



## Chemical Modification of Chitosan for Metal Ion Removal

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### Abstract

This study is interested with a significant application of surface chemistry in the fields of treatment of pollution. It deals with adsorption systems of chemical pollutants (some heavy metal ions) on surface (modified chitosan). Atomic absorption spectrophotometry technique have been used to results adsorption data at different conditions of (contact time, pH). Chitosan were modified from benzoyl chloride reaction with ammonium thiocyanate and then its resulting composite reactor with carboxylic acids at room temperature, the chemical structures of modified polymer was to elucidated using FTIR and <sup>1</sup>HNMR. Chitosan modified compounds have been evaluated as a good material for adsorption of heavy elements in water solutions.

### Introduction

In the historical development process of human society, water is one of the most important resources for humans' living and development. However, water contamination has become a serious environmental issue and has caused international concern in recent years, especially for various pollutants that are entering aquatic systems as a result of the rapid growth of the world population, industrialization, unplanned urbanization, agricultural activities as well as the excessive use of chemicals [1].

An ideal adsorbent for heavy metal ions removal possesses the following properties: large surface area and high adsorption capacity, suitable pore size, mechanical stability, compatibility, easy accessibility, ease of regeneration, cost effectiveness, environmental friendliness, simple processing procedures and high selectivity [2].

Therefore, some groups have recently focused on developing polymer materials such as chitosan and its modifications, which is an abundant biopolymer obtained from alkaline N-deacetylation of chitin and has higher adsorption capacity for heavy metal ions than some conventional adsorbents due to the presence of amounts of reactive hydroxyl (OH) and amino (NH<sub>2</sub>) groups.

One of the most commonly used techniques

involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of solid. Bio-adsorption is a good alternative to traditional processes. Widely available biopolymers are also being used for adsorption mainly because they are a cheap resource or an available resource [3].

### Experimental

#### Materials and Reagents

The chemicals were supplied from Reagent World, BDH, Scharlan, HIMEDIA, Merck-Germany and Aldrich chemicals Co.

#### Instrumentation

FT-IR-Spectra were recorded on a (Shimadzu FTIR- 8400s) using KBr disk, Melting point have been measured by using electro thermal Gallenkamp melting point apparatus, <sup>1</sup>HNMR spectra were carried out Ultra Shield 400 MHz and Ultra Shield 500 MHz, Bruker, University of Tehran, Center Lab. (in Iran), Atomic absorption Spectrometer (AAS) Shimadzu (A680) to measured the concentration of metal ions (Co<sup>+2</sup>, and Ni<sup>+2</sup>), pH meter.

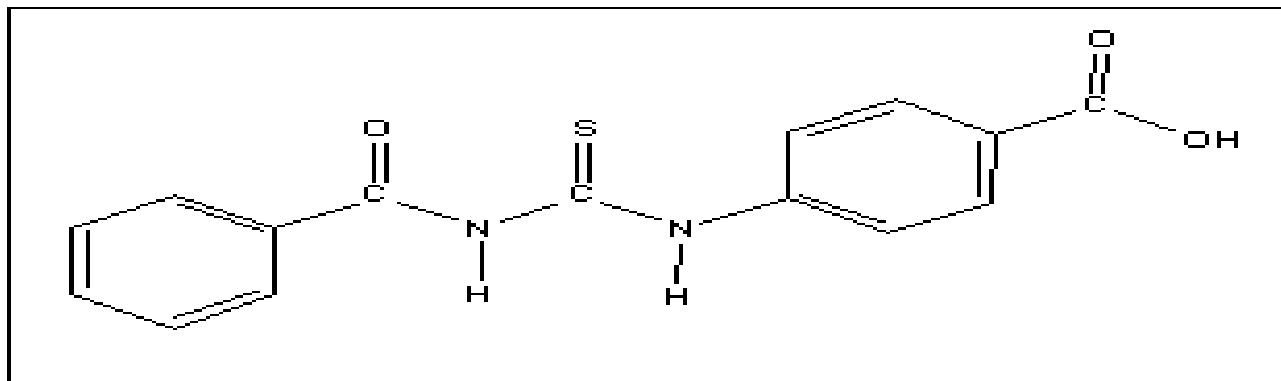
#### Synthesis of Process

#### Synthesis of 4-(3-benzoylthioureido) benzoic acid [1] [4]

A solution of benzoyl chloride (1.4gm,

0.01mol.) in acetone (15ml) was added gradually to a cool solution of ammonium thiocyanate (0.76gm, 0.01mol.) in acetone (10ml) at (0-5°C) during 30 minutes and the reactants were stirred for 2 hrs, the formed

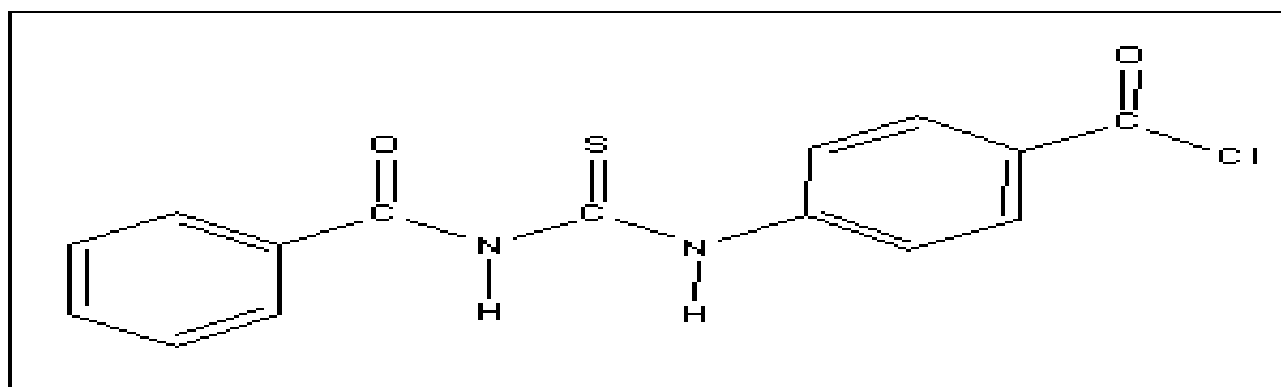
precipitate remove by filtration. The filtrate was reaction with p-amino benzoic acid (1.37gm, 0.01mol.) in acetone (15ml) gradually at 25 °C and the reaction mix was left to stirred overnight.



