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Nanochitosans for Removal of Heavy Metals from Wastewater

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Abstract—*This paper was to demonstrate to the scientific community how to obtain chitosan nanoparticles with these properties. Ionic Gelation Technique was applied to form nanoparticles through linkages between tripolyphosphate (TPP) and chitosan (CTS). The characterization of the nanoparticles was done by using the X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Thermal Gravimetric Analysis (TGA).*

In this paper describes the removal of heavy metals ions from industrial waste water by the use of chitosan nanoparticles. These particles were then used to study their adsorption behavior for the removal of heavy metal ions namely Ni (II) and Co (II). The concentration determination of the above mentioned heavy metal ions was done with the help of 797 VA Computrace.

Keywords*: Chitosan, Nanotechnology, Voltammetry, XRD, FTIR, SEM, TGA.*

1. INTRODUCTION

Water is one of the most important resources for human life. 60% of the total surface of earth is water. Most of the water of pond, lakes, rivers, sea and oceans, have become polluted due to population inflation, industrial and technological expansion, and waste generation from domestic and industrial sources and hazardous to human and other living resources [1]. Hence many industries discharge untreated waste water into water ways. Different contaminants are released to waste water with the rapid industrialization of human society, including heavy metal ions, organic, bacteria, viruses and so on, these effluent are ultimately going to stream along with rain water, which serious harmful to human health.

Among all water impurities, heavy metal ions, such as Zn, Cd, Cu, Pb, Ni, Co, have high toxic and non bio degradable properties, can cause severe health problem in animals and human being[2].

Heavy metals are natural component of earth's crust. The presence of heavy metals in environment has been great concern due to their toxic nature and other harmful effect on receiving water. Heavy metal toxicity causes serious health effects such as; cancer, nervous system damage, organ damage, and in extreme cases, at the last death. Furthermore, heavy metals are toxic to the sensitive, rapidly developing systems of fetuses, infants, and young children. Excessive amounts of Cr, Cd, Zn, Ni, also in water can great affect biosystems and pose a threat to human beings.

Hence their removal and recovery from wastewater is important to protect the living environment. Several methods adopted to remove heavy metal ions from the industrial waste water are reduction, chemical precipitation, solvent extraction cementation, electrolysis, ion exchange; each method has its own limits [1]. In recent year research adsorption is recognized as an emerging technique for the treatment of waste water containing heavy metal. The 'Adsorption' term was suggest by Bois-Reymond but introduced into literature by Kayser [3]. So researchers are working on developing new techniques to increase the possibilities of removing metal ion contaminants from wastewater.

Some of the adsorbents include chitosan and chitosan nanoparticles. Chitosan is a linear polysaccharide which is obtained from the deacetylation of chitin in sodium hydroxide solution (NaOH), in deacetylation reaction in which amino acetyl group is changed in to amino group. Chitosan is also found in some microorganism, yeast and fungi.

Some chemical properties of chitosan: chitosan has three reactive group, primary and secondary hydroxyl group on each repeat unit, and the amino group on each deacetylated unit. Chitosan is hydrophilic polymer with positive charge. Chitosan is beta-1, 4-linked unit of N-acetyl-D-glucosamine [4]**.** Molecular weight and degree of deacetylation are the main factors affecting the particle size, particle formation and aggregation.

Due to the presence of positive charge on the chitosan polymer chain, these particles are able to attract negatively charged metal ions and thus adsorbed heavy metal ions from water. Size is known to have a great impact on the adsorption capacity of chitosan polymer. Studies have revealed that adsorption is inversely related to particle size, this means smaller the size of the adsorbent, greater will be the magnitude of adsorption. This is because the decrease in size increases the surface area of adsorbent and in turn more particles are adsorbed. Therefore in this study we aim at using chitosan nanoparticles for heavy metal ion adsorption.

Nanotechnology is the science of small; the very small. It is the use of matter at a tiny scale. During the past years Nanotechnology and nanoscience studies have emerged rapidly [5].

Application of nanotechnology in different field is [6]

- Nanomedicine: nanodrugs, tissue engineering.
- Food science: processing, nanocapsules.
- Materials: nanoparticles, biopolymers, coating.

