Batch Adsorption Studies for the Removal of Copper from Wastewater using Natural Biopolymer

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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. 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. Characterizations of the binary blends were investigated by Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), X-ray diffraction (XRD) and scanning electron microscope (SEM). 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. TGA studies reveal that the thermal stability of the blend is enhanced by glutaraldehyde as crosslinking agent. Finally, the results of scanning electron microscopy (SEM) indicated that the morphology of the blend is smooth and large surface area for better adsorption, further it confirms the interaction between the functional groups of the blend components.
Keywords: chitin, biosorption, copper, adsorption isotherm, composites, crosslinking.

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. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. These industries also release heavy metals like Cu, Cr, Cd, Hg, Pb etc.

Even very low concentrations[1-3] 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[4], fertilizers, tanneries 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[5]. 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[6] and be extremely harmful, even fatal[7]. 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. High concentration of copper causes enzyme inhibition leading to Wilson's diseases (Accumulation of copper in liver and kidneys). It was estimated that the annual industrial discharges of copper into fresh water environments was at 1.4×10^{10} g/year, and the amounts of copper in industrial wastes and sewage sludge that have been dumped into the ocean was 1.7×10^{10} g/year worldwide [8]. The world health organization (WHO) recommended a maximum acceptable concentration of copper in drinking water to be 1.5 mg/l [9]. Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent.

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 [10-11] 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 [12-14] 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 [15].

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 derivates of chitin have played significant role in their capacity as adsorbent and complexing agent by virtue of their hydroxyl, acetate, amido and amino groups. Research and development work on chitin and CS has reached a status of intense activities in many parts of the world [4-6]. The positive attributes of excellent biocompatibility and admirable biodegradability with ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity have provided ample opportunities for further development[7-12]. It has become of great interest not only as an under-utilized resource but also as a new functional biomaterial of high potential in various fields[13-15]. With data emerging from not less than 20 books, over 300 reviews, over 12,000 publications and innumerable patents, the science and technology of these biopolymers are at a turning point where one needs a very critical look on its potential to deliver the goods[16,17]. Chitin has been reported to be the second most abundant natural polysaccharide in nature[16] and is commonly found in crab and shrimp shells containing 10-15% of chitin[17]. Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (7.21%) compared to synthetically substituted cellulose (1.25%) [18]. As most of the present-day polymers are synthetic materials, their biocompatibility and biodegradability are much more limited than those of natural polymers such as cellulose, chitin, chitosan and their derivatives. However, these naturally abundant materials also exhibit a limitation in their reactivity and process ability[19-20]. In this respect, chitin and chitosan are yield recommended as suitable functional materials, because these natural polymers have excellent properties such as biocompatibility, biodegradability, non toxicity, chelating properties, etc. Chitin consists mainly of β-(1→4)-2- acetamido- 2- deoxy- glucopyranose 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 [21].

The blending of polymers, which results in preparation of new materials with improved physico chemical and mechanical properties[22], has received considerable attention of researchers in the past several decades. Hence, the mechanical properties of chitin blend can be improved by blending with other natural[23] or synthetic polymers[24]. In this project the chitin was blended with the inorganic material such as bentonite (clay). Bentonite

is a naturally occurring material consisting predominantly of the clay mineral montmorillonite. It mainly composed of montmorillonite with a composition of SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, Na_2O, and K_2O [25-26]. Crosslinking is a process where polymeric chains are linked either by covalent bonds via a chemical reaction or by strong physical interactions (e.g. ionic interactions) between the polymer and the crosslinking agent or between two different polymers[27]. Crosslinking agents can be incorporated into linear polymers to improve such properties as stiffness, surface hardness, resistance to temperature and resistance to solvent attack. [28]. In the present investigation bentonite was treated with chitin biopolymer in the presence of formaldehyde as cross-linking agent and used for adsorption studies of Cu (II) from wastewater.

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 Characterization

The chitin composite films before and after cross linking were characterized using FT-IR, TGA, SEM and XRD studies. X-ray diffractometer was used to characterize the crystallinity of pure and the blend films. Chemical structure of pure chitin and the composite films were investigated by FTIR measurement. The thermo gravimetric analysis of the chitin/bentonite blends was carried out on SDT Q500 V20.10 Build 36 instrument at the temperature range from 300-350° C at a heating rate of 10° C per minute in nitrogen atmosphere. In this technique the mass of the substance and thermal decomposition of polymer blend were measured as a function of temperature. The surface morphology and cross sectional morphology of chitin/ bentonite blends were observed with Scanning Electron Microscope to verify the compatibility of the mixtures of chitin and bentonite.

