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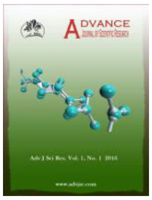

A novel Adsorbent Based on Chitosan and Tanninfor the Removal of Heavy Metals from wastewater

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ABSTRACT

The adsorption of Cd , Co , Pb and Zn by novel adsorbent polymer based on Chitosan and Tannin was investigated. The adsorption of Cd , Co , Pb and Zn by prepared polymer was studied. Polymer was characterized using FTIR, UV, GC-Mass , X-ray spectra DSC and TG. All characterization techniques confirm the existence of Chitosan and Tannin. Adsorption of Cd , Co , Pb and Zn ions by prepared polymer was investigated under different conditions. The effect of pH, Dose of polymer and agitation time were studied. The removal efficiency under different conditions was evaluated using atomic adsorption spectroscopy. To improve uptake and make in an industry workable process, this study suggests that modification of the native polymer would be required.

Keywords:Chitosan, Tannin, heavy metals, adsorption

Received: 23 December 2015 *Accepted: 26 Feproary 2016* *Available online: 14 May 2016*

1. Introduction

Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment. Copper, Nickel, Mercury, lead, Zinc, Arsenic etc. are such toxic metals which are being widely used. They are generated by dental operation, electroplating, tanning, textile, paper and pulp industry and are potentially toxic to humans. [1] These heavy metals are used in many industries for different purposes and released to the environment with industrial wastage. Therefore the effluents being generated by these industries are rich in heavy metals should be treated before discharge in to the common waste water. On the other hand aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chain. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms.[2]

The current physico-chemical processes for heavy metal removal like precipitation, reduction, ion-exchange etc. are expensive and inefficient in treating large quantities. They also cause metal bearing sludges which are difficult to dispose off.[2]

The application of biopolymers such as chitosan is one of the emerging adsorption methods for the removal of heavy metal ions, even at low concentrations.[3] Chitosan is a type of natural polyaminosaccharide, synthesized from the deacetylation of chitin, which is a polysaccharide consisting predominantly of unbranched chains of (1→4)-2-acetoamido-2-deoxy-d-glucose. Chitin is the second most abundant polymer in nature after cellulose. It can be extracted from crustacean shell such as prawns, crabs, fungi, insects and other crustaceans.[4] Widely available biopolymers are also being used for adsorption mainly because they are a cheap resource or a freely available resource.[5] Chitosan is a biopolymer, which is extracted from crustacean shells or from fungal biomass. The structure of chitosan is presented schematically in Figure 1.

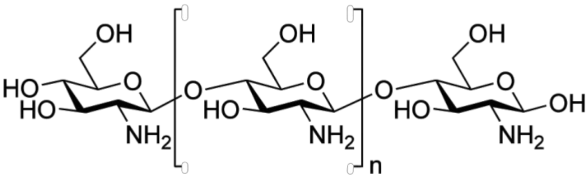


Figure (1): Structure of chitosan

To improve chitosan's performance as an adsorbent, cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycondiglycidyl ether and isocyanates have been used.[6] Cross-linking agents do not only stabilize chitosan in acid solutions so that it becomes insoluble but also enhance its mechanical properties.[7] Chitosan derivatives have been extensively investigated as adsorbents.[8] Recently, chitosan composites have been developed to adsorb heavy metals from wastewater. Different kinds of substances have been used to form composite with chitosan such as montmorillonite,[9] polyurethane, [10] activated clay, [11] bentonite, [12] poly vinyl alcohol, poly vinyl chloride, kaolinite, [13] oil palm ash, [14] and perlite. [15]

The high porosity of this natural polymer results in novel binding properties for metal ion such as cadmium, copper, lead, uranyl, mercury and chromium. Chitosan has been used for about three decades in water purification processes.[16] It has an amine functional group which is strongly reactive with metal ions. [17]

Tannins are high molecular weight polycyclic aromatic compounds widely distributed through the plant kingdom. Tannins can be classified into two groups,[18] the proanthocyanidins (or condensed tannins) and the polyesters of gallic acid and (or) hexahydroxydiphenic acid (hydrolysable tannins, respectively, gallo- and ellagitannins). The co-occurrence of both kinds of tannins in the same plant or plant tissue is often observed. Tannins are found in the leaves, fruits, barks, roots and wood of trees. [19] The structure of tannin is presented schematically in Figure2 .Complex polysaccharide tannin derivatives have been used extensively in potable water, wastewater and industrial effluent treatment applications. [20] In addition tannin helps the filtration process .[21]

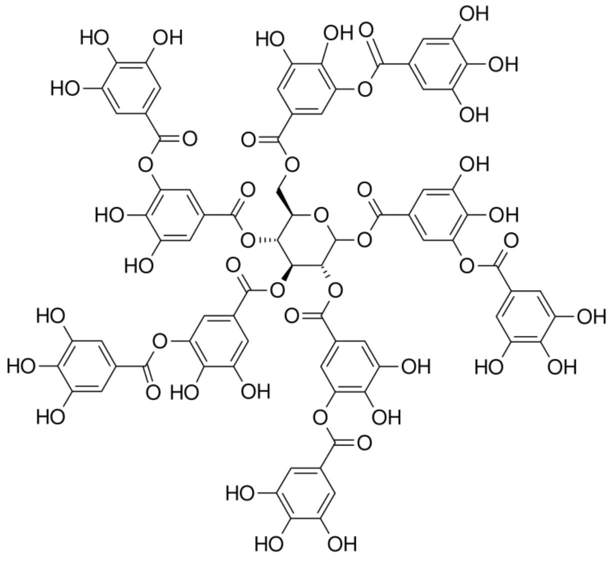


Figure (2) : Structure of Tannin

The idea of using a tannin to purify industrial wastewater, connected to the natural ability of polyphenols to entrapped metal ions with the easy removal system of such a new products. [22] The scavenging behaviour of tannins for several kind of metal ions is well-known. [23] The study of the adsorption by tannin of copper and lead, which are two of the most common metals in factory's wastewater, afford to understand the general affinity of tannin for metal ions, [24] today they are also widely used in tannin-modified adhesive formulations, [25] as adsorbents for pollution control of industrial effluent, [26] and as flocculants. [27] Their natural origin is as secondary metabolites of plants, [28] occurring in the bark, fruit, leaves, etc. Tannin derivatives have been used extensively in potable water ,wastewater and industrial effluent treatment applications. [29]

The aim of this study is to investigate the heavy metals removal from wastewater by adsorption and to evaluate factors affecting on the removal of heavy metals (Cd , Co , Pb and Zn) using as a bio-adsorption material.