This paper describes the removal of heavy metals ions from industrial waste water by the use of chitosan nanoparticles. Chitosan nanoparticles gained more attention as waste water treatment because of their better stability, non-toxicity, biodegradability, biocompatibility, antibacterial activity, and versatile physical and chemical properties. The main factors that affect the adsorption capacity of chitosan is its particle size, molecular weight and degree of deacetylation.

Chitosan nanoparticles were prepared by cross linking crab shell chitosan with polyanion sodium tripolyphosphate (STPP). Chitosan interacts with polyphosphate ions to form nanoparticles with different diameters depending on the mutual ration among them. With the increase in the concentration of TPP solution, the size of nanochitosan decreases because of ionic gelation interaction between positively charged amino group of chitosan and negatively charged tripolyphosphate [7]. Therefore different sizes of chitosan nanoparticles can be prepared by using different ratios of TPP-Chitosan. Tripolyphosphate is being widely used because of its non toxic nature [8].

Removal of heavy metal ions like Ni (II) and Co (II) with nanochitosan from waste water is established by studying the adsorption of these metal ions on the chitosan surface .This process is completed via 797 VA computrace.

2. MATERIALS AND METHOD

A. Chemical

Chitosan crab shell (75% deacetylated), sodium tripolyphosphate, Nickel chloride hexahydrate ($NiCl_2.6H_2O$), cobalt(ous) nitrate hexahydrate ($Co(NO_3)2.6H_2O$) from sigma aldrich ,Delhi and Dimethyl glyoxime (DMG) from CDH, New Delhi, Glacial acetic acid and Ethanol were also stalked up, Double Distilled water was used for all the experiments. All the above chemicals used in the present research work were of analytical grade.

B. Preparation of nanochitosan

Chitosan nanoparticles have been synthesized on the basis of Ionic Gelation method [9]. Chitosan nanoparticles were prepared by crosslinking crab shell chitosan (CS) with polyanion sodium tripolyphosphate (STPP) in the following ratios 1:3 (CS/TPP). The adsorption capacity of chitosan was found to be increased with the addition of cross linking agent. The tripolyphosphate (TPP), a good cross linking agent is non-toxic polyanion. Due to this nature, this cross linking agent is suitable for water purification.

C. Procedure of preparing chitosan nanoparticles

$3x10^{-6}$ m^3 of glacial acetic acid was diluted in $5x10^{-4}$ m^3 of distilled water to form a solution, to this solution $3x10^{-3}$ kg. of previously prepared crab shell chitosan is added slowly along with constant stirring using a magnetic stirrer. To another beaker $2x10^{-3}$kg. of sodium tripolyphosphate (sTPP) is added along with $1x10^{-4}m^3$ of distilled water. The sodium tripolyphosphate solution is then added in the chitosan mixture solution drop by drop using a titration tube according in the following ratio (CS/TPP) 1:3.

The solution was continuously stirred for 1200 sec. so that proper precipitate is formed. Once the complete sTPP solution is added to the prepared previous solution (acetic acid + chitosan) the resulting mixture is kept in a deep freezer for 1 day. After keeping it overnight, the frozen solution is taken out and allowed to melt. After melting, the precipitate that gets settled at the bottom of the melted solution is stored. That settled precipitate is kept out and then dried in hot oven.

The dried precipitate is then crushed using mortar and pestle. This crushed precipitate is the chitosan nano particles. Which are stored in a glass tube for further use.

D. Characterization of Chitosan Nanoparticles

Chitosan nano particles were characterized by X-Ray powder diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra-red (FTIR), Thermo- gravimetric analysis (TGA).

E. Voltammetric Measurement

A 797 VA Computrace,metrohm ion analysis (Switzerland).

VA computrace is voltametric analyser computrace. It works through basic principles of polarography," potential is applied and current is measured''. This instrument provides current versus voltage graph of the metal ion present in given sample. It gives qualitative and quantitative analysis of metal ion. It concists of three electrodes namely Auxiliary electrode (AgCl), Working electrode and Reference electrode (Pt).

Voltammetric analysis has long been known as a powerful technique for trace metal detection, especially in environmental sample. In voltammetry we are using Hanging Mercury Drop Electrode (HMDE). HMDE have been extensively used for voltammetry, the main reason being its reliability. A new electrode surface is produced with the formation of new drop each time. Hanging mercury drop electrode has been most frequently used to achieve high reproducibility and sensitivity. Due to their distinctive ability to preconcentrate target metals during the accumlation step [10].

