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# Synthesis and characterization of cross linked chitin/bentonite polymer blend and adsorption studies of Cu (II) and Cr (VI) on chitin

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# ABSTRACT

Mixing of two or more polymers to produce blends is a well established strategy for achieving specific combination of physical properties. Polymer blend films of chitin and bentonite were prepared from homogeneous solutions in trichloroacetic acid at various ratios of chitin and bentonite. The cross linking agent glutaraldehyde was incorporated into the polymer blends to improve the properties such as surface hardness, stiffness, resistance to temperature and solvent attack. 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. Glass transition temperature and the crystallization of the polymer blends were investigated on the basis of studies differential scanning calorimetry (DSC). By TGA and DTG experiments, enhancement in the thermal stability of polymer blend in presence of cross linking agent (glutaraldehyde) was found out. Adsorption of Cu (II) and Cr (VI) on chitin was studied by the Longmuir and Freundlich method. The influence of dosage of adsorbent, contact time & pH were experimentally verified. The results revealed that the adsorption of Cu (II) and Cr (VI) on chitin is spontaneous, endothermic and favorable. This blended polymer was used as an adsorbent in dye effluent treatment.

Keywords: Chitin, Cross linking Agent, Thermal stability, Polymer blend Adsorption studies.

## **INTRODUCTION**

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-D-glucopyranose units. It carries one acetamido group and hydroxyl group per glucose ring, thus allowing excellent complexation capacity with metal ions (Lerivrey et al., 1986).

Chitin possesses many beneficially biological properties such as biocompatibility, biodegradability, non-toxicity, adsorption properties. Nowadays natural polymeric materials have become increasingly important due to their natural abundance and low costs. However, due to its low mechanical strength and flexible behavior, chitin has limited in application water treatment, (Sudha, 2010) while addition of synthetic polymers increased its properties tremendously. The mechanical properties of chitin film can be improved by blending with other natural (Bianchi, et al., 1995) or synthetic polymers (Lee et al., 1996).

Chitin exhibits a strong tendency to form intra- and inter-molecular hydrogen bonding between the polymer chains and is water insoluble due to its rigid crystalline structure (Minke and Blackwell, 1978; Gozalez et al., 2000) with a network of organized fibers; this structure confers rigidity and resistance to organisms that contain it. Chitin is known as potential useful biomedical materials for wound healing, artificial skin, suture and drug carrier (Lee et al., 1996). Chitin is a well-known adsorbent for transition and post- transition metal ions (Gavrilescu, 2004; Ravikumar, 2000). Since the lone pair of electrons available on nitrogen in acetamido group and hydroxyl group can serve as chelating sites. The formation of a coordination complex between the metal and chitin nitrogen or oxygen has been reported (Reddad et al, 2002).

Conventional methods employed for the removal of heavy metal ions from industrial effluents include chemical precipitation, filtration, electrochemical treatment, and ion exchange. Most of these methods are expensive and incapable of removing trace levels of heavy metal ions (Do, 1998). In recent years this situation has led to a growing interest in the application of biomaterials including algae, bacteria, fungi, higher plants, and products derived from these organism, have been demonstrated to remove certain chemicals species (Domszy and Roberts, 1985). Chitin is widely used in food and pharmaceutical industry and in biotechnology. Thus polymer has been extensively studied in the field of biomaterials and because of its biological properties, biodegradability, bioactivity, and biocompatibility it has attracted much attention (Aksu et al., 2005).

The optimum experimental conditions and mechanism of adsorption such as pH were investigated for the qualitative recovery of Cr and Cu on chitin. In this paper, we will report on thermal properties of chitin-zeolite polymer blend systems. We will also report on the miscibility of the two polymers in the solid state due to intermolecular interaction by means of FTIR, wide angle X-ray diffraction (WXRD), DSC etc.

Langmuir and Freundlich adsorption isotherms were applied to the experimental data.

The pseudo first-order, pseudo second -order were used for determining of the adsorption Kinetics.

## MATERIALS AND METHODS

#### **2.1 Materials**

Chitin was obtained from India sea foods, Cochin which is 99% pure. All other materials such as glutaraldehyde 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 at room temperature with moderate agitation for 30 minutes.

## 2.3 FTIR analysis

The films were dried at 60 °C overnight before measurement. Chemical structure of pure and the blend 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>.

# 2.4 X-ray diffraction

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 Ka radiation using a Rigaku X-ray diffractometer operated at 40kV and 30mA in the 2 $\theta$  scanning mode from 5° to 80°.