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 represents 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^{-1} corresponding to OH group of chitin is significantly shifted to lower wave number at 3402 cm^{-1} in the chitin/bentonite composite in the presence of cross linking agent[29-30], 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.
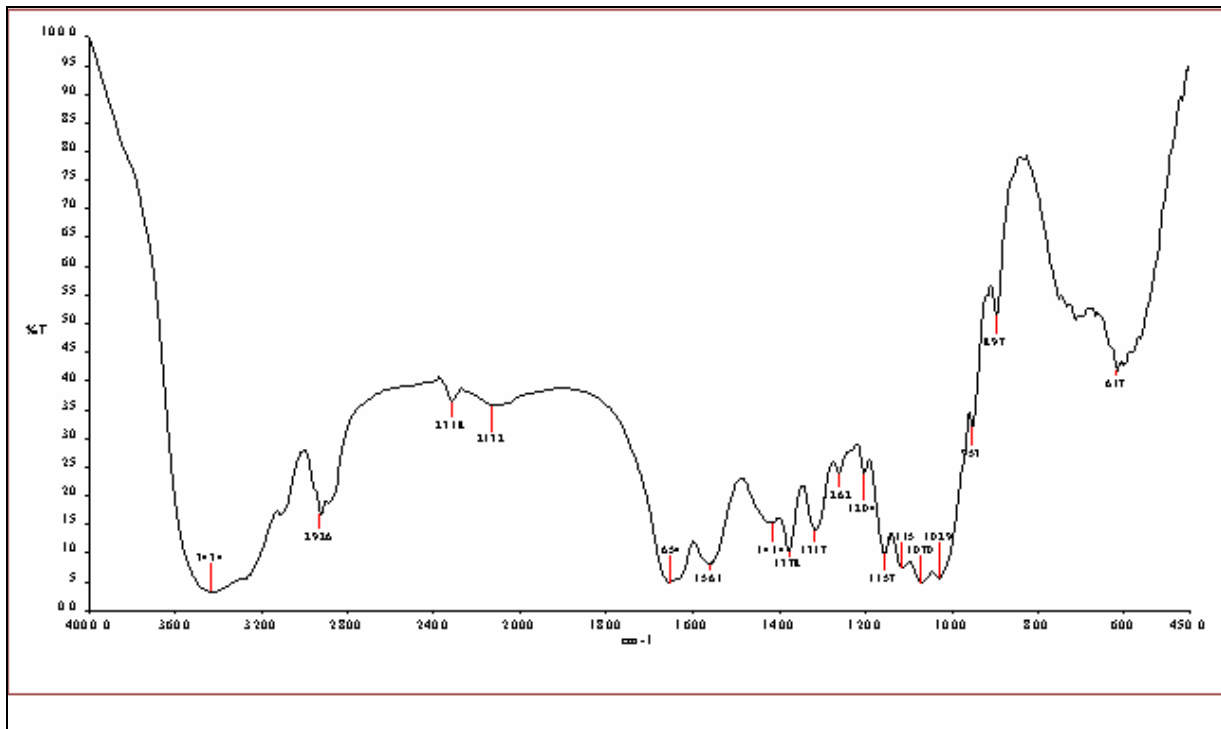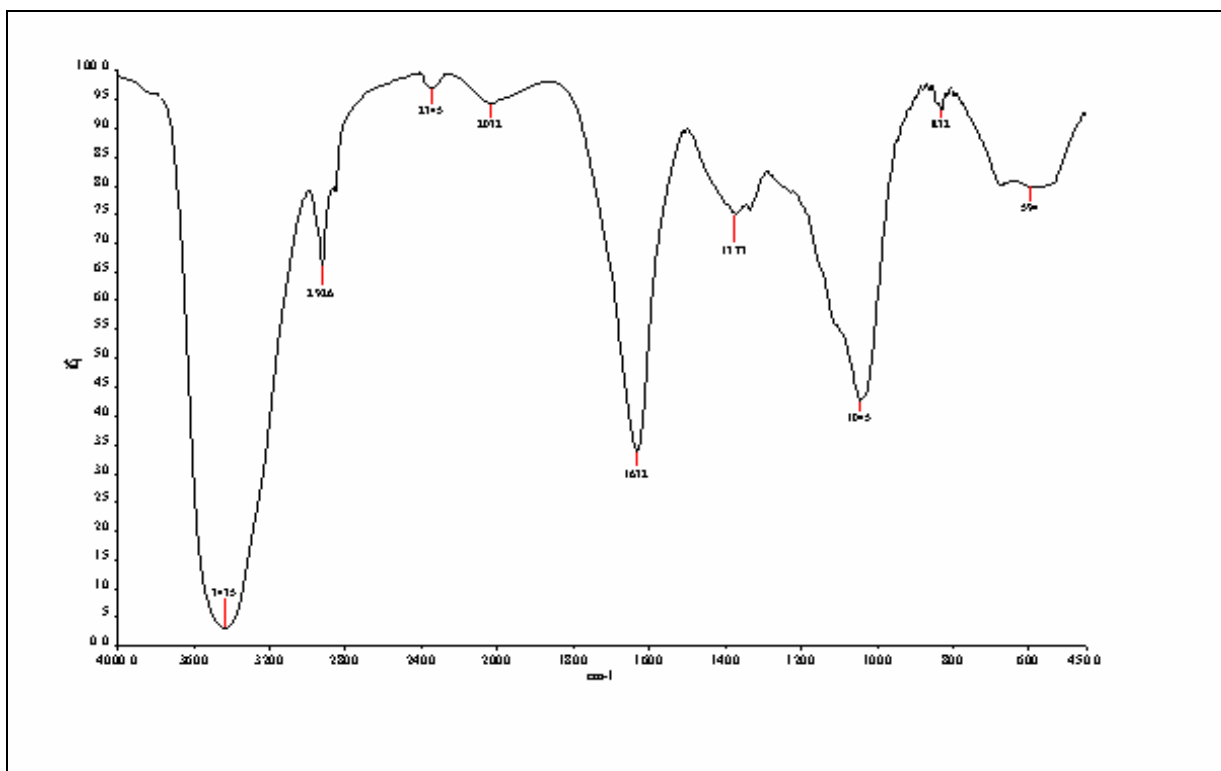
Fig 1: FTIR spectrum of pure chitin