3. RESULT AND DISCUSSION

A. X-Ray Diffraction (XRD)

In XRD the relative intensity were recorded within the range of 10°-90° degree (2° theta) at a scanning rate of 2 degree per minutes.

The crystalline behavior and size of particles is determined by using XRD studies. The XRD spectrum of nanochitosan is shown in (Fig. 2). It shows a broad peak around 2 theta 20.13^0 .The pure chitosan shows a peak at around 2ϴ 19.7°.

On comparing nano chitosan with pure chitosan (Fig. 1), it was observed that there was a significant shift in diffraction pattern. In pure chitosan an intense peak is recorded, while nanochitosan shows a broad amorphous peak. The appearance of broad peak in nanochitosan may be due to the increase in packing of the chitosan polymer chain by the ionic crosslinking which can deform the crystalline regions [11]. In addition to this, the weakening of the rigid crystalline nature of chitosan, interpenetrating polymer chains cross linked to each other by TPP counterions. Due to hydrogen bonding, these results obtained and indicate an effective cross linking and molecular miscibility [12].

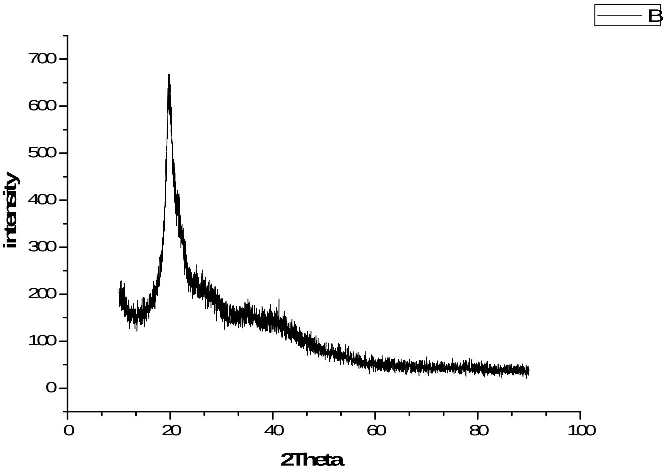


Figure 1: XRD Pattern of chitosan

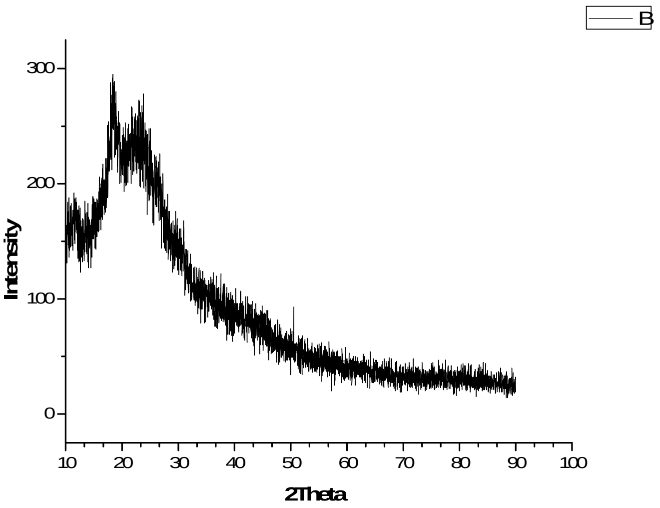


Figure 2. XRD Pattern of Chitosan Nanoparticles

B. Fourier Transform Infrared Spectra (FTIR)

In FTIR spectra the KBr pellets were used .The spectra was scanned over the wave range of 4000 to 400 cm-1. In FTIR spectra, chitosan and chitosan/TPP nanoparticles shown in (Fig.3 and Fig. 4) were recorded. In crab shell chitosan spectrum a band at 3430.58cm-1 was attributing to the -OH and $-NH_2$ group stretching vibration. In nano chitosan a shift from 3430.58 cm-1 to 3436.06 cm-1 was recorded. Another alternation in FTIR spectra that indicate the nanoparticles formation is shift of band at 1658.23 cm^{-1} to 1640.47 cm^{-1} in nanoparticle spectrum, representing the $CoNH_2$ group. Which suggest the ionic interaction between the positively charged amino groups of the CTS and the negatively charged group of the TPP. Absorption bands around 1422-603 cm-1 region confirmed the presence of CH_3, CH_2, and CH groups.