## 2.5 Thermo gravimetric analysis

The thermo gravimetric analysis of the bentonite/chitin blends without and with cross linking agents such as glutaraldehyde was carried out on TGA Q500 V20.10 Build 36 instrument. The thermal properties of samples were measured by NET Z SCH - Geratebau GmbH thermal analyzer. Samples were dried in vacuum desiccators and powdered in a standard Aluminum panel. 2.0mg of this sample was heated about 30 °C – 350 °C at a heating rate of 10 °C per min under N<sub>2</sub> atm in the DSC analysis.

TGA were recorded with 2.0mg of this sample was heated from 30 °C to  $870^{0}$ C at a heating rate of 10 °C/min at N<sub>2</sub> atm. In this technique thermal decomposition of polymer blend are measured as a function of temperature.

## 2.6. Dyeing industry effluent

Dyeing industry effluent was collected from an effluent canal outside a leather dyeing unit of Ambur Industrial area, India in a polythene container. pH and Temperature were noted on the spot.

## 2.7. Physico- chemical characterization of effluents

Physico-chemical factors such as pH, Electrical Conductivity, Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand, Total Dissolved Solids, Total Solids, Alkalinity, Chloride, Hardness, Sodium and Heavy Metals such as Copper, Chromium were analyzed as per the methods of APHA(1998), Heavy metals were analyzed using Varian AA200 Atomic absorption spectrophotometer(AAS) in air-acetylene flame.

# **RESULTS AND DISCUSSION**

## **3.1 FTIR**

As shown in Figure.1, the spectrum of pure chitin film shows a broad band at  $3434 \text{ cm}^{-1}$  which is due to the OH stretching. The band at  $1561 \text{ cm}^{-1}$  is assigned for the NH bending (amide II) (NH<sub>2</sub>)

while the small peak at 1654 cm-1 is attributed to the C=O stretching (amide I) O=C-NHCH<sub>3</sub>. The bands at 2926, 1414, 1317 and 1262 cm<sup>-1</sup> are assigned to CH<sub>2</sub> bending due to pyranose ring. The band at 1378 cm<sup>-1</sup> is due to CH<sub>3</sub> wagging. The characteristic features of chitin spectrum in this study are similar to that of previous reports.



Figure 1. FTIR of Pure chitin

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Figure.2 represents the FTIR spectrum of chitin/bentonite (1:1) blend. 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 blend, 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. As can be seen, the presence of bentonite in the chitin caused remarkable shift for the C=O stretching peak at 1654 cm<sup>-1</sup> of chitin to a higher wave number at 1658 cm<sup>-1</sup>. In addition, the bands at 2926 and 1317 cm<sup>-1</sup> of chitin disappeared in the spectrum of chitin/bentonite blend. These observations indicate the existence of good miscibility between chitin and bentonite.







Figure 6. XRD of CT/BE (1:1) with glutaraldehyde



Figure 7. TGA of pure chitin



### 3.2 X-ray analysis

The XRD spectrum of chitin shown in Figure 4. It has high crystallinity and the characteristic peak at  $2\theta=10^{\circ}$  and  $20^{\circ}$  are assigned to crystal forms I and II. In comparison with chitin, CT/BE does not have the peak at  $10^{\circ}$ , but CT/BE (1:1) with glutaraldehyde polymer have the peak at  $2\theta=20^{\circ}$  in Figure.6. The intensity of the peak descends sharply. Hence crystallanity of the blended polymer had decreased much.

#### 3.3 Thermo gravimetric analysis

The TGA thermograms of chitin, CT/BE (1:1) and CT/BE (1:1) with glutaraldehyde 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.



Figure 9. TGA of CT/BE (1:1) with glutaraldehyde



Figure 10. DSC of pure chitin







Figure 12. DSC of CT/BE (1:1) with glutaraldehyde

#### 3.4 DSC analysis

The Fig.10 shows the DSC curves of pure chitin and Figure.11 is CT/ BE (1:1) Polymer blend. Broad endothermic peaks are observed at various temperatures indicating the crystallization of the polymer blend as well as evaporation of water and decomposition of side chain. The glass transition temperature of pure chitin is 75.1°C; whereas the glass transition temperature of CT/BE blend (1:1) is 91.7°C. On comparing the DSC curves of chitin, CT/BE (1:1) has higher glass transition temperature. Hence, it was found that the endothermic peaks and the glass transition temperatures of chitin/bentonite blend shifted to higher values. It confirms that the blended polymer has higher thermal stability than pure chitin with the formation of different crystalline forms.