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

3.2 X-Ray Diffraction

The X-ray diffraction analysis is used to determine the structure, complexation and crystallization of the polymer matrix[31-32]. 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 2Θ= 10-30° region, which demonstrated that the conjugation of bentonite suppressed the crystallization to some extent due to the loss of hydrogen bonding [19] and diffraction pattern with a broad amorphous peak indicated that there was a molecular miscibility and interaction between the components[33].
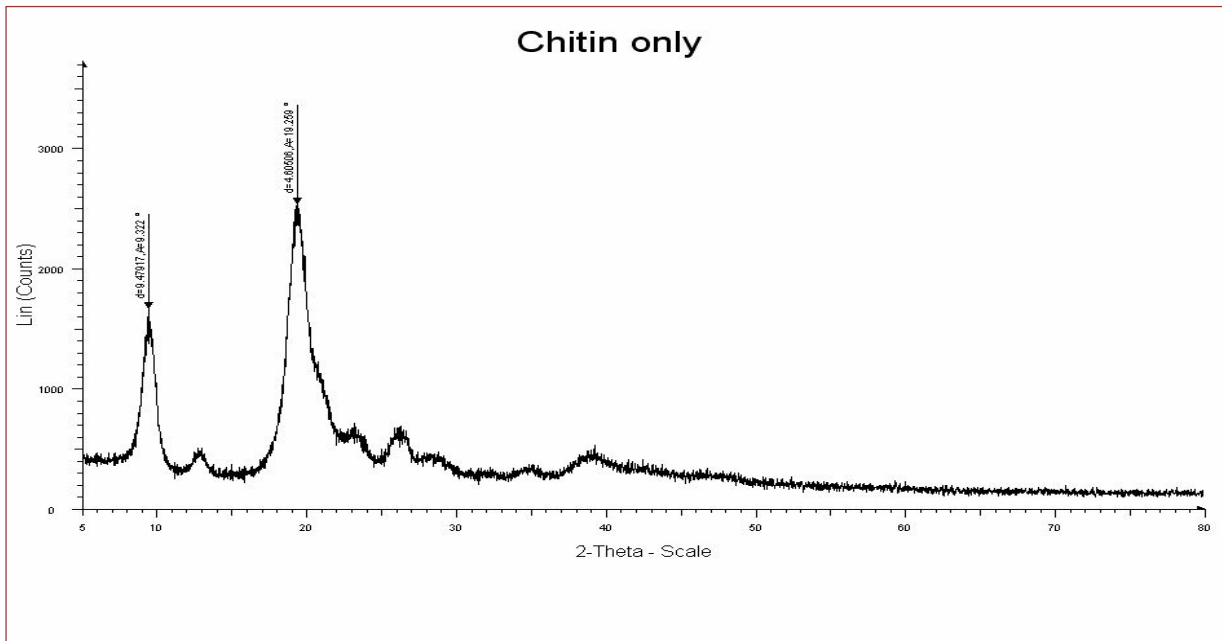
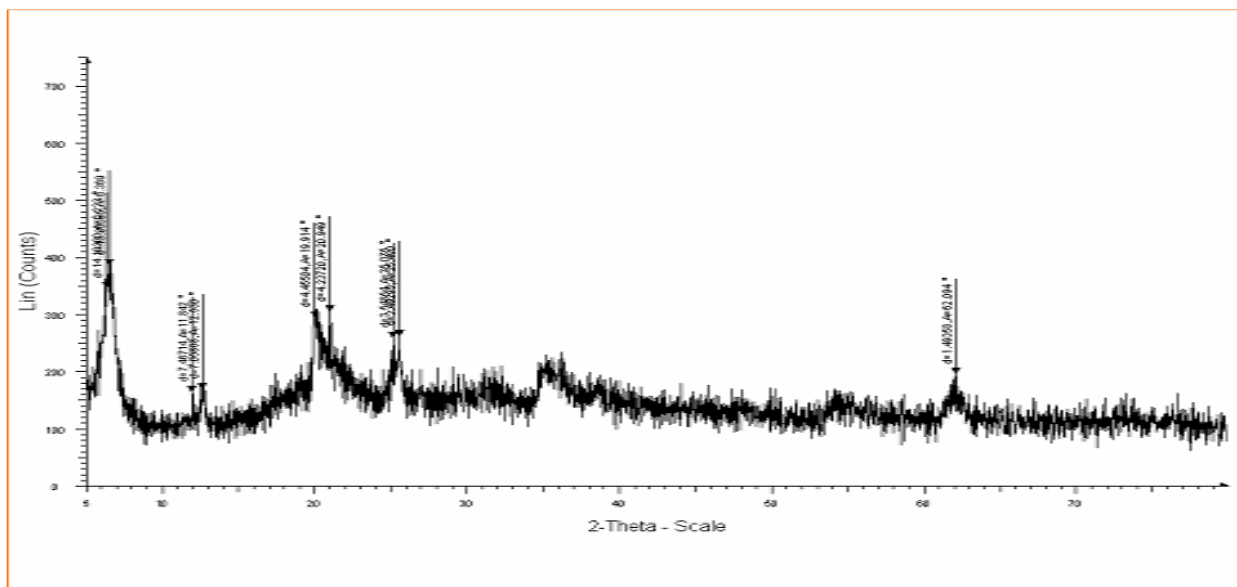**Fig 3: XRD spectrum of pure chitin**

