

**ADSORPTION OF COPPER FROM WASTEWATER USING BIOPOLYMER****Dr.D. Saravanan<sup>1</sup>, P. N. Sudha<sup>2</sup>**Professor and Head, Department of Chemistry, Arunai Engineering College,  
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[saravanan\\_1974@rediffmail.com](mailto:saravanan_1974@rediffmail.com), [drparsu8@gmail.com](mailto:drparsu8@gmail.com)**Abstract**

Water is a basic human need, a finite life support system and a key to prosperity and sustenance of the life cycle. Unplanned industrialization, urbanization, rapid growth of population affects the aquatic environment. Large scale industrial, agricultural and environmental pollution generates volumes of wastewater which in turn affects the flora, the fauna, air, water and the soil. Among the industries, dyeing and printing industrial effluents discharge dyes loaded with heavy metals into aquatic ecosystems. The heavy metals render the water unsuitable for drinking and are also highly toxic to human beings. Removal of these metals is therefore essential. Adsorption studies have been used to remove Copper from aqueous solution was tested using chitin biopolymer. The sorption data obtained from batch method at optimized conditions have been subjected to Freundlich and Langmuir isotherm studies. The data were suitable for both Freundlich and Langmuir isotherm models indicating favorable and monolayer adsorption. FTIR study revealed that there is intermolecular molecular hydrogen bonding interaction between the two polymer components. XRD studies shows that the films to exhibit an amorphous character.

**Keywords:** biosorption, copper, adsorption isotherm, composites, cross linking.

**1. Introduction**

Dyes are used widely in leather and tanning industries. Most of them are inert and difficult to biodegrade when discharged into wastewater streams due to their synthetic origin and complex aromatic molecular structures. Even small quantities of dyes can change the color of large water bodies. Majority of industries are water - based and a considerable volume of wastewater emanates from them, which is generally discharged into water courses, either untreated or inadequately treated. As a result, it is not only affects the aesthetic merit but also reduces sunlight penetration and photosynthesis. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. These industries also release heavy metals like Cu, Cr, Cd, Hg, Pb etc. Even very low concentrations (Kadirvelu et al., 2001; Descalzo et al., 2003; Xiao and Thomas, 2005) of heavy metals in water bodies may alter the quality of aquatic environment. This can cause physiological, chemical and biological deterioration of aquatic bodies. Copper ions are mainly found in wastewaters of industries such as metal

cleaning, plating baths, refineries, paper and pulp, (Moinum Islam Sharif and Khandaker Mainuddin, (2003), fertilizers and wood preservatives.

Copper is an essential element for living organisms, including human and is also necessary in small amounts in our diet to ensure good health. However, too much of copper can cause adverse health effects including vomiting, diarrhea, stomach cramps and nausea (Ng et al., 2002). Copper is stored mainly in liver, brain, heart, kidney and muscles. There are evidences to suggest that copper may be carcinogenic and acute doses and intake could accumulate in the liver or kidney (Gundogan et al., 2004) and be extremely harmful, even fatal (Tseng et al., 1999). Marine and aquatic organisms can also be at great risk because copper is highly toxic to them, even at low concentrations. Although it is an essential element to plants, exceptionally high copper concentrations may be toxic to plants by affecting mainly the growth of the roots. It was estimated that the annual industrial discharges of copper into fresh water environments was at  $1.4 \times 10^{10}$  g/ year, and the amounts of copper in industrial wastes and sewage sludge that have been dumped into the ocean was  $1.7 \times 10^{10}$  g/year worldwide (Nriagu et al., 1979). The world health organization (WHO) recommended a maximum acceptable concentration of copper in drinking water to be 1.5 mg/l (Rao, 1992).