## **3.5. Tannery effluent treatment**

The physico – chemical parameters and heavy metals content of the tannery industry effluent collected from an industry from Ambur industrial area. All the parameters along with the heavy metal contents were found to be high than the accepted limits.

#### 3.5.1. Effect of adsorbent dose on the tannery effluent

Table.1. Effect of adsorbent dose (chitin/ zoelite 1:1 – glutaraldehyde) on the physico – chemical factors and
heavy metals of tannery effluent

Denometers		Adsorbent Dose					
Parameters	Raw Effluent	1g	2g	3g	4g	5g	6g
Electrical Conductivity dSm <sup>-1</sup>	12.49	4.77	2.9	1.75	1.15	0.98	0.82
BOD mg/L	1250	544	369	271	177	121	120
COD mg/L	4210	2100	1450	925	514	225	220
TDS mg/L	8140	1120	955	520	415	340	318
Alkalinity mg/L	798	420	240	149	132	111	95
Chloride mg/L	1200	597	379	242	132	79	75
Total Hardness mg/L	3610	1151	642	245	147	140	140
Calcium mg/L	1010	779	385	224	121	119	111
Magnesium mg/L	2600	1180	851	410	144	121	120
Sodium mg/L	2140	1176	712	450	199	110	109
Potassium mg/L	840	482	275	192	106	100	99
Total Nitrogen mg/L	258	144	115	90	64	42	42
Chromium mg/L	1200	651	240	113	96	54	50
Copper mg/L	141	71	44	27	11	9.5	9.0

 Table.2. Effect of contact time of an adsorbent (chitin/ zoelite 1:1 – glutaraldehyde) on the physico – chemical factors and heavy metals of tannery effluent

Panamatang	<b>Raw Effluent</b>	Contact time					
rarameters		1hr	2hrs	3hrs	4hrs	5hrs	6hrs
Electrical Conductivity dSm <sup>-1</sup>	12.49	9.5	5.2	3.33	2.7	1.6	1.5
BOD mg/L	1250	767	385	122	118	109	99
COD mg/L	4210	1422	977	517	299	145	111
TDS mg/L	8140	2116	1412	62.0	37.5	25.0	25
Alkalinity mg/L	798	222.5	120.5	642	411	277	124
Chloride mg/L	1200	721	319	254	197	147	117
Total Hardness mg/L	3610	1221	867	545	255	115	77
Calcium mg/L	1010	512	377	215	111	66	61
Magnesium mg/L	2600	1123	731	449	295	155	59
Sodium mg/L	2140	1115	744	322	177	110	95
Potassium mg/L	840	322	244	116	76	41	27
Total Nitrogen mg/L	258	145	89	57	44	43	41
Chromium mg/L	1200	724	447	245	113	125	77
Copper mg/L	141	102	65	41	28	25	21

Various dosages of the prepared chitin-bentonite blend cross linked with glutaraldehyde have been used to treat tannery effluent. Table. 1 explains the parameters such as COD, TS, BOD, and also heavy metals such as copper, chromium, have been decreased drastically with the increase in the adsorbent dosage. The purification of water has been found at minimum amount of sample required (5 g/L). Hence 5 g was found to be the optimum dosage treating the tannery effluent (Singh et al., 2009).

## 3.5.2. Effect of contact time on tannery effluent

The Table. 2 shows the effect of time on the treatment of tannery effluent by the chitin –Zeolite (1:1) with glutaraldehyde. On increasing the time the initial concentration reduces. After the treatment for 6 hrs all parameters reduced to the maximum extent. Hence 6 hrs was found to be an optimum treatment time

## 3.5.3. Effect of pH on tannery effluent

 Table.3. Effect of pH of an adsorbent (chitin/ zoelite 1:1 – glutaraldehyde) on the physico – chemical factors and heavy metals of tannery effluent