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

3.3 Tga Analysis

TGA has been used to investigate the thermal degradation, phase transition and crystallization of the polymers. In order to ascertain the thermal stability, the prepared films were subjected to TGA analysis. The TGA thermograms of chitin and CT/BE (1:1) with formaldehyde polymer blend are presented in Figures 5 – 6. Chitin has two degradation temperatures which the temperatures lower than 100°C indicating the loss of water [34]. 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 [29].
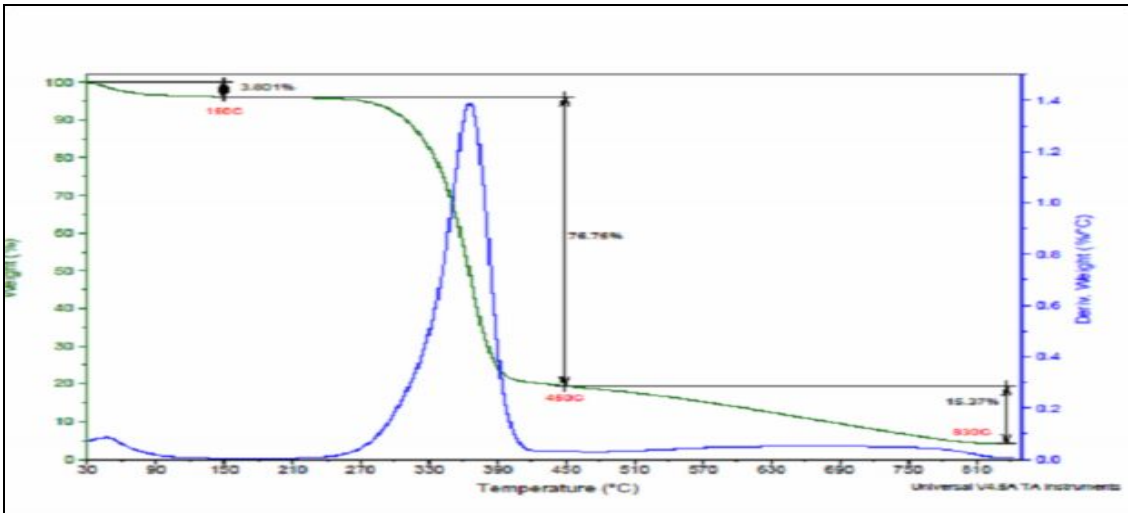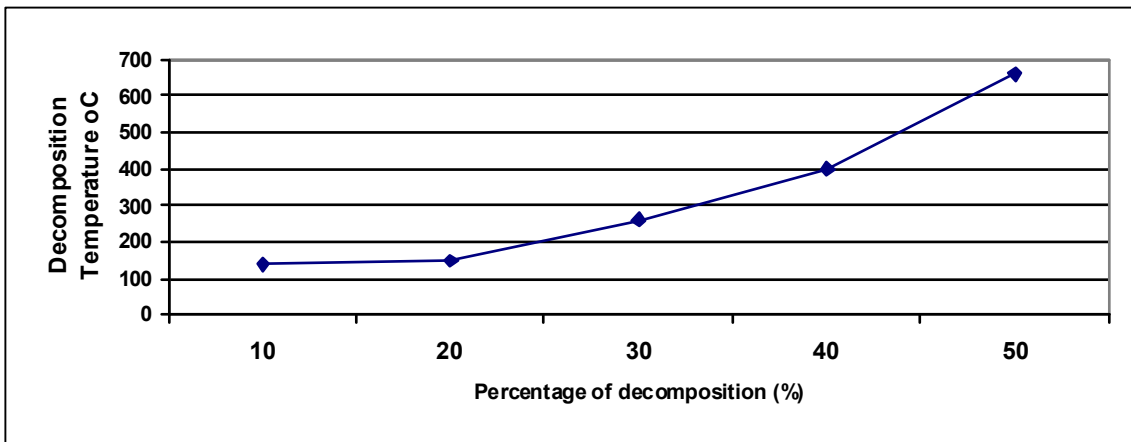
Fig 5: TGA spectrum of pure chitin