2. Experimental

2.1.Materials and methods

2.1.1.Materials

All reagents in this work were of analytic grade and were used as received without further purification and then tested and prepared in order to be suitable for real experiments. The prepared reagent consist of: (1) reagent for isolation of chitosan, i.e. 45% (w/v) NaOH and 1 M HCl (2) reagents for preparation of chitosan – tannin polymer beads, i.e 1% acetic acid , HCl and buteraldehyde (3) Stock solution of 100 mg/ml Cd(II), Co(II), Pb(II) and Zn(II) from $CdCl_2$, $CoCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$crystal, respectively (4) standard solutions for preparing standard curve for the determination of Cd(II), Co(II), Pb(II) and Zn(II) using atomic absorption spectrometer (AAS).

2.1.2.Methods

2.1.2.1. Isolation of Chitosan

The shrimp shells which were used for chitosan isolation was purchased from local seafood processing industry . Chitin, isolated from shrimp shell, was ground to powder form.This powdered chitin was then deacetylated with NaOH (45% w/w) in 100°C water bath for 60 min and the reaction was terminated by an ice bath. Following that, the product was cleaned several times with deionized water until the pH of the suspension reached 7. The suspended particles were collected with a membrane filter and dried at 80°C for 48 h. The chitosan powder was modified with a novel method different from the previous one to achieve better performance.

2.1.2.1.2. Isolation of Tannin:

The Laurus nobilis leaves was cut into pieces and powdered using grinding machine.The powdered sample was sieved through a pair of 40 and 60 mesh sieve. In order to obtain maximum quantity of tannin , extraction was carried out at elevated temperature. The extraction of 50 gram of sample was carried out with water-ethanol mixture (1:1) in soxhlet apparatus. The tannin extract obtained from different cycles of reflux was collected in a flask and its volume was reduced in rotary evaporator. The concentrated tannin extract was dried at 50°C. The dried tannin extract which contains 64-67% tannin was ground in a morter with a pestle. The powdered sample was sieved (60 mesh) and stored in sample bottle.

2.1.2.1.3. Chitosan- Tannin Polymer Synthesis

A 250 mL 2-necked round-bottom flask containing 1% acetic acid, 2 gm of chitosan were added and a magnetic stirring bar and mixed at 100 rpm for 60 min or until dissolved to make. after that an aqueous solution of 2 gm tannin in 25 ml distilled water were added, and then 0.5 ml of buteraldehyde was added into the reactor by controlling the dropping speed. The reaction was continued for 3hrs at room temperature (25°C). Adjusted the pH to 2 by HCl, the chitosan - tannin was obtained. The structure of chitosan-tannin polymer is presented schematically in Figure 3.

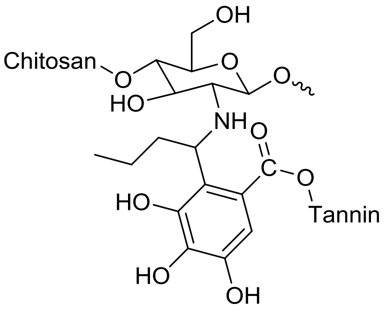


Figure (3): Chitosan - Tannin polymer structure.

3. Characterization techniques and instruments

Six methods were used for the characterization of the chitosan, tannin and chitosan – tannin polymer:

The UV-visible spectra were recorded over the range of 200–700 nm using the T60 U PG Instrument Limited UV-visible spectrophotometer (UK).

Fourier transform infrared (FTIR) spectra were obtained with a FTIR- RX1 spectrometer (Perkim Elmer, USA) with samples incorporated into KBr discs in the range of 400 to 4000 cm^{-1}.

Gas chromatography-mass spectrometry (GC-MS) were performed using an Agilent Technologies 7890 GC with 5975 MSD1μL of reconstituted sample was injected through a 7683B Series Injector using a split mode of 50%. The GC separation was done using a DB5 column at a flow rate of 1mL/min He 99.999%. The oven temperature was programmed as follows: 50 °C (hold 1 min), 25 °C/min to 150 °C, 20 °C/min to 170 °C and 80 °C/min to 250 °C for 3 min. (The total run time was 10 min). Products were detected using a 5975C VLMSD with TripleAxis Detector (m/z 50-250).

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instruments DSC 30 (Mettler Toledo, Switzerland) Differential Scanning Calorimeter. Samples (5–10 mg) were loaded into standard aluminium pans and run using a heat/cool/heat cycle with a heating rate of 10 °C min^{-1} and a cooling rate of 5 °C min^{-1}.

Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments TGA (Mettler Toledo , Switzerland) Thermogravimetric Analyzer. Samples (8–14 mg) were weighed out on platinum pans and heated to 600 °C at 10 °C min^{-1}under a nitrogen atmosphere. All thermal analysis employed duplicate runs for each sample. Working temperature range was 25–800°C with a efficiency of 10°C min^{-1}. Air was used as environmental medium at100 ml min^{-1}flux.

The crystallinity of materials in powder form was studied by X-ray diffraction method (Empyrean series 2) PAN analytical (Netherland) using Cu Kα radiation generated at 40 kV and 40 mA at scanning speed of 0.3 2/ min within a range of 10°to 60°.

4. Study of heavy metal adsorption by synthesized Chitosan – Tannin Polymer

For the adsorption experiments, a 100 mg/l of cadimium , cobalt , lead, , and zinc solutions at different concentrations were prepared and different pH (2 ,4,6,8) were tested. The pH of solution was adjusted to desired values with 0.1 N HNO_3 and 0.1 N NaOH. Adsorption experiments were developed placing (0.1- 1) gm of the dry polymer and 50 ml of corresponding solution with metal ions in a 100 ml glass-stoppered flask. The mixture was shaken at 175 rpm for different mixing time(0.25 , 0.5 , 1 , 2 , 4 , 6 , 8 , 24)hour using a thermostated shaker. The temperature was controlled at 25°C . Samples were filtered at equilibrium. The remaining concentration of metal ions was determined in the filterate by Atomic Absorption Spectrometry.