Many biological, physical and chemical methods have been used for wastewater treatment. The type of the process to be employed may depend on the nature of pollutant. Conventional metal removal techniques such as reverse osmosis, solvent extraction, lime coagulation and ion exchange methods (Alfassi, 1992; Walton, 1990) are encountered with certain major disadvantages such as high energy requirements, incomplete removal and generation of large quantity of toxic waste sludge due to various reagents used in a series of treatments. Adsorption techniques

are proved to be an effective and attractive process for removal of non-biodegradable pollutants (Blais et al, 1999; Sigg et al, 2001; Fiset, et al, 2000) from wastewater. Adsorption process is being effectively used for the removal of contaminants such as dyes and pigments which persist in the environment and are resistant to biological and physico-chemical treatment methods. It has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity, ease of operation, insensitivity to toxic substance and no generation of secondary toxic chemical species (Mckay, 1984).

Biopolymeric materials include cellulose, alginates, carrageenan, lignins, proteins, chitosan and chitin derivatives. The salient feature of bio polymers is that they possess a number of different functional groups, such as hydroxyls and amines to which the metal ions can bind either by chemisorption or by physisorption. Among the bio polymers worked with for adsorption of metal ions, chitin and the derivatives of chitin have played significant role in their capacity as adsorbent and complexing agent by virtue of their hydroxyl, acetate, amido and amino groups. Chitin has been reported to be the second most abundant natural polysaccharide in nature (Gregorio, 2006) and is commonly found in crab and shrimp shells containing 10-15% of chitin (Austin and Brine, 1977). It consists mainly of  $\beta$  - (1  $\rightarrow$  4)-2- acetamido- 2- deoxy- Dglucopyranose units. It carries one acetamido group containing lone pair of electrons on nitrogen and hydroxyl group per glucose ring, thus allowing excellent complexation capacity with metal ions (Lerivrey et al., 1986).

## 2. Experimental Details

### 2.1 Materials

Chitin was obtained from India sea foods, Cochin which is 99% pure. All other materials such as formaldehyde and

powdered bentonite are of analytical grade.

## 2.2 Blend Preparation

A known weight of chitin and bentonite were dissolved in trichloro acetic acid separately. The chitin and bentonite solutions were mixed at various ratios with moderate agitation for 30 minutes. The blend films were prepared by casting the mixed solutions onto polystyrene plated and allowing the solvent to evaporate at room temperature. Similar experiments were performed in the presence of formaldehyde.

## 2.3 Characterizations

The chitin composite films before and after cross linking were characterized using FT-IR and XRD studies. X-ray diffractometer was used to characterize the crystallinity of pure and the blend films. X-ray diffraction (XRD) patterns were recorded by reflection method with nickel-filtered Cu K $\alpha$  radiation using a Rigaku X-ray diffractometer operated at 40kV and 30mA in the 2 $\theta$  scanning mode from 5° to 80°. Chemical structure of pure chitin and the composite films were investigated by FTIR measurement, FTIR measurements were performed using KBr pelleted samples with a Perkins Elmer 200 FTIR spectrophotometer with a resolution of 4cm<sup>-1</sup> in the range of 400 – 4000 cm<sup>-1</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1 FTIR analysis

IR spectra are a powerful tool to identify functional groups in a molecule and to study the strength and the fraction of hydrogen bonding and miscibility. Fig. 1 presents the FTIR spectrum of pure chitin and fig.2 is chitin/bentonite (1:1) composite in the presence of cross linking agent (formaldehyde). The peak at 3434 cm<sup>-1</sup> corresponding to OH group of chitin is significantly shifted to lower wave number at 3402 cm<sup>-1</sup> in the chitin/bentonite composite in the presence of cross linking agent, which indicates that both the chitin and bentonite have good interaction through intermolecular hydrogen bonding.

Two peaks in the range of 3650-3400 were observed due to OH group of bentonite and OH group of chitin. These observations indicate the existence of good miscibility between chitin and bentonite.