On the other hand, in nano chitosan which is obtained from chitosan by ionotropic gelation method showed some different bands when compare to pure chitosan . A shift from 3430.58 cm^{-1} to 3436.06 cm^{-1} corresponding to the presence of NH, OH stretching in chitosan to lower wave number (3436 cm-1) in nano chitosan sample may indicate an interaction of sodium tripolyphosphate with the pure chitosan. In addition to this appearance of some new peaks in nanochitosan when compared to the pure chitosan conclude that the nanochitosan was formed from the pure chitosan used.

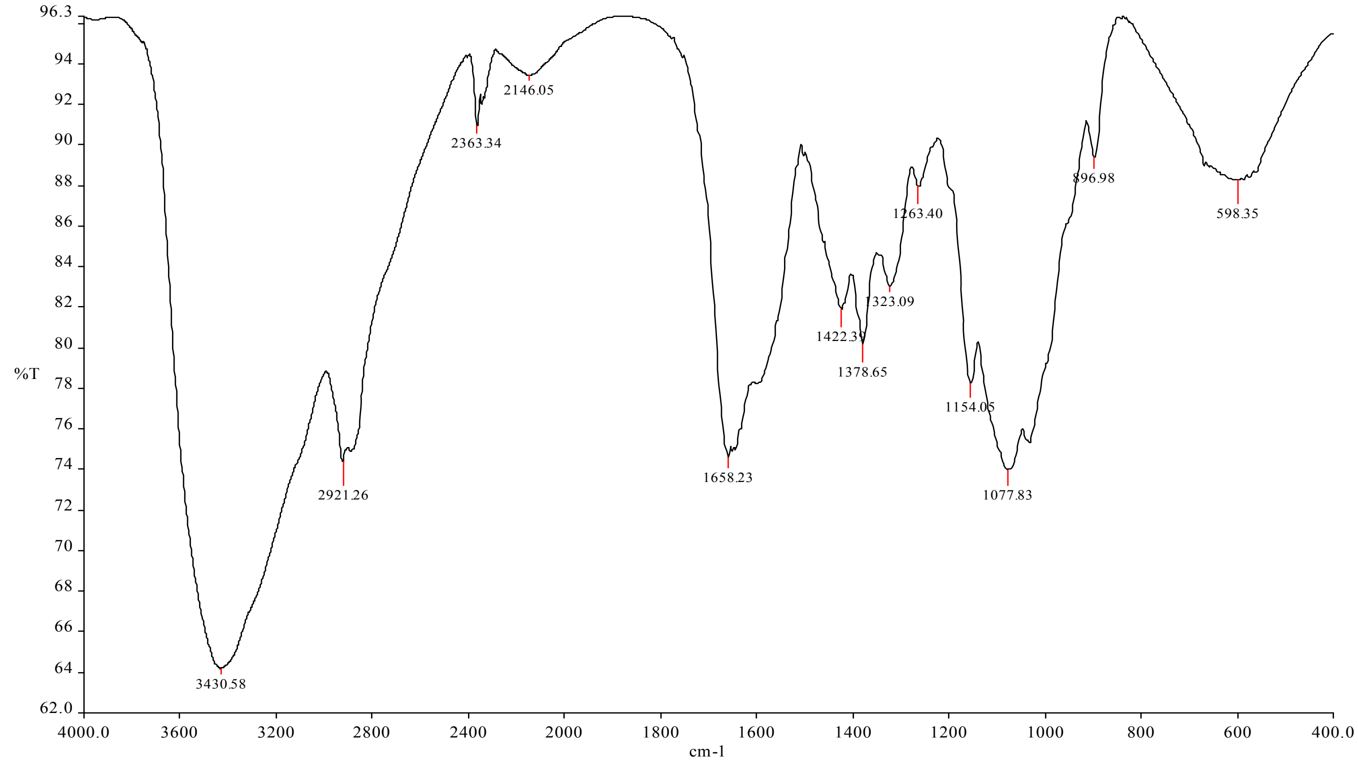


Figure 3. FTIR Spectra of Crab Shell Chitosan

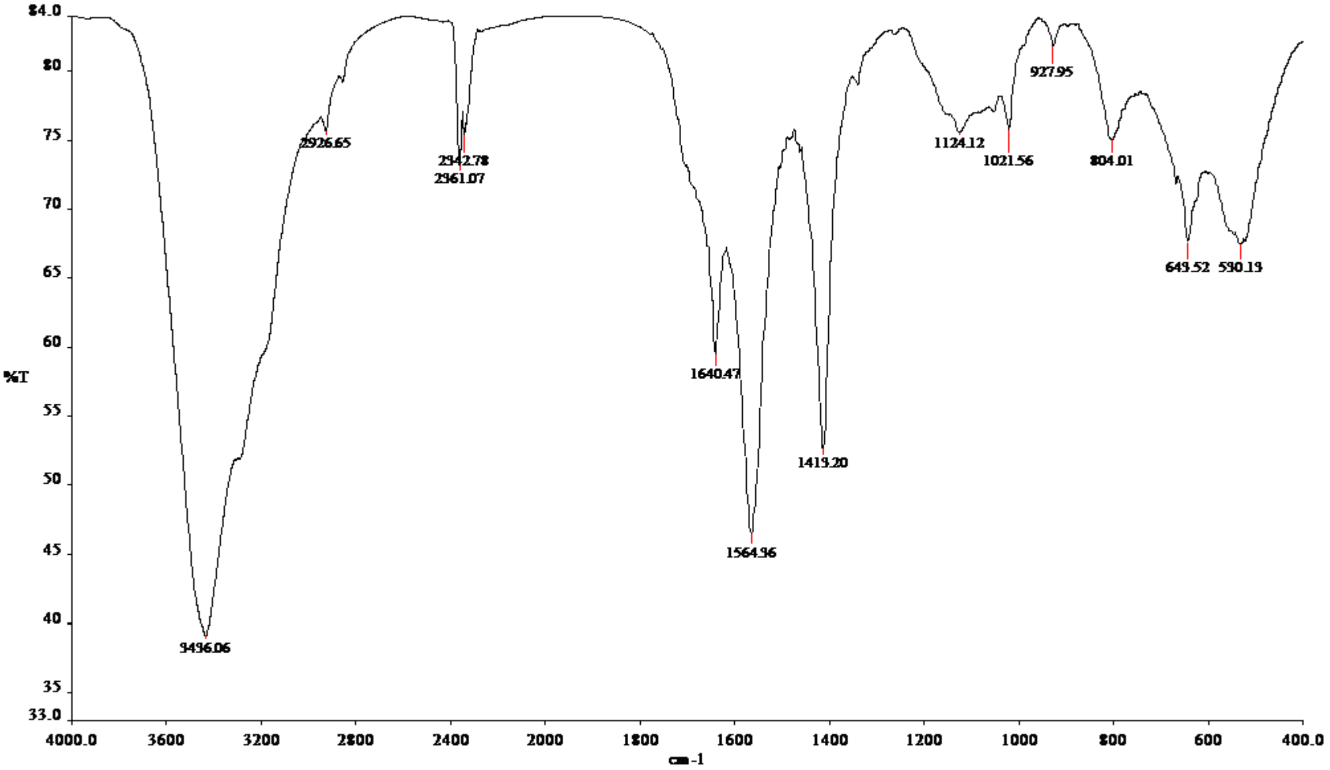
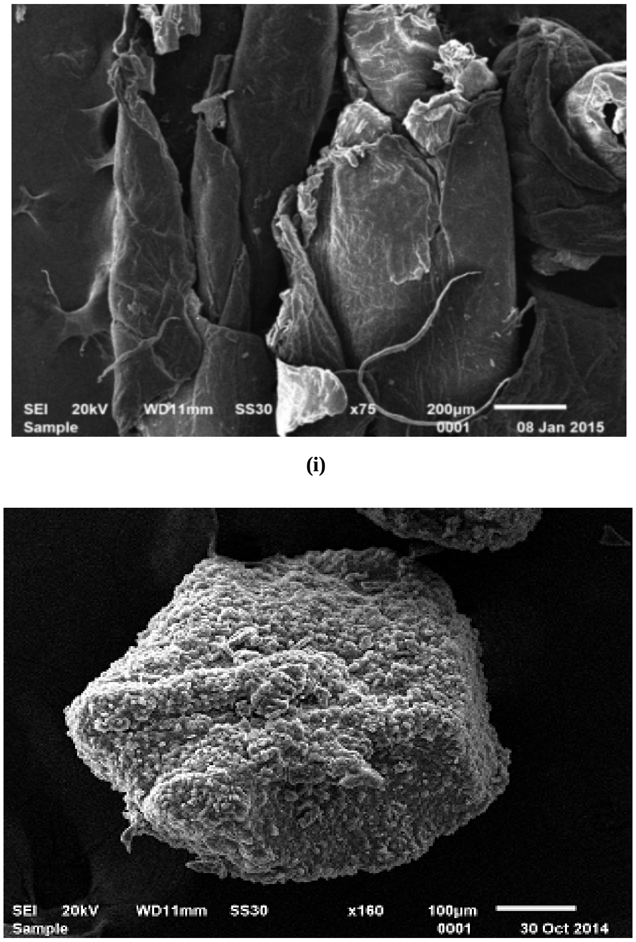