5. Results and Discussion

5.1. Ultraviolet –visible study of the Compounds

Ultraviolet/visible (UV-Vis) spectroscopy is useful as an analytical technique for two reasons. Firstly, it can be used to identify certain functional groups in molecules, and secondly, it can be used for assaying. UV-Vis spectroscopy involves the absorption of electromagnetic radiation from the 200–800 nm range and the subsequent excitation of electrons to higher energy states. The absorption of ultraviolet/visible light by organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy . The UV of the studied compounds: chitosan and tannin was carried out in double beam UV-visible photometer , using dilute solution (3.5×10^{-3}) .

UV-Vis spectra of chitosan are usually recorded in aqueous acetic acid solutions in a 1.0 cm quartz cell at ambient temperature . Chitosan include various ratios of two far-UV chromophoric groups, N-acetylglucosamine (GlcNAc) and glucosamine (GlcN); as a result, their extinction coefficients for wavelengths shorter than approximately 225 nm is non-zero. Because GlcNAc and GlcN residues show no evidence of interacting within the chitin/chitosan chain, the monomer units contribute in a simple, additive way to the total absorbance of this polymer at a particular wavelength. The UV spectra of chitosan was shown in Figure 4 and the λmax is 201 nm in 0.1 M HAc solution . The U.V. spectra for tannin, show an intense bands at λmax 270 nm for π→ π* transition due to the high conjugation between the π electrons of the benzene ring and the carbonyl group through the carbon-carbon double bond.

5.2. Gas Chromatography- Mass Spectrometry

Mass spectrometry (MS) is a destructive analytical technique used for measuring the characteristics of individual molecules. The basic information obtained from mass spectrometric analysis is the molecular mass of a compound, which is determined by measuring the mass to charge ratio (m/z) of its ion. With the ionization method, full particulars about a molecule’s chemical structure can be found. MS can analyze chemicals with a wide mass range–from small molecules to complicated biomolecules such as carbohydrates, proteins, peptides or nucleic acids. The GC-MS analysis detected all organic species quantitatively. Each peak area in the chromatogram was propotional to the amount of the organic compounds forming that peak.

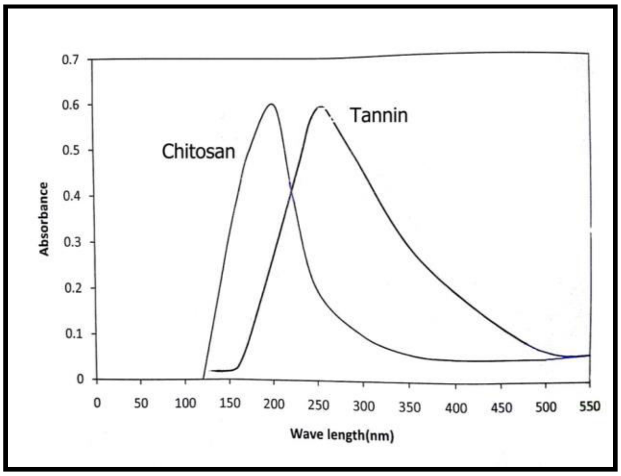


Figure (4): UV-Vissible Spectra of chitosan and Tannin

GC-MS spectra of chitosan is shown in Fig.5 , from the mass spectra it is possible to identify volatile compounds obtained from chitosan . The peaks at m/z 537.9 with retention times under our chromatography conditions around ~15 mins is derived from glucosamine. The molecular weight of the obtained chitosan was 2561.1 . Conditions could be found for tannin that giving peaks at 647.2 m/z with retention times under our chromatography conditions around ~15 mins as shown in Fig. 6. Tannin consists of a ratio of gallic acid to glucose units of approximately 12:13. Therefore this tannin could be considered a hydrolysable tannin. The molecular weight of the obtained lignin was 2836.7.

5.3. Fourier Transformer Spectroscopy(FTIR):

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency of the functional groups in the three different polymers. The spectra were measured by an FTIR spectrometer within the range of 400–4000 cm−1 wave number. The dry amount of polymers (about 0.1 g) was thoroughly mixed with KBr and pressed into a pellet and the FTIR spectrum was then recorded.

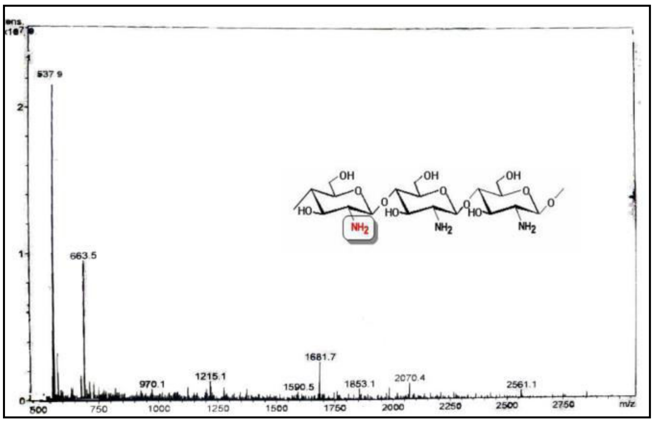


Figure. (5): GC-MS spectra of Chitosan.

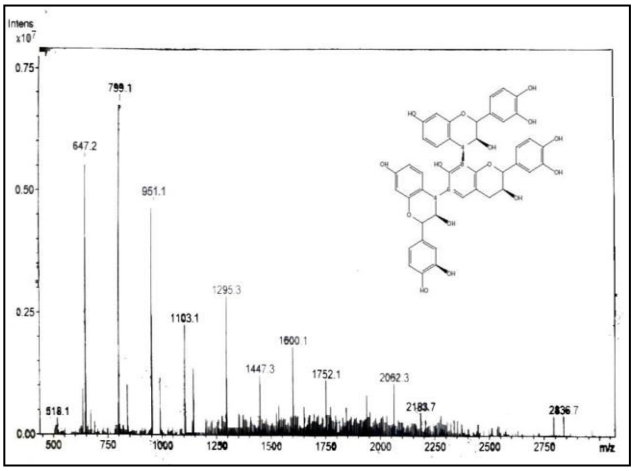


Figure (6): GC-MS spectra of Tannin

5.4. FTIR of Chitosan

The characteristic IR absorption peaks of chitosan were observed (Fig. 7) ,which include a broad and strong band ranging from 3200-3700 cm^{-1} (stretching vibration of O-H and extension vibration of N-H). The peaks located at 2920 and 2881 cm^{-1} can be assigned to asymmetric and symmetric $-CH_2$ groups.The peak located at 1642 cm^{-1} is characterstic of amine deformation. The prominent peak at observed at 1383 cm^{-1} represents C-N stretching. The peak at 1164 cm^{-1}