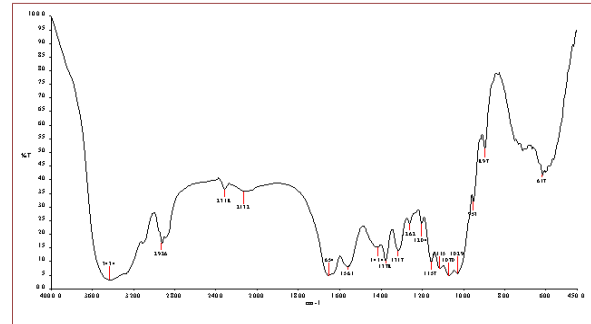


Fig 1: FTIR spectrum of pure chitin

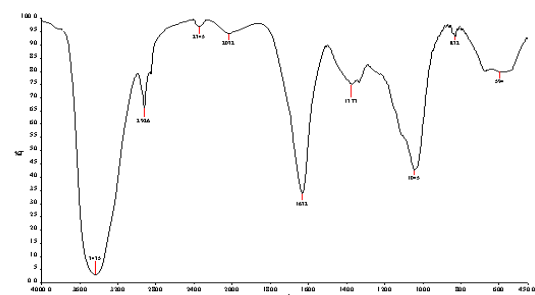


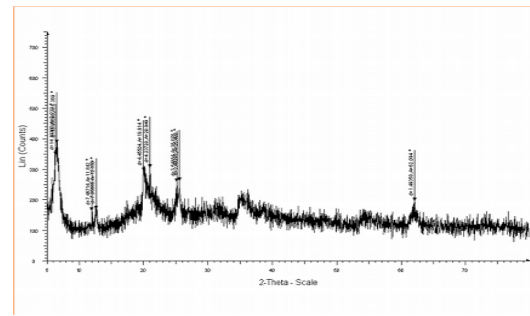
Fig 2: IR spectrum of CH/BE (1:1) with crosslinking

### 3.2 X-ray diffraction

X- Ray diffractograms (XRD) of chitin/bentonite composite films are shown in the Fig.3-4. As compared with chitin, CT/BE (1:1) in the presence of cross linking agent shows a weaker and broader peak in the 2 $\theta$ = 10-30° region, which demonstrated that the conjugation of bentonite suppressed the crystallization to some extent due to the loss of hydrogen bonding (Zong et al., 2000). In the CT/BE blend films, the intermolecular interactions

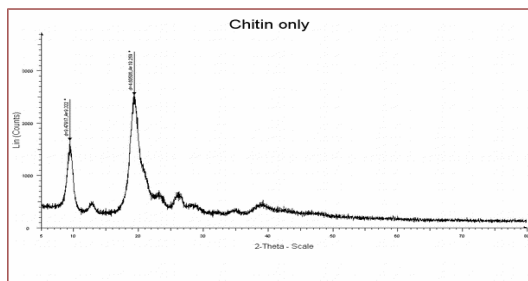
between the amide and OH groups in chitin limited the molecular movement of chitin chain and reduced its crystallization.

**Fig 3: XRD spectrum of pure chitin**

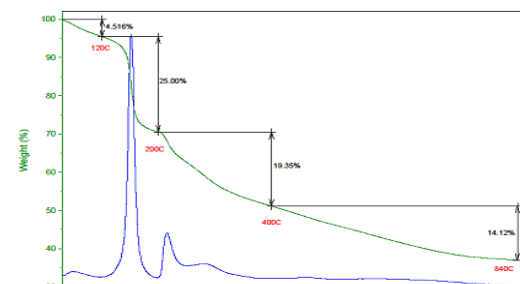


**Fig 4: XRD spectrum of CH/BE (1:1) with crosslinking**

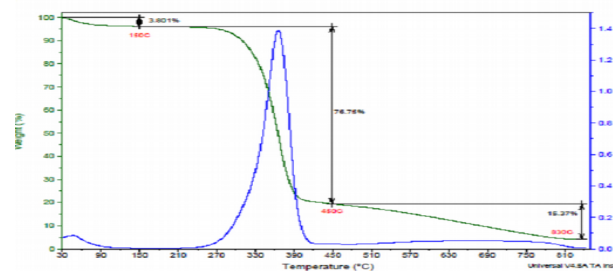
### 3.3 TGA analysis



The TGA thermograms of chitin, CT/BE (1:1) and CT/BE (1:1) with formaldehyde polymer blend are presented in Figures (7 – 9). Chitin has two degradation temperatures which the temperatures lower than 100°C indicating the loss of water. The temperature above 100°C indicates the decomposition of pyranose ring structure. The TGA of blended polymer shows five decomposition temperatures. Maximum decomposition was observed around from 350°C, which may be due to the decomposition of side chains.