Raw Effluent					pН			
Parameters		3	4	5	6	7	8	9
Electrical Conductivity dSm <sup>-1</sup>	12.49	4.2	1.7	1.5	1.66	2.1	3.25	4.10
BOD mg/L	1250	470	295	144	177	195	241	259
COD mg/L	4210	2142	1194	223	447	610	725	1120
TDS mg/L	8140	4217	1212	440	599	795	1310	1442
Alkalinity mg/L	798	312	116	44	72	198	277	359
Chloride mg/L	1200	467	224	135	299	377	413	774
Total Hardness mg/L	3610	1555	1131	310	566	622	830	835
Calcium mg/L	1010	495	390	177	520	699	848	922
Magnesium mg/L	2600	1110	640	177	434	595	822	1100
Sodium mg/L	2140	991	565	214	492	577	714	744
Potassium mg/L	840	540	266	121	356	426	511	511
Total Nitrogen mg/L	1458	1255	877	312	820	975	960	981
Chromium mg/L	1200	474	340	140	288	460	522	525
Copper mg/L	141	69	60	41	61	79	85	85

The effect of pH on tannery effluent treatment was studied. The reduction of all the parameters in the effluent by the blended polymer was found to be pH dependant. Table 3 showed that the there was maximum adsorption of all the parameters in the effluent by chitin –Zeolite with glutaraldehyde at pH 5.

## **3.6. Kinetics**

The rate constants for adsorption of reactive orange dye onto bagasse activated carbons were treated with Lagergren first order model which is generally expressed as

 $dq_t/dt = k_1 (q_e - q) - (1)$ 

Where k1 is the first-order-rate constant. Integrating Eq. (1) with respect to integration conditions

 $\log (q_e - q_t) = \log q_e - k_1 t/2.303 - \dots (2)$ 

The first-order-rate constant  $k_1$ , can be obtained from the slope of the plot log (qe - qt) vs time.



Figure.14 Pseudo-first-order kinetics for Copper

The coefficients of correlation for the first-order-kinetic model were not high for all adsorbents and concentrations. Also, the estimated values of qe calculated from the equation differed from the experimental values (Table. 4), which shows that the model is not appropriate to describe the adsorption process.

Adsorption kinetics were explained by the pseudo-second-order model

 $t/q_t \; = \; 1/k_2 {q_e}^2 \, + t/q_e \; \ldots \ldots \ldots \ldots \ldots (3)$ 

Where  $K_2$  is the second-order-rate constant (g mg-1 min-1). The values of  $k_2$  at different initial dye concentrations for all adsorbents were calculated from the slopes of the respective linear

plots of t/qt vs. t (Fig.15&16). The correlation coefficients were, 0.9848 and 0.9406 suggest a strong relationship









Table.4 Comparison between Lagergren pseudo-first-order and pseudo- Second-order kinetic models for Copper and Chromium

Metal ion	Pseudo-first-order kinetic model		Experimental value	Pseudo-sec	cond-order kinetic	model	
	qe (mg/g)	$k_1 (min^{-1})$	$\mathbf{R}^2$	qe (mg/g)	qe (mg/g)	$k_2 (g mg^{-1} min^{-1})$	$\mathbf{R}^2$
Cr(VI)	455.76	0.005195	0.9065	187.17	122.12	0.003897	0.9848
Cu(II)	428.32	0.005685	0.9909	170.21	204.89	0.003576	0.9406

#### **3.7.** Sorption isotherms

#### **3.7.1.** Langmuir sorption isotherm

The Langmuir model, which is one of the most widely used, was initially proposed for the adsorption of a gas on the surface of a solid, nevertheless it has been extended to include the sorption of solid at a solid – liquid interface. The Langmuir model suggests that the sorption occurs on the surface of the solid that is made up of elementary sites, each of which can adsorb one sorbate molecule, i.e. Monolayer sorption. It was also assumed that every sorption site is equivalent and the ability of sorbate to get bound there is independent of whether (or) not the neighboring sites are occupied (Langmuir, 1918).

The Langmuir model is given as follows,

 $Qe = Q^0 bCe/1 + bCe$  (4)

The linearised form is,

 $Ce/qe = 1/Q^0b + Ce/Q^0$ (5)

Where, qe (mg/g) and Ce (mg/L) are the sorbed metal ion on the sorbent and the metal ion concentration in the solution at equilibrium b (L/mg) is the constant related to the affinity of binding sites.  $Q^0$  (mg/g) is known as the Langmuir constant, which represents the monolayer sorption capacity. Figures 17 &18 explained the linearization of Langmuir model. In general for good sorbents, high values of  $Q^0$  and low values of b are required (Kratochvil and Volesky, 1998). The calculated values are reported in the Table.6.



Figure. 17. Langmuir isotherm of chromium.



