostatic attraction between positively charged H_3N^+ and negatively charged bacterial cells is necessary for the antibacterial effectiveness of the chitosan composite and this attraction is possible by the charge of the chitosan and the microbials. This kind of attraction is depends upon such factors such as size and shape that can influence the bacterial cell death. Since it having SCA of smallest size, inducing of positive charge amine group from chitosan and influence the antibacterial activity has also been depicted in the mechanism of antibacterial activity as shown in the Figure 7(c). All the bacteria's cell membrane is negatively charged due to the presence of carboxyl, phosphate, and amino groups. Hence the electrostatic interaction is takes place between the cell wall and amine groups to initiate the inhibition on bacteria effectively [23].

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. The mechanism antifungal activity as same as in the antibacterial activity as shown in the Figure 8(a-c)

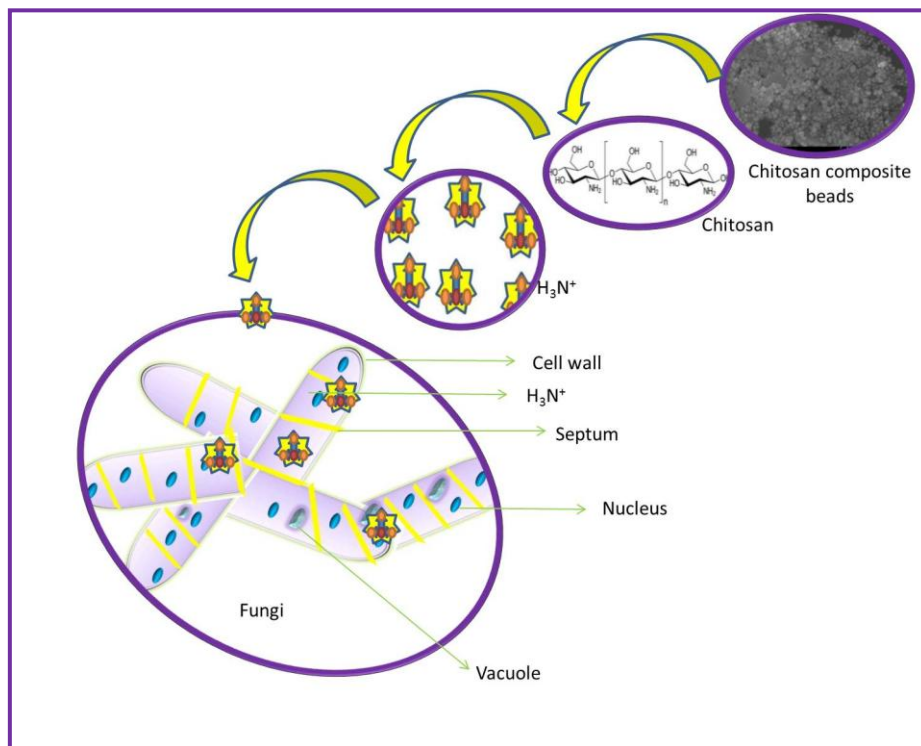
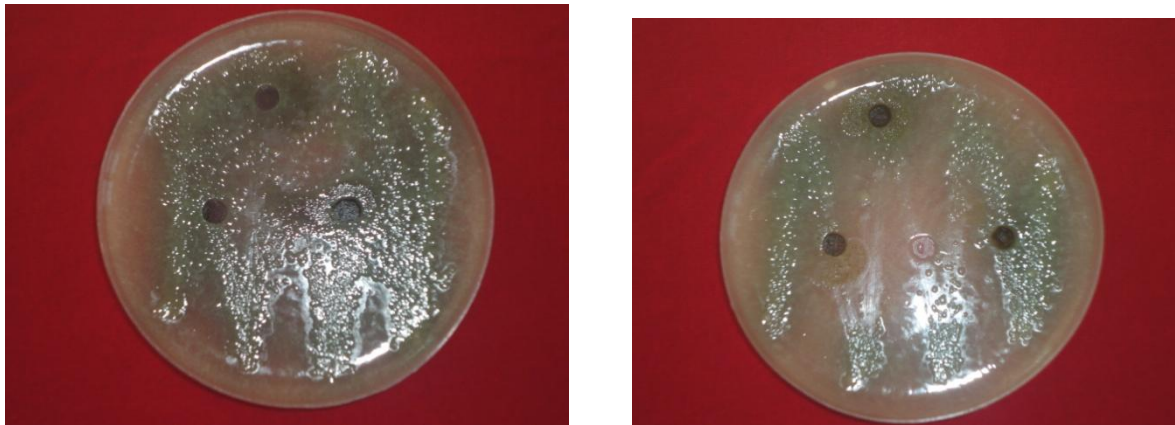


Figure 8(a-c). Antifungal activity of activated Carbon adsorbent for 3 different dosages 100, 200 & 500 mg

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 ($\text{O}_2^{\cdot-}$), which in turn react with H^+ to generate (HO_2^{\cdot}) radicals, which upon subsequent collision with electrons produce hydrogen peroxide anions (HO_2^-) [24]. 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. When the crystallite size is small the antibacterial effects are larger Cu^{4+} has higher ionic radius than that of the host ion Carbon [25].

4. 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 this field of removal. The generation of ROS further makes the damage and cell became deformed. Moreover the activated carbon adsorbent in this system is also contributed to damage all the bacterial cell systems. The variation of activated carbon concentrations in distribution systems was affected by copper ions and bacterial activity: the former resulted in an increase of activated carbon value while the latter led to a reduction in activated carbon adsorbent

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