Fig 5a: TGA thermogram of CH/BE (1:1) blend with crosslinking
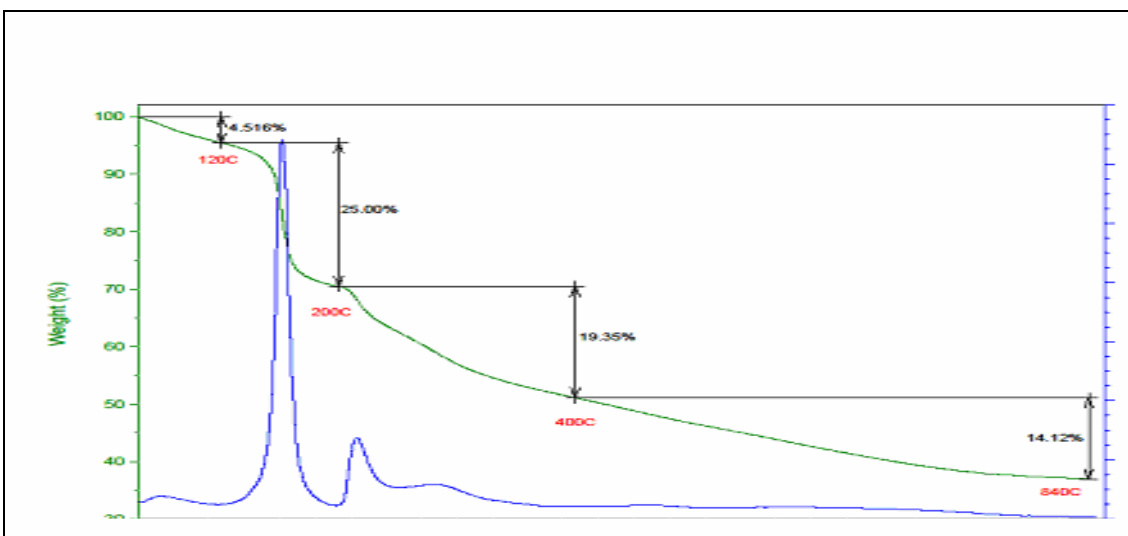