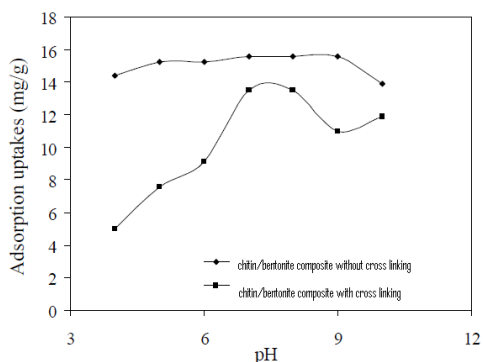
**Fig 6: TGA spectrum of chitin (1:1) with crosslinking**



**Fig 5: TGA spectrum of pure chitin**

### 3.4 Effect of pH on copper adsorption

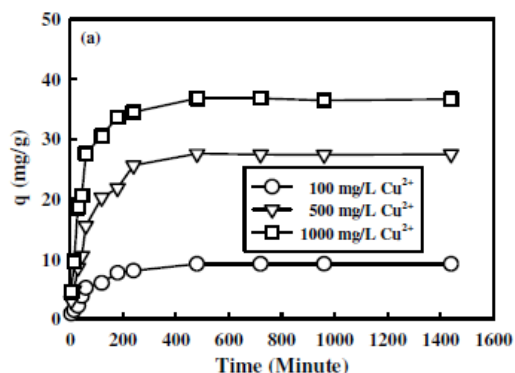
Figure 5 shows the amounts of copper ion adsorption on the chitosan-bentonite and the crosslinked chitin-bentonite beads in solutions of initial pH values from 4 to 10 (copper ions mainly existed as  $\text{Cu}^{2+}$  in this pH range). In general, the adsorption capacities increased with the increase of the solution pH values for both the chitin-bentonite beads and the crosslinked chitin-bentonite beads and the maximum adsorption uptakes reached about 13-15 mg/g in this case. It is also observed that the chitin-bentonite beads always had greater adsorption capacities than the cross linked chitin-bentonite beads in the pH range studied.



**Figure 7:** Effect of initial solution pH values on copper adsorption uptakes on the chitin/ bentonite composite with and without cross linking (initial copper ion concentration in the solution 50 mg/l)

### 3.5 Effect of contact time

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration of the adsorbate. The effect of contact time on the heavy metal ions adsorption by chitin biopolymers was investigated for 24 hours. The kinetic studies were carried out for different initial concentrations 100, 500 and 1000 mg/L for  $\text{Cu}^{2+}$  ions on chitin at 298 K. In Figure 6, it was observed that the uptake amount of  $\text{Cu}^{2+}$  ions on chitin increases rapidly with increasing of the contact time 0 to 180 minute and then reaches the equilibrium after 480 minutes. The initial rapid phase is due to the presence of large number of vacant sites and, as a result there exists increased the concentration gradient between adsorbate in solution and adsorbate in the adsorbent surface. As time proceeds, this concentration is reduced due to the accumulation of  $\text{Cu}^{2+}$  ions on the vacant sites, leading to decrease in gradient the adsorption rate after 180 to 480 minute.