Figure. 18. Langmuir isotherm of copper.

The affinity between adsorbate and adsorbent can be predicted using the Langmuir parameter to form the dimensionless separation factor  $R_L$ 

 $R_L = 1/1 + bC_o$  ----- (6)

Where  $C_o$  is the initial metal ion concentration and b is the Langmuir isotherm constant, the adsorption process as a function of  $R_L$ . Table. 5 show 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

Metal ions	Initial concentration C <sub>0</sub>	Final concentration C <sub>f</sub>	R <sub>L</sub> values
	$(mg/dm^3)$	$(mg/dm^3)$	
	1000	395	0.4034
	500	185	0.5908
Cr(VI) ion	200	66	0.8019
	100	27.5	0.9067
	50	13	0.9536
	1000	387.5	0.3024
	500	161	0.5107
Cu(II) ion	200	42.5	0.7981
	100	15.5	0.9155
	50	8	0.9545

 Table.5 R<sub>L</sub> values based on Langmuir adsorption

#### **3.7.2. Freundlich 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,

$Qe = K_F Ce^{1/n.}$	 (7)
$\log qe = \log K_F + 1/n \log Ce.$	 (8)

where,  $K_F$  and n represent the Freundlich constants.  $K_F$  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. Figures (19&20) correspond the Freundlich isotherm of copper and chromium. Using mathematical calculation that n values between 1 and 10 represent beneficial sorption (Febrianto et al., 2009). Langmuir and Freundlich constants are represented in the Table. 6.



Figure .19. Freundlich isotherm of chromium.

Copper



Figure .20. Freundlich isotherm of copper

Madaliana	Langmuir constants				Freun	dlich con	stants
Metal lons	$K_L (dm^3/g)$	b (dm <sup>3</sup> /mg)	C <sub>max</sub> (mg/g)	$\mathbf{R}^2$	K	n	$\mathbf{R}^2$
Cr(VI)	1.949	0.003744	520.57	0.8417	0.9471	1.2384	0.9989
Cu(II)	1.020	0.005952	171.37	0.9379	2.4361	1.5110	0.9907

Table.6. Adsorption isotherm constant,  $C_{\text{max}}$  and correlation coefficients

According to the regression coefficients proved that the correlation of Freundlich model was strong with respect to the Langmuir model.

## 3.8. Sorption efficiency

The distribution coefficient of an adsorbent is defined as the ratio of the metal ion adsorbed to the amount in the liquid phase. Values of the distribution coefficient lower than 1.0 shows low sorption efficiency. In this study the values of distribution coefficient is higher than 1.0 as presented in Tables 7&8. The estimated values of the distribution coefficient indicated high efficiency of the chitosan graft co polymer for the treatment of wastewater containing Cu (II) and Cr (VI) ions (Bamgbose et al., 2010).

Table.7. Equilibrium sorption of copper and chromium on chitosan blend at 25°C pH 6

Initial concentration	Metal ion adsorbed (mg/				
of metal ions (mg/l)	Cu(II)	Cr(VI)			
200	122.5	121			
100	67.8	63			
40	31.5	26.8			
20	16.9	14.5			
10	8.4	7.4			

 Table.8. Distribution coefficient of copper and chromium at 25°C

Metal ions	Equilibrium concentration of metal ion (mg/l)	Distribution coefficient Kd
Cu(II)	71 - 1.9	1.8169 - 4.2631
Cr(VI)	69 – 1.2	1.8985 - 7.3333

# CONCLUSION

The results suggest that there is strong interaction between the molecular chains of chitin and bentonite, which may lead to the miscibility at specific ratios of the two polymer components blended. From the FTIR results, it was found that the C=N type of linkage were observed in the cross linked polymers showing the cross linking between the polymer and the cross linking agents. From the results of DSC and TGA analyses, it was observed that the cross linking agents enhanced the thermal stability of the polymer blend.

The effects of dosage, time and pH of the medium on adsorption efficiency of chitin-zeolite polymer blend were studied for wastewater tannery effluent. According to regression coefficient the Freundlich adsorption isotherm was more fitted for copper and chromium than Langmuir, and also the value of E < 8, it indicates that the adsorption was physisorption. The adsorption

distribution coefficient is greater than 1; it indicates that the adsorption of copper and chromium on to the chitin-zeolite polymer blend is more efficient.

A significant result has been found for the industrial application. Hence the chitin-zeolite polymer blend can be used for waste water treatment at industrial level.

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