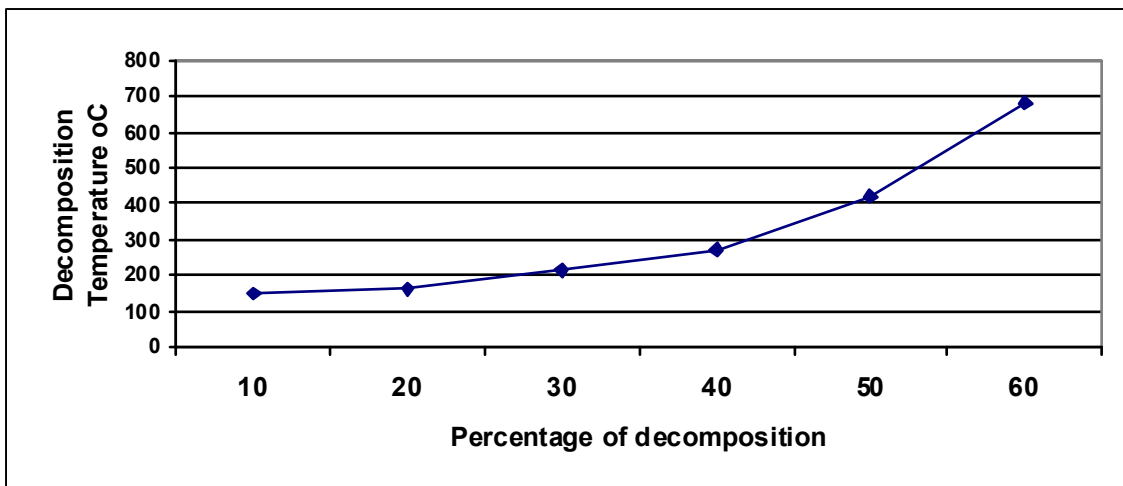**Fig 6: TGA spectrum of chitin (1:1) with crosslinking**

Fig 6a: TGA thermogram of CH/BE (1:1) blend with crosslinking

3.4 Scanning Electron Microscopy

Scanning Electron Microscope (SEM) is commonly used to study surfaces, structures, morphologies, and forms of materials. The SEM micrographs of the chitin/bentonite blend (1:1). Figure 7b showed the proper dispersion of film with complete miscibility on the chitin matrix in a uniform manner[35]. It was observed that chitin/bentonite blends had porous and fibrous structures with large surface area for better adsorption. The Scanning Electron Micrograph of crosslinked chitin/bentonite blend (1:1) with formaldehyde is shown in Figure 7a. After Formaldehyde treatment, the surface of the blends became very porous and after the amine groups release the surface of the blends became dense again, somewhat similar to the surface of the previous blend. SEM image of crosslinked chitin/bentonite with formaldehyde blend was smooth on the surface. All these observations confirm that blending of bentonite in the presence of crosslinking agent allows better compatibility between chitin and bentonite. This characteristic copolymer may responsible to allow water with greater adsorbing property.
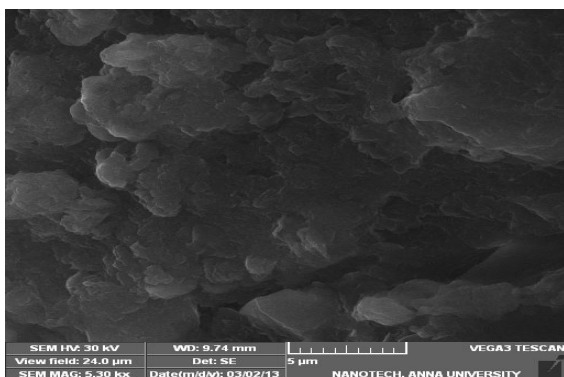

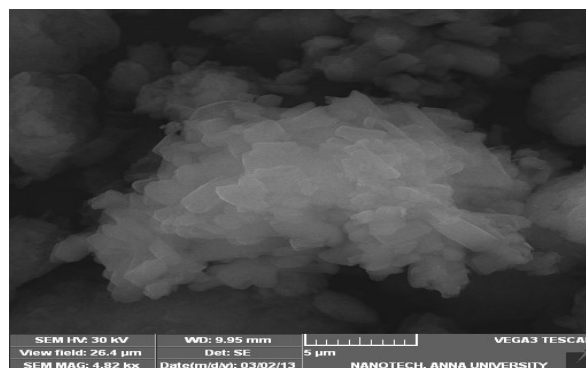**Figure 7a: Scanning Electron Micrographs of CH/BE (1:1) blend with formaldehyde**