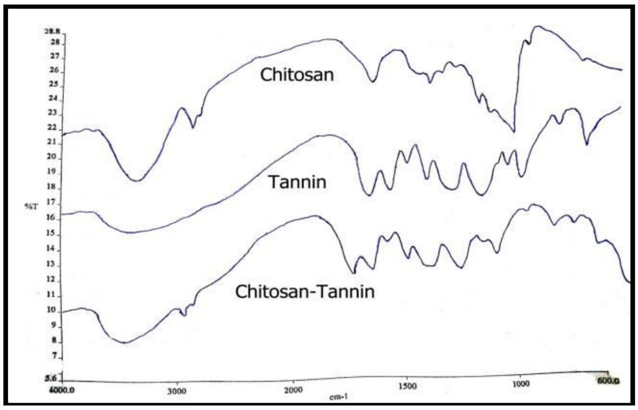
can be attributed to the C-O-C stretching. The peak at 1022 cm^{-1} is characteristic of C-O stretching vibration. The absorption band at 896 cm $^{-1}$, corresponds to the characteristic absorption of β-D- glucose unit.

5.5. FTIR of Tannin:

The poly phenolic tannin compound have many characteristics bands at certain frequencies. Its FT-IR spectrum is shown in Fig.(7) broad peak at 3412 cm-1 is attributed to polymeric O-H group, the frequency at 2935 cm-1 corresponds to C-H stretching frequency and the peak at 1614 cm-1 has been assigned to C=O , and the wideness of the 1709 cm-1 band can be related to the presence of conjugated carbonyl groups . The presence of the functional group C-O-C in tannin is confirmed from the band at 1207 cm-1 ,C-H bending frequency is noted at 1340 cm-1 . A notable band at 1031 cm-1 can be assigned to C-O stretching. At 759 cm-1 shows the result distortion vibration of C=C in benzene rings. Around 1449 cm-1 streching vibrations of C-C aromatic groups appear in spectrum. The absorption band at 869 cm-1, corresponds to the characteristic absorption of β-D-glucose unit Table 3.2 shows the important main bands of tannin.

5.6. FTIR of Chitosan – Tannin Polymer

Some functional groups of tannin were also present in chitosan. Therefore, the same vibrations were observed but with different intensities (Fig.7). The absorption intensity of –NH_2 group and –OH group (peak 3200 – 3700 cm^{-1}) from chitosan – tannin polymer is obviously lower than that of –NH_2 group and –OH group from chitosan , which indicates a cross-linked reaction occurred between chitosan and tannin. Moreover, the reduction in the intensities at 1450 cm^{-1} peak (primary amino group, -NH_2) showed that most of the primary amino groups were involved in the cross – linking process.



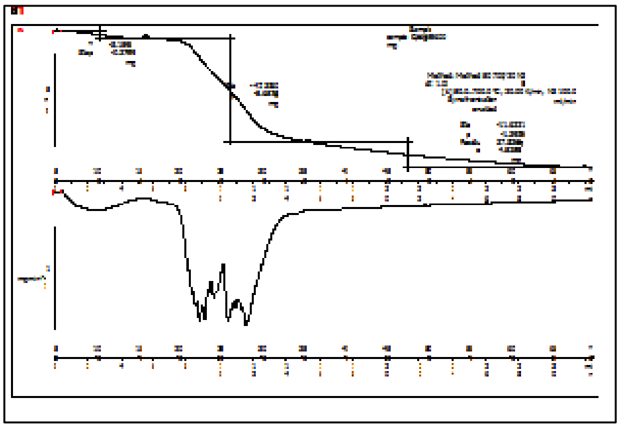
Figure(7): FTIR of Chitosan, Tannin and Chitosan-Tannin polymer

5.7. The Thermal Stability Study of the compounds:

In the present study the thermal stability characteristics of the compounds was investigated by TG and DTG technique. TG is one of the familiar techniques for systematic assessment of polymers thermal stability. It is very useful tool and help to indicate the relative order of stability of various polymers. TG is defined as a continuous measurement of sample weight as a function of time or temperature at a programmed rate of heating. The resulting weight change v.s. temperature (or time) curve gives information about the thermal stability and decomposition of the materials.

The thermogravimetric analysis traces obtained for the polymers heated at a rate of 10°C/ min, which show the dependence of the mass loss of the sample expressed as a percentage of the initial mass and temperature. Also the first derivative is below of them.

From thermogram of weight loss vs. temperature one suggest a mechanism for the degradation of chitosan in the review of the decomposition temperature. Fig.(8) shows the dynamic thermogravimetric analysis of chitosan which showed wt.% loss of 3.15% at 100°C, which can be related to the loss of water molecule from the backbone chain of chitosan . The second loss peak of about 47.3% at 260°C correspond to the cleavage of the NH_2 and OH bond of chitosan moiety forming (NH_3, H_2O) molecules and the loss of this groups for each repeating unit .The third loss peak found in thermogram is propotional to 11.62% wt. loss at 480°C which are attributed to the cleavage of polymer and gaseous products leaving the carbon residue about 37.8% wt.



Figure(8): Thermogravimetric digram of Chitosan.

From thermogram of the tannin degradation , three distinct mass loss peaks can be seen in Fig.(9), a week peak centered at 150 oC where almost 2.35% of weight due the postcuring, thermal reforming , preliminary oxidation steps and elimination of volatile fractions. The second peak is sharper and more pronounced and it is found at 305 oC which about 63.3% where the degradation tannin begins and it could be the result of partial breakdown of the intermolecular bonding . Third degradation of tannin takes place after 450 ^{o}C with remark peak at 580 ^{o}C, in this section is seen a mass loss of 6.56% with 27.73% of carbon residue.