Figure 4. FTIR Spectra of Chitosan Nanoparticles

C. Scanning Electron Microscopy (SEM)

Surface properties of the sample was analysed with SEM. The morphology of chitosan and chitosan naoparticles was non porous. The SEM images of nano chitosan reveal a spherical shape structure. On comparing the SEM micrograph details of nano chitosan with pure crab shell chitosan (Fig. 5) it was observed that the analyzed by scanning electron microscopy (SEM).

Under has relatively a rough surface with uneven structure which exhibited amorphous feature. Spherical shape of nanoparticles was thus confirmed through scanning electron microscopy.



(i)

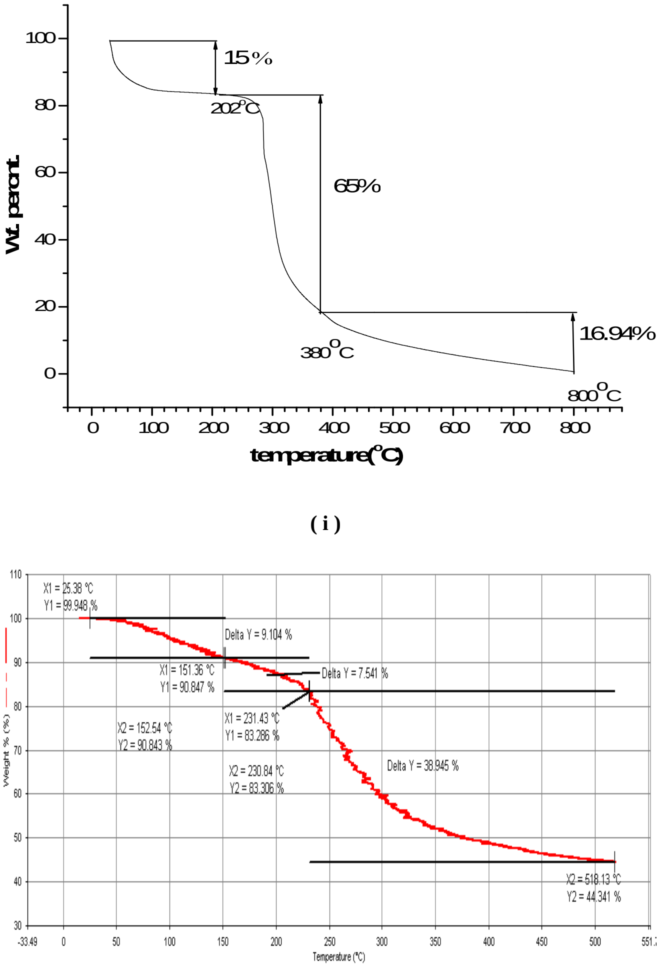
(ii)

Figure 5. SEM Images of (i) Crabshell chitosan (ii) CS/TPP nanoparticles

D. Thermo Gravimetric analysis

The TGA thermo gram of the pure crabshell Chitosan (Fig. 6) shows three weight losses one before 475K (202°C), second after 523K (250°C) and another after 653K (380°C) in polymer mass. The first degradation is due to the water molecules elimination, second degradation is due to the depolymerisation and third one is decomposition of products. Around 96.94 % of crabshell chitosan gets decompose within 1073K (800°C). Maximum weight loss occur 475K – 653K (202°C- 380°C). At the end of experiment around 3.06% of the crabshell chitosan remain as a residue.