Figure 7b: Scanning Electron Micrographs of CH/BE (1:1) blend

3.5 Effect of Ph On Copper Adsorption

Figure 8 shows the amounts of copper ion adsorption on the chitin-bentonite and the crosslinked chitin-bentonite blend in solutions of initial pH values from 4 to 10 (copper ions mainly existed as Cu^{2+} in this pH range). At low pH, the amine group on blend was protonated to varying degree resulting in a decrease in the sorption of heavy metal ions. After pH 5 the adsorption values found to increase. In general, the adsorption capacities increased with the increase of the solution pH values for both the chitin-bentonite blend and the crosslinked chitin-bentonite blend and the maximum adsorption uptakes reached about 13-15 mg/g in this case. It is also observed that the chitin-bentonite blend always had greater adsorption capacities in the pH range studied.
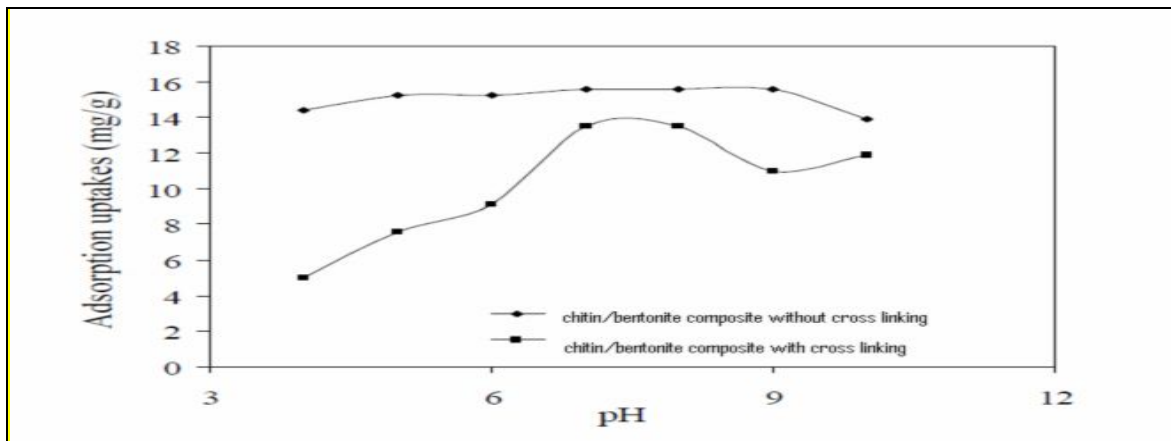
Figure 8: Effect of initial solution pH values on copper adsorption uptakes on the chitin/ bentonite blend with and without cross linking.

3.6 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 Cu^{2+} ions on chitin at 298 K. In Figure 9, it was observed that the uptake amount of 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 Cu^{2+} ions on the vacant sites, leading to decrease in gradient the adsorption rate after 180 to 480 minute.
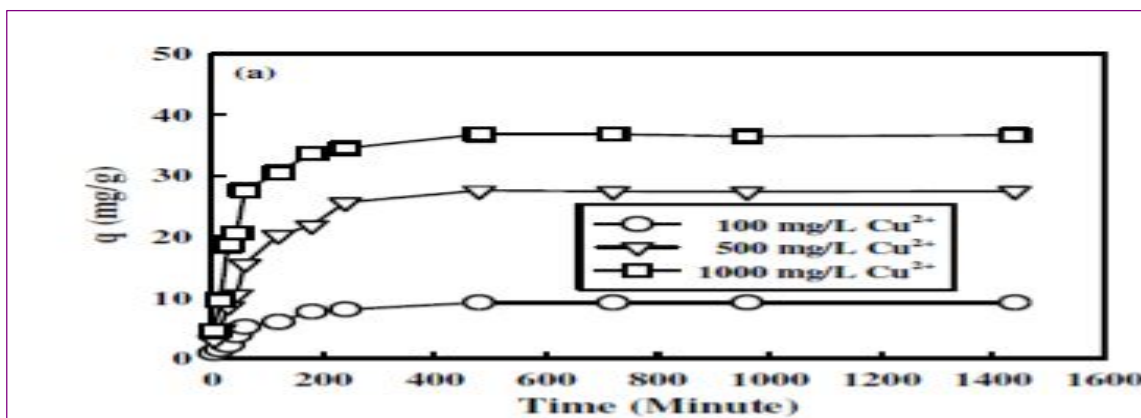

Figure 9: Effect of contact time on adsorption of Cu^{2+} ion for chitin blend (1:1) at 298.15 K (pH= 8)

3.7 Sorption Isotherms

Sorption isotherms describe how adsorbates interact with adsorbents. In order to successfully represent the equilibrium adsorption behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Two kinds of several isotherms equations were tested [36].

3.7.1 Langmuir adsorption isotherm

The most important model of monolayer adsorption came from the work of [37]. 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

$C_{ads} = (K_L C_{eq})/1+bc_{eq})$ ----------- (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.

$C_{eq}/C_{ads} = bc_{eq}/K_L + 1/K_L$ ----------------- (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.