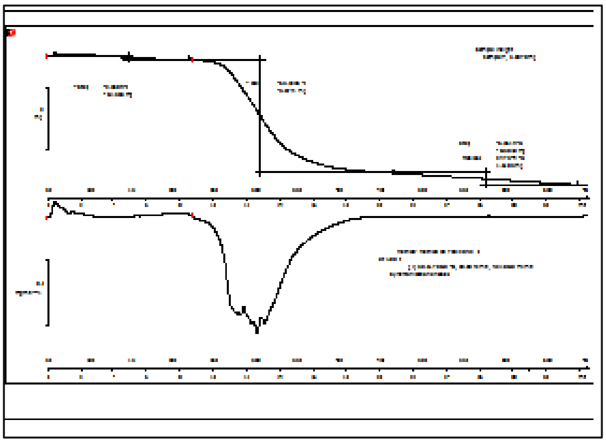
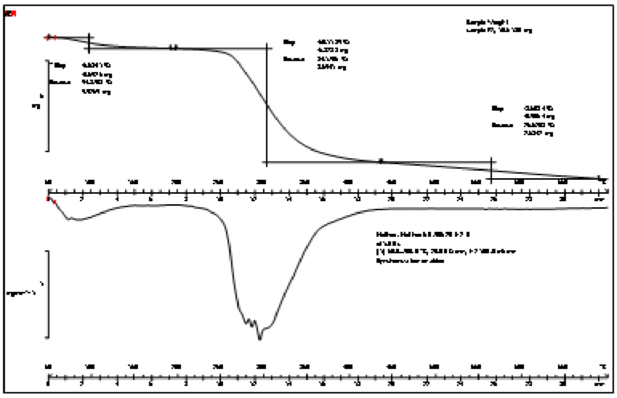


Figure (9): Thermogravimetric digram of Tannin

The chitasan-tannin polymer showed approximately the same degradation behavior as for tannin with little difference in the wt.% loss of water.Three stages of degradation could be recognized (Fig.10) corresponding to wt.% loss of 5.63% related to the loss of water molecules at 100 ^{o}C .The cleavage of –N-C-C- bond of the Chitosan – Buteraldehyde – Tannin is seen in peak at 300°C with weight loss about 60.11% . In the third loss peak found in thermogram is propotional to 8.6% wt. loss at 560°C which are attributed to the cleavage of chitosan and tannin and remains 25.5% wt. of carbon.



Figure(10): Thermogravimetric digram of Chitosan-Tannin polymer

5.8. Differential scanning calorimetry(DSC)

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. This technique is used widely for examining polymeric materials to determine their thermal transitions. The sample undergoes a physical transformation such as phase transition which is exothermic or endothermic depending on the type of sample. DSC may also be used to observe more physical change such as glass transition temperature (Tg), crystallization temperature (Tc) , melting of polymers (Tm) , heat capacity , thermal of expansion and for studying polymer curing. From DSC thermo grams several parameters can also be determined like curing reactions , energy of curing , melting temperature, activation energy of curing , degree of crystallization , charging enthalpy and degree percentage of curing(124). Using it is possible to Glass transitions may occur as the temperature of an amorphous solid is increased. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (Tc). This transition from amorphous solid to crystalline solid is an exothermic process (the cross-linking of polymer molecules that occurs in the curing process), and results in a peak in the DSC signal that usually appears soon after the glass transition. As the temperature increases the sample eventually reaches its melting temperature (Tm). The melting process results in an endothermic peak in the DSC curve.

The DSC curve of pure chitosan (Figure 11) showed three endothermic peaks, the first one (96.86 ºC) corresponds to a dehydration process of chitosan. The second peak (355.21 ºC) was the melting of the sample, and the last one (458.31 ºC) corresponding to the evaporation of melted chitosan.

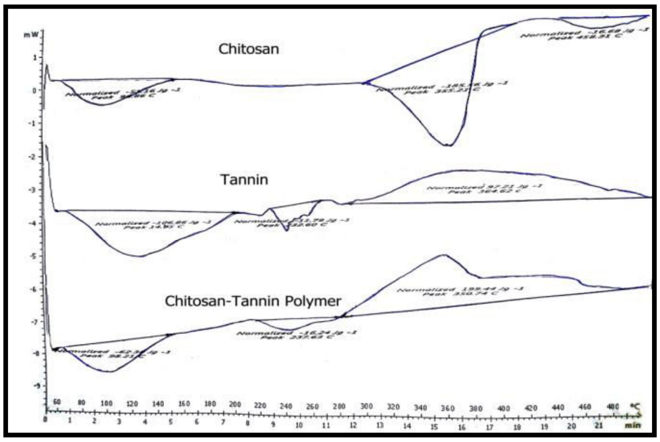
Figure 11 shows the DSC thermogram of tannin which showed two endothermic peaks. The first one is a wide peak which occur at 114.96 ºC corresponding to a dehydration. The second endothermic peak (232.6ºC) corresponded to the chemical bonds decomposition of tannin chains. At temperature 364.62 ºC, the presence of one exothermic peak is corresponding to the melting of tannin.

The DSC thermogram of chitosan-tannin polymer is shown in Fig.(11) which showed a medium endothermic peak below 100 ºC, which corresponded to the removal of moisture. The glass transition temperature is appeared in a small endothermic peak at about 237.63 ºC and an a broad exothermic peak with maximum peaks between 280-480 ºC corresponds to the decomposition of the chitosan-tannin polymer.7

5.9. X-ray Diffractometry:

X-ray spectroscopy is unarguably the most versatile and widely used means of characterizing materials of all forms. There are two general types of structural information that can be studied by X-ray spectroscopy: electronic structure (focused on valence and core electrons, which control the chemical and physical properties, among others) and geometric structure (which gives information about the locations of all or a set of atoms in a molecule at an atomic resolution). This method encompasses several spectroscopic techniques for determining the electronic and geometric structures of materials using X-ray excitation: X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), X-ray photoelectron spectroscopy (XPS) and X-ray

Auger spectroscopy. Which type of X-ray spectroscopy is employed depends on whether the target information is electronic, geometric or refers to oxidation states. X-ray spectroscopy is thus a powerful and flexible tool and an excellent complement to many structural analysis techniques. The properties of polymers depended mostly on the molecular weight, polydispersity and crystallinity. XRD Commonly used to measure crystallinity,