The TGA thermo gram of chitosan nanoparticles indicate that first thermal event occur at temperature range 323K-428K (50^0 -155^0 C), with mass loss 9.1% is due to the evaporation of water in the nano particles. The second degradation stage occur in range of 473K-803K (200 ^{0}- 530^0C) with mass loss of 38.9% where occur nanoparticles decomposition. The TGA thermo gram of nanochitosan shows that total mass loss around 55.69% and the sample remained as a residue around 44.31%. According to above studied, it was found that the nanochitosan was found to be thermally more stable and at the end of experiment, this was confirmed from the amount of residue remained and the initial decomposition of temperatures.



(i)

(ii)

Figure 6. TGA Thermogram of (i) crabshell chitosan (ii) nanochitosan

E. Metal Adsorption Study

We prepared stock solutions of metal Ni (II), Co (II) for VA computrace analysis. In simultaneous analysis all two metal ions are present or mixed together in the same solution. The stock solution of 10^{-2} Kg/m^3 (Ni and Co) prepared by ($NiCl_2.6H_2O$ and Co $(NO_3)_2.6H_2O$). $2.5x10^{-5}$ m^3 of each solution mix because want to combined co-relation concentration graph. The signal response (peak current) of each metal ion obtained by measuring peak height of each. The calibration plots of concentration *versus* current were prepared by determining the peak currents of the metal ions from the voltammogram for two metal ions (Fig.7) in supporting electrolyte (Ammonia buffer pH 9.8) and also use a complexing agent Dimethylglyoxime disodium salt octahydrate (DTPA). Adsorption was carried out in a $5x10^{-5}$ m^3 of metal solution in which $1.3x10^{-5}$ Kg. of chitosan nanoparticles were added. The concentration of metal ions was determined after a time period of 600 sec. for approx 3600 sec. The result is shown in (Table I).

Table I: Concentration of Metal Ions at different Time Intervals

Time(Sec x 10-2)	Concentration of Metal ions in Kg/m3	
	Ni+2	***Co+2***
Initial	4.1x10-5	.37x10-6
6	.7x10-5	.24x10-6
12	.5x10-5	.11x10-6
18	.3x10-5	.12x10-6
24	.2x10-5	.01x10-6

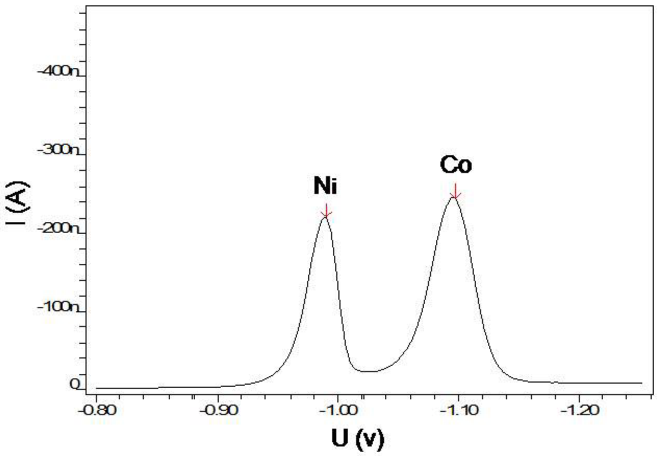


Figure 7: Voltammograms of Ni^{+2} and Co^{+2}

4. CONCLUSION

In summary a method for the preparation of chitosan nanoparticles from crabshell chitosan were developed using the ionic gelation technique. The present study was mainly to synthesize and characterize the CHS/TPP nanoparticles (1:3). The results of FTIR studies of prepared chitosan nanoparticles indicate that TPP were effectively cross linked with the chitosan. The XRD studies explain the amorphorous nature of the nanochitosan when compared with pure crab shell chitosan. The TGA studies of nanochitosan indicate clearly that the prepared nanoparticles were found to be highly thermally stable. In addition to this, surface morphology of nanochitosan was also identified from the SEM studies. In above studies, result found that the dose of 1.3x10-3Kg of chitosan nanoparticles were the optimum dose for maximum simultaneously removal of Ni, Co treatment. The concentration result calculated by using regression equation. It was observed that concentration of metal ions is decreasing due to their adsorption by chitosan nanoparticles which are put in the solution.

5. ACKNOWLEDGMENT

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