**Figure 8.** Effect of contact time on adsorption of  $\text{Cu}^{2+}$  ion for chitin beads at 298.15 K (pH= 8)

### 3.6 Sorption isotherms

#### Langmuir adsorption isotherm

The most important model of monolayer adsorption came from the work of Langmuir (1918). Langmuir considered the adsorption of an ideal gas onto an idealized surface. It is based on the assumptions namely, adsorption can only occur at a fixed number of definite localized sites, each site can hold only one adsorbate molecule (monolayer) all the sites and no interaction between adsorbed molecules even on adjacent sites. The Langmuir equation (Eq. 1) which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed as

$q_e = q_{\max} C_e / 1 + b C_e$  which can also be written as

$$C_{\text{ads}} = (K_L C_{\text{eq}}) / 1 + b C_{\text{eq}} \quad \text{--- (1)}$$

Fresh metal salt solutions of copper with different initial concentrations were prepared. Equal volumes of these solutions were treated with the adsorbents at equilibrium conditions (1gm/L at a pH 5). The results were tabulated and fitted into the Langmuir adsorption isotherm equation. In this study the following linearized form of the Langmuir isotherm was used.

$$C_{\text{eq}} / C_{\text{ads}} = b C_{\text{eq}} / K_L + 1 / K_L \quad \text{----- (2)}$$

composite bentonite chitin/	Initial concentration of Cu(II) mg/L	1000	500	200	100	50
	Initial amount of Cu (II) in 200ml solution	200	100	40	20	10
	Eqm adsorption in 1 gm of sorbent (ye) $C_{ab}$	172	89	36	18.6	9.5
	Amount of Cu left in 200ml of solution	28	11	4	1.4	0.5
	Eqm concentration in 1000ml (Ce) $C_{eq}$	140	55	20	7	2.5
	Ce/Ye	0.8	0.6	0.5	0.3	0.2

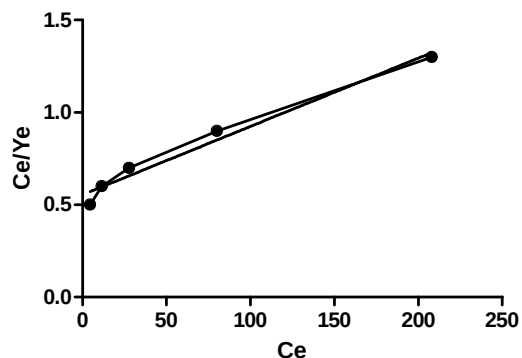
and  $C_{max} = K_L/b$  ----- (3)

Where,  $C_{ads}$  = amount of metal ions adsorbed ( $mg.g^{-1}$ )  
 $C_{eq}$  = equilibrium concentration of metal ion in solution ( $mg.dm^{-3}$ )  
 $K_L$  = Langmuir constant ( $dm^3.g^{-1}$ )  
 $b$  = Langmuir constant ( $dm^3.mg$ )  
 $C_{max}$  = Maximum metal ion to adsorb onto 1g adsorbent ( $mg.g^{-1}$ )

The constant  $b$  in the Langmuir equation is related to the energy or the net enthalpy of the sorption process. The constant  $K_L$  can be used to determine the enthalpy of adsorption.

**Table: 1 Distribution of Cu (II) ions between sorbent and solution at equilibrium.**

Metal ions	Initial concentration $C_0$ ( $mg/dm^3$ )	Final concentration $C_f$ ( $mg/dm^3$ )	$R_L$ values
Cu(II) ion	1000	378	0.3841
	500	168	0.5839
	200	58	0.8025
	100	26.5	0.8989
	50	9.5	0.9613



**Figure – 9:** Effect of initial concentration on the Langmuir adsorption of Copper by CH/BE (1:1) composite – formaldehyde

The affinity between adsorbate and adsorbent can be predicted using the Langmuir parameter to form the dimensionless separation factor  $R_L$  that is used to predict if an adsorption system is “favorable” or “unfavorable (Ngha et al., 1998, Sharma et al 2007; Meena et al 2003)

$R_L = 1/1+bC_0$  ----- (4)

Where  $C_0$  is the initial metal ion concentration and  $b$  is the Langmuir isotherm constant, the adsorption process as a function of  $R_L$ . Table 2 shows the  $R_L$  values for copper and chromium.

$R_L > 1$  Unfavorable,  $R_L = 1$  Linear,  $0 < R_L < 1$  Favorable,  $R_L = 0$  Irreversible

**Table 2:**  $R_L$  values based on Langmuir adsorption. In the present study, the values of  $R_L$  (Table 2) are observed to be in the range 0–1, indicating that the adsorption process is favorable for chitin- bentonite composite.