Figure(11): DSC thermogram of chitosan, Tannin and Chitosan – Tannin polymer

The crystallinity index (CI) can be calculated on the basis of X-ray diffractograms. Postulating the following equation for determining the crystallinity index (CI):

$$\mathbf{CI\ (\%) = [(\mathit{I}m - \mathit{I}am)/\mathit{I}110] \times 100}$$

Where: *I*m (arbitrary units) is the maximum intensity of the crystalline peak at around 2θ = 51°, and *I*am (arbitrary units) is the amorphous diffraction at 2θ = 15°. In most cases, CI provides information about the crystal state. Crystallinity could also be assigned from an X-ray diffractogram by dividing the area of the crystalline peaks by the total area under the curve (background area). In these calculations, the crystallinity percentage supplied information on relative crystallinity.

The typical chitosan diffraction pattern is given in angle form. Fig.12, showed strong reflections at 2θ around 42° and 2θ of 51°, However, differently indexed crystalline peaks (90%), the chains form hydrogen-bonded sheets linked by C=O...H–N bonds approximately parallel to the a axis, and each chain is stabilized by an C(3') O–H····OC(5) intramolecular hydrogen bond, as in cellulose.

These data also indicated that a statistical mixture of CH_2OH orientations was present, equivalent to half an oxygen on each residue, each forming inter and intramolecular hydrogen bonds.

Figure (12) shows the X-ray diffraction patterns of the tannin sample showed strong reflections at 2θ around 42° and 2θ of 51°. The crystallizations of tannin were 50% . Tannin have crystalline region and non-crystalline region. Compared to chitosan , the X-ray diffraction patterns of the chitosan-tannin polymer showed that the bands at 2θ = 42° and 51°, the crystallization decreasing of chitosan-tannin polymer (86%) indicates that the interaction force of polymer molecular chains has become weaker and the degree of regularity is decreased. The molecular flexibility of chitosan-tannin polymer is higher than that of chitosan and lower than tannin. It was therefore concluded that the crystallizations is influenced by components, reaction condition and so on.

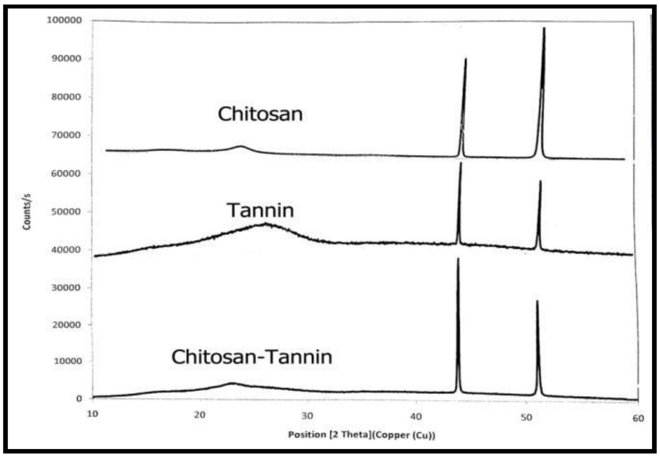


Figure (12): X-Ray Spectra of Chitosan, Tannin and Chitosan-Tannin polymer

Table (1): The optimum conditions for the studied metal ions

	Slit width (cm)	Lamp current (mA)	Wave length (nm)	Linearity (ppm)	Air flow rate (L/min)	Acetylene flow rate (L/min)
Cd(II)	0.2	4	228.8	5	8	2
Co(II)	0.2	4	242.5	5	8	2
Pb(II)	0.2	5	217.0	5	8	2
Zn(II)	0.2	5	213.9	4	8	2

Treatment of an artificial solution by the prepared polymers:

A 100 ppm solution of Cd(II), Co(II), Pb(II) and Zn(II) were prepared by dissolving an accurate weight of the metal salt in distilled water. The metal content of the standard solution was then determined by using flame atomic absorption spectrometry.

The adsorption experiment of all polymers under investigation were prepared by mixing 50 ml of 100 ppm of Cd(II), Co(II), Pb(II) and Zn(II) ions separately with appropriate amounts of chitosan- lignin. The samples were subjected to stirring for a period of time then filtered, after filtration the samples were analyzed for their heavy metal ions content by using flame atomic absorption spectrometry at the optimum conditions for the studied ions listed in Table (1).

Preliminary experiments were carried out to assess the optimum conditions for the removal of Cd(II), Co(II), Pb(II) and Zn(II) ions from prepared solutions as well as from wastewater samples drained from Paper production factory. These conditions include: (1) the effect of pH, and (2) Amount of polymer used, (3) The effect of time of agitation.
The initial metal ions concentration of synthetic solution flow was 100 ppm of Cd(II), Co(II), Pb(II) and Zn(II) ions. In these experiments dry polymer powder was carefully transferred into four 100 ml glass-stoppered flask containing 50 ml of Cd(II), Co(II), Pb(II) and Zn(II) ions solutions separately and shaken at 175 rpm for 24 hrs. After filtration of the mixtures 25 ml aliquots were used to determine unreacted metal contents of the solutions. From the difference of the metal contents in the initial and final synthetic solutions, the removal efficiency of chitosan- lignin polymer was calculated by using the following equation:

$$\textbf{Removal efficiency} = \frac{Co-Ci}{Co} \times 100$$

Where, Co(mg/l) is the initial concentration of metal ions in the solution, Ci (mg/l) is the final concentration of metal ions in the solution.

5.10. Effect of pH on adsorption of metal ions using Chitosan-Tannin polymer

The dependence of amount of adsorption of Cd(II), Co(II), Pb(II) and Zn(II) ions on pH values is shown in Fig. (13), The adsorption increased with an increase of pH of the solution, in case of Cd(II) ion which shows an optimum adsorption 94 % at pH 6, and it shows an optimum adsorption 95% at pH 6 in case of Co(II) ion, while in case of Pb(II) it shows an optimum adsorption 92% at pH 6 and it shows an optimum adsorption 98% at pH 6 in case of Zn(II) ion. This could be explained on the basis that at low pH, amine and hydroxyl groups in the chitosan-tannin polymer easily form protonation that induced an electrostatic repulsion with Cd(II), Co(II), Pb(II) and Zn(II) ions. At low pH value of solutions increase of H_3O^+ concentration and intensifies the competition between $H_3O^+$and heavy metal ions for complexation sites. This behavior can be explained by the nature of chitosan-tannin polymer at different pH values and the type of ionic state of functional group of the chitosan-tannin polymer. However, there is some removal at pH 6-8 but above this value the rate of removal is reduced, which could be considered as due to the presence of other mechanism such as physical adsorption on the surface of sorbent.