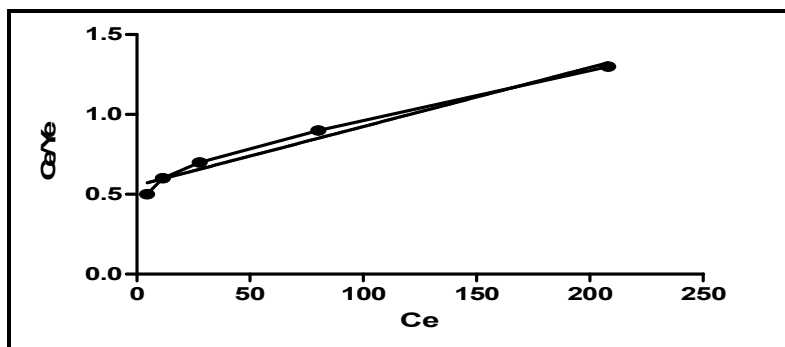|						
	Initial concentration of Cu(II) mg/L	1000	500	200	100	50
chitin/ bentonite composite	Initial amount of Cu (II) in 200ml solution	200	100	40	20	10
	Eqm adsorption in 1 gm of sorbent (ye) C_{ab}	172	89	36	18.6	9.5
	Amount of Cu left in 200ml of solution	28	11	4	1.4	0.5
	Eqm concentration in 1000ml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

Figure 10: Effect of initial concentration on the Langmuir adsorption of   Copper by
**   CH/BE (1:1) blend – 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 [38-40].

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

Where Co 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

Metal ions	Initial concentration C$_0$ (mg/dm^3)	Final concentration C$_f$ (mg/dm^3)	R$_L$ values
	1000	378	0.3841
	500	168	0.5839
Cu(II) ion	200	58	0.8025
	100	26.5	0.8989
	50	9.5	0.9613

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.

3.7.2 Freundlich's Sorption Isotherm

A brief empirical equation often used to represent adsorption data is called the Freundlich equation. The Freundlich isotherm model, which is also very widely used. The Freundlich model proposes a multilayer sorption with a heterogeneous energetic distribution of active sites, and/ or interactions between sorbed species [41].

The Freundlich model can be expressed by,

$$Qe = KFCe \ 1/n. \text{-------------} (5)$$

$$\log qe = \log KF + 1/n \log Ce. \text{-------------} (6)$$

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 [42].
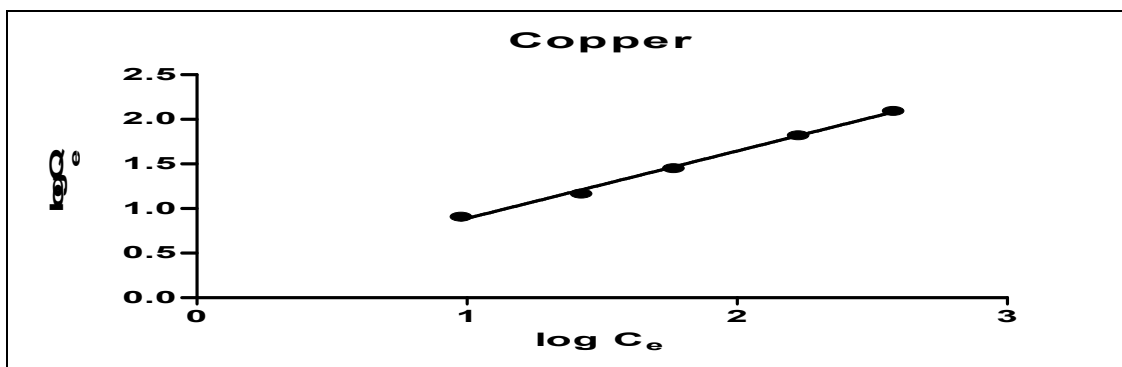

Figure 11: Effect of initial concentration on the Freundlich adsorption of   Copper by CH/BE (1:1) blend – formaldehyde

Table 3: Adsorption isotherm constant, C $_{max}$ and correlation coefficients

Metal ions	Longmuir constants				Freundlich's constants		
	Q$_0$ (dm^3/g)	b (dm^3/mg)	C$_{max}$ (mg/g)	R^2	K$_F$	1/n	R^2
Cu(II)	1.572	0.004232	361.75	0.8351	1.3631	1.3223	0.9972

This study showed that the chitin - bentonite composite adsorb heavy metals in particular Cu(II) ions at a higher range (C $_{max}$ – 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.

3.8 Thermodynamic Parameters

The thermodynamic parameters, the standard enthalpy change (ΔH^o), standard entropy change (ΔS^o), and standard Gibbs energy (ΔG^o) 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 [43]. Gibbs free energy was calculated by the following equation.

$$\Delta G^o = -2.303RT \log C_{ad}/C_{eq} \quad \text{--------------- (7)}$$

The ΔG^o 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.

Acknowledgement

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