**Freundlich’s sorption isotherm**

The Freundlich isotherm model, which is also very widely used. The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of



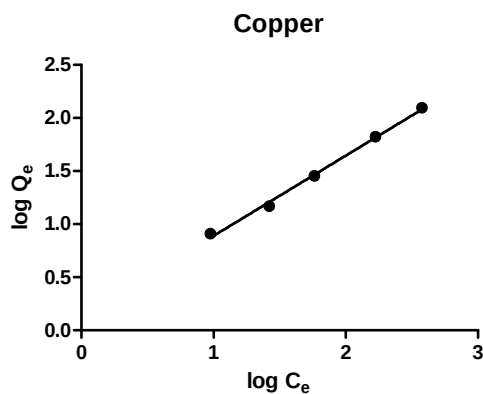
active sites, and/ or interactions between sorbed species (Freundlich, 1907).

The Freundlich model can be expressed by,

$$Q_e = KF C_e^{1/n} \text{----- (5)}$$

$$\log q_e = \log KF + 1/n \log C_e \text{----- (6)}$$

Where, KF and n represent the Freundlich constants. KF is indicative of the relative sorption capacity, where n is the measure of the nature and strength of the sorption process and the distribution of active sites. Figure (8) corresponds the Freundlich isotherm of copper. Using mathematical calculation that n values between 1 and 10 represent beneficial sorption (Febrianto et al., 2009).



**Figure – 10:** Effect of initial concentration on the Freundlich adsorption of Copper by CH/BE (1:1) composite – formaldehyde

**Table 3:** Adsorption isotherm constant, C<sub>max</sub> and correlation coefficients

Metal ions	Langmuir constants				Freundlich's constants		
	Q <sub>0</sub> (dm <sup>3</sup> /g)	b (dm <sup>3</sup> /mg)	C <sub>max</sub> (mg/g)	R <sup>2</sup>	K <sub>F</sub>	1/n	R <sup>2</sup>
Cu(I)	1.572	0.004 232	361.7 5	0.835 1	1.363 1	1.322 3	0.997 2

This study showed that the chitin - bentonite composite adsorb heavy metals in particular Cu(II) ions at a higher range (C<sub>max</sub> – 361.75 Cu ) These results are in good agreement with the results obtained for copper remediation from tannery effluent. The removal was at a higher rate when the metals were taken in the pure form than when they are present in the effluent. This is mainly because of the influence and competition of the other ions present in the effluent which inhibit the chelation of the metals on to the adsorbents.

### 3.7. Thermodynamic parameters

The thermodynamic parameters, the standard enthalpy change (ΔH°), standard entropy change (ΔS°), and standard Gibbs energy (ΔG°) of adsorption are useful in defining whether the adsorption reaction is endothermic or exothermic, comment of the system undergoing adsorption, and spontaneity of the adsorption process. Gibbs free energy was calculated by the following equation.

$$\Delta G^\circ = -2.303RT \log C_{ad}/ C_{eq} \text{----- (1)}$$

The ΔG° value of Cu (II) was -38.25. The negative value of Gibbs free energy indicates the spontaneous nature of adsorption process.

## 4. Conclusion

FTIR and XRD study shows that there is intermolecular molecular hydrogen bonding interaction between the two polymer components and the films exhibit an amorphous character. The effect of contact time and pH of the medium on adsorption efficiency of chitin-bentonite polymer blend were studied for wastewater tannery effluent. It is also observed that the chitin-bentonite composite always had greater adsorption capacities than the cross linked chitin-bentonite composites in the pH range were studied. According to regression coefficient the Freundlich adsorption isotherm was more fitted for

copper than Langmuir, it indicates that the adsorption was physisorption. The negative value of Gibbs free energy indicates the spontaneous nature of adsorption process. Hence the chitin-bentonite polymer blend can be used for waste water treatment at industrial level.

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