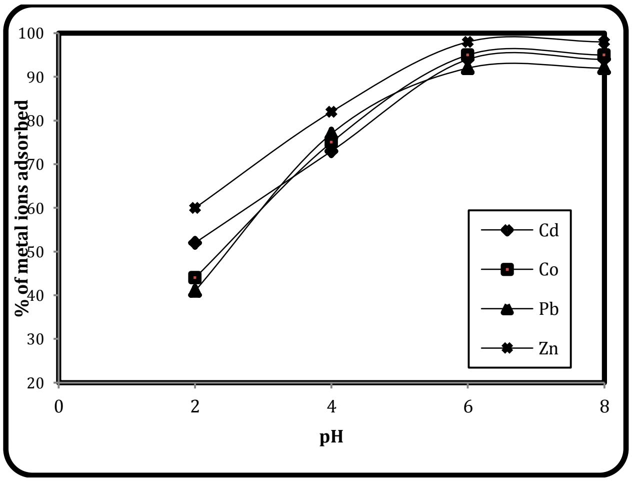


Figure (13) : Adsorption of metal ions using of Chitosan-Tannin polymer as a function of pH .

5.11. Effect of amount of chitosan- Tannin polymer on the adsorption of metal ions

Fig. (14), represents Cd(II), Co(II), Pb(II) and Zn(II) ions removal efficiency as function of Chitosan-Tannin polymer of metal ions. The dose of the P2 was varied between 0.1 g to 1 gm for 100 ppm. Other operational parameters (pH, agitation time) were kept at the optimum values, the agitation speed were kept at 175 rpm.
As shown in Fig. (14) the increasing dose of Chitosan-Tannin polymer increases Cd(II), Co(II), Pb(II) and Zn(II) ions removal efficiency. This is expected because more binding sites for ions are available at higher dose of adsorbents. The percentage removal of Cd(II), Co(II), Pb(II) and Zn(II) ions by the adsorbents initially increased with increasing as the Chitosan-Tannin polymer amount is increased from 0.1 g to 0.2 g, after which there was no further increase of the percentage removal at pH 6 with shaking 175 rpm for 4 h. This is expected because more binding sites for ions are available at higher dose of Chitosan-Tannin polymer.At the high removal efficiency of Chitosan-Tannin polymer for all the studied ions, Chitosan-Tannin polymer amount of 0.3g is taken as optimum adsorbent dose because no appreciable change in the removal efficiency occurs at higher doses greater than 0.3 g.
It is clear that the percent of removal of Cd(II), Co(II), Pb(II) and Zn(II) ions in better in case of Chitosan-Tannin polymer than in case of free chitosan and free tannin itself, as it takes

less amount of doses, this depends on other effects like pH and agitation time.

At the high removal efficiency of chitosan- tannin polymer for all the studied ions, chitosan- tannin polymer amount of 0.3 g is taken as optimum adsorbent dose because no appreciable change in the removal efficiency occurs at higher doses greater than 0.3 g. It is clear that the percent of removal of Cd(II), Co(II), Pb(II) and Zn(II) ions in better in case of synthesized polymer than in case of free chitosan and free tannin itself, as it take less amount of doses, this depends on other effects like pH and agitation time.

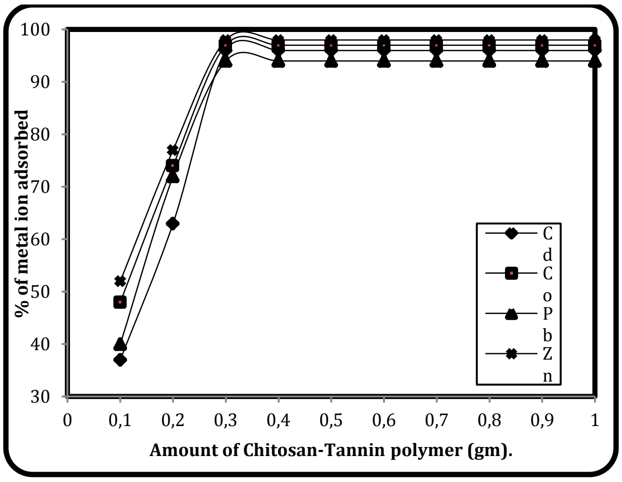


Figure (14): Effect of the weight of Chitosan-Tannin polymer on metal ions adsorption

5.12. Effect of time of agitation on adsorption of metal ions using chitosan – tannin polymer

The optimum period for the adsorption of Cd(II), Co(II), Pb(II) and Zn(II) ions on chitosan- tannin polymer can be observed by looking for the behavior of adsorption of heavy metal ions solution after adding chitosan- tannin polymer. Fig.(15) shows the effect of agitation period on the adsorption of Cd(II), Co(II), Pb(II) and Zn(II) ions using chitosan- tannin polymer. The adsorption of Cd(II), Co(II), Pb(II) and Zn(II) ions increases with agitation period and attains equilibrium at about 4 h /175 rpm for an initial concentration 100 ppm of metal ions at pH 6 .This behavior may be explained by the availability of the active surfaces for adsorption. Initially, the number of active sites available for adsorption on the adsorbent surface is high but this number starts to decrease with the progress of adsorption. Finally, adsorption will stop when all active surfaces are covered with the metal ions. This implies that the four heavy metal ions adsorbed using chitosan- tannin polymer, possibly by chemical adsorption because chemical adsorption takes places as a monolayer surface coverage rather than multilayer adsorption as in case of physical adsorption. Initially adsorption rate is very high because of the large surface area of the beads available for adsorption. But after the coverage of this surface area by the adsorbed metal ions as a monolayer its adsorption capacity was exhausted and the rate of adsorption will be controlled by the diffusion rate of adsorbate from external sites to the internal sites.

Under the optimum conditions ,the obtained results shows the highest removal efficiency at an initial concentration of 100 ppm was 98%, 99% , 97% and 99% for Cd(II), Co(II), Pb(II) and Zn(II) , respectively.

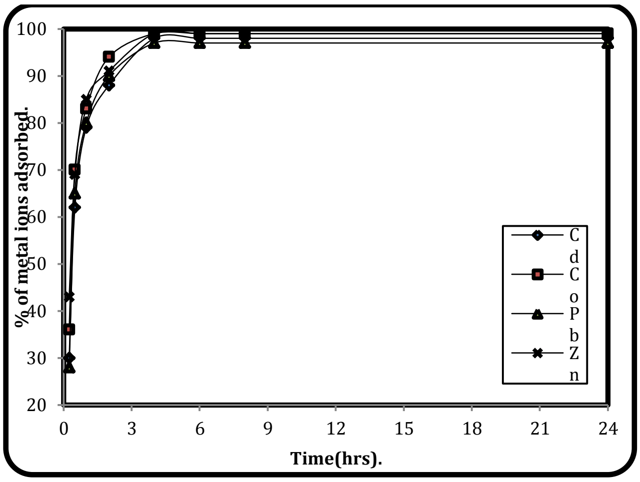


Figure (15): Effect of agitation time using of Chitosan-Tannin polymer on metal ions adsorption

5.13. Desorption study for Chitosan – Tannin polymers

The desorption experiments were performed by suspending 0.3 gm of loaded polymers in 10 ml of 3 M HCl and shaking on shaker at 200 rpm at 25°C. After constant time intervals (0.5-24 hrs) the samples were filtered (Whatman filter paper No. 42) and the filterate was analyzed by flame atomic absorption spectrometer (FAAS) for the metal contents. Figure 16, shows the recovery percentage of the test metals from the synthesized polymer as a function of the contact time with (3M HCl). The obtained results show that

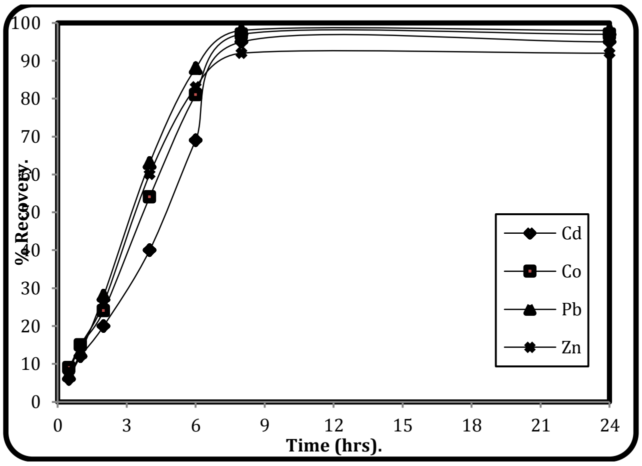


Figure (16): Effect of contact time on the recovery percentage of ions from Chitosan-Tannin polymer with (3M HCl) the orders of recovery percentage of metal ions was in sequence: Pb > Co > Cd > Zn. This could be related to the strong binding between polymers and ions.

5.14. Treatment of wastewater samples by the prepared polymers.

A wastewater sample drained from paper production factory for contains Cd(II), Co(II), Pb(II) and Zn(II)ions solution. The wastewater was treated with the optimum amount of the prepared polymer for 50 ml from wastewater samples and time of agitation as discussed previously with 175 rpm, agitation speed and pH was adjusted to be 6. The concentration of metal ions of the wastewater before treatment was 8 ppm for Cd(II) ion, Co(II) ion was 5 ppm, Pb(II) ion was 12 ppm and Zn(II) ion was 25 ppm, the amount of the synthesized polymer was 0.3 gm.

The data of removal of each metal ion are given in Fig. (17). Inspection of the data for metal ions in wastewater samples before and after treatment given in Fig. (17) using the synthesized polymer, the order of removal of heavy metal ions in wastewater samples in a separately treatment was Co(II) > Zn(II) > Cd(II) > Pb(II).

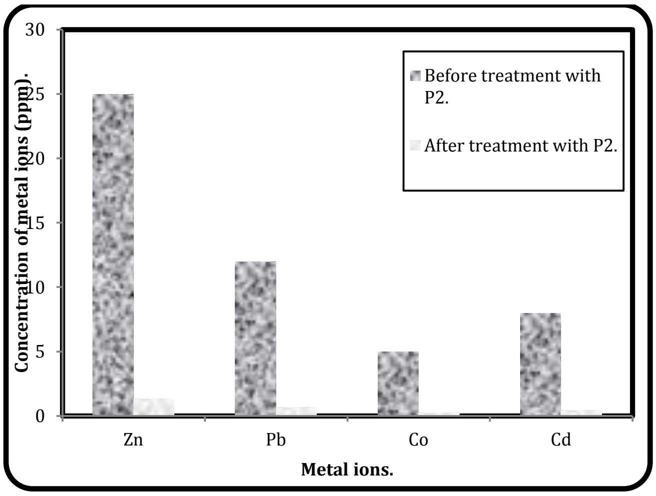


Figure (17): Treatment of industrial wastewater sample contains metal ions using Chitosan-Tannin polymer

6. Acknowledgment

The authors gratefully acknowledge the contributions of Prof Dr.S.Archibald in the University of Hull, UK for his benefic contribution of this study..

7. Conclusion

Natural polymer “Chitosan-Tannin polymer” based sorbent provides axcellant method for metal removing. The characterization of material gives information about molecular weight, crystallinity , good chemical and thermal stability which revels applicability towards metal removing . This low-cost adsorbent is effective for the removal of metal ions from aqueous solutions shows order of % removal effeciency i.e. Co(II) > Zn(II) > Cd(II) > Pb(II). The batch method was employed parameters such as pH, polymer dose and agitation time were studied at an ambient temperature 25^{o}C. The optimum pH corresponding to the maximum adsorption of Cobalt, Cadimium, lead and Zinc removal was pH 6 Cobalt, Cadimium, lead and Zinc ions were adsorbed onto the adsorbents very rapidly within the 0.3 gm of polymer for 4 hrs.

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