### Synthesis of 4-(3-benzoylthioureido)benzoyl chloride [2] [5]

A mixture of compound [1] (3gm, 0.01mol.) in

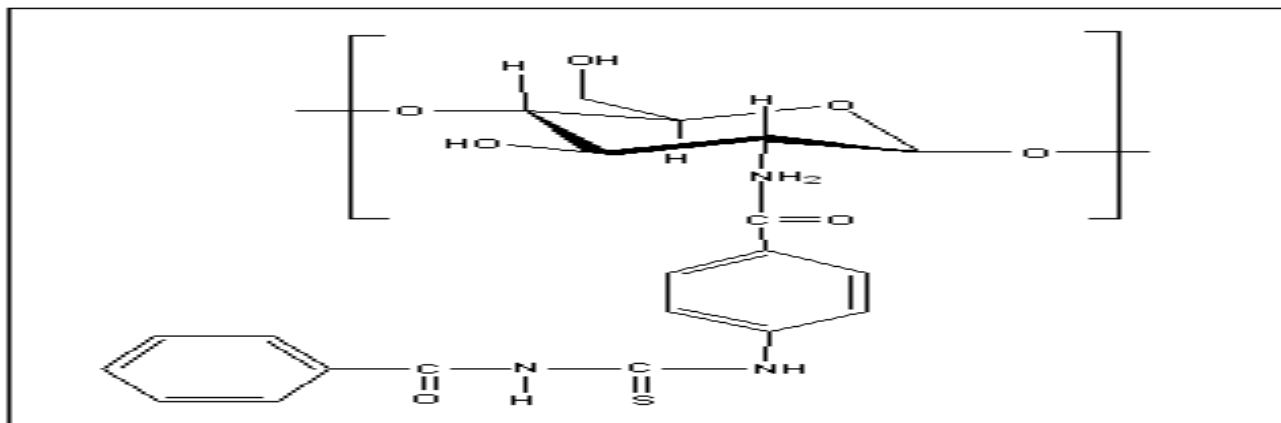
benzene dry (10ml), and thionyl chloride (10ml) was reflux for (7 hrs.) After cooling the excess of thionyl chloride and benzene were remove under vacuum.



### Modification of Chitosan [3]

Chitosan was modified at 25°C and stable stirring, with the compound [2] thawed in dry pyridine, and dissolved (1gm) of chitosan in methanol / acetic acid / water was diluted with an excess from methanol and cooled to

(0-5°C) with stable stirring. A (3gm, 0.01mol). From compound [2] of thawed in dry pyridine was slowly added to chitosan dissolved under vigorous stirring. The reactions proceeded overnight, and after were pouring in a Petri dish; the formed film was dried under vacuum at 35°C at 24 hrs.



### Preparation of Buffer Solution

The buffer solutions were prepared by adding drops of each of the solutions 0.1M

hydrochloric acid and 0.1M sodium hydroxide and were checked by using of pH-meter.

**Adsorption Experiments**

The adsorption of Ni<sup>+2</sup> and Co<sup>+2</sup> ions has been studied in sequential steps: the standard

solutions were prepared by dissolving the necessary weights of metals chlorides and sulfates in the ionic water. The adsorption of Ni<sup>+2</sup>and Co<sup>+2</sup>ions on the studied polymers was analyzed using atomic absorption spectroscopy.

**Table 1: shows the weights taken from each salt and required for obtain 100 ppm from ion the element**

No.	Molecular formula for salts the elements	Weight for salts the elements
1.	CoCl <sub>2</sub> .6H <sub>2</sub> O	0.464
2.	NiCl <sub>2</sub> .6H <sub>2</sub> O	0.405

**Effect of Contact Time**

50 mg of the polymer and 10ml of copper solutions were placed in 10ml volumetric flask and shaken continuously for 2,5,10,20,30 and 180 minutes at 25°C. The polymer samples were filtered, a similar

procedure have been used for Ni<sup>+2</sup> and Co<sup>+2</sup> ions studies. The metal ion concentrations in the filtrate were measured by atomic absorption spectroscopy. The removal efficiency R%, was Calculated by using the equation (1-1).

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \dots\dots\dots (1-1)$$

Where C<sub>i</sub> and C<sub>e</sub> is the initial and equilibrium

concentrations (mg/L) of copper ions, respectively.

**Table 2: Show the impact of connect time on adsorption of Co<sup>+2</sup>and Ni<sup>+2</sup> ions on the synthesized polymer [3]**

Metal ion	Time (min)	C <sub>e</sub>	R %
Co <sup>+2</sup>	2	298	31.7
	5	205.6	53
	10	324.8	51
	20	212	51.6
	30	426.7	50
	180	294.6	52
Ni <sup>+2</sup>	2	147.67	67
	5	145.86	67.5
	10	132.1	70.6
	20	181.3	70
	30	201.6	69
	180	128	71

From the experimental results show above, the contact time for experiment, was found to be: Co<sup>+2</sup>(5 minutes) and Ni<sup>+2</sup>(10 minutes) for polymer [1].

polymers was evaluated within a pH of 4,7 and10.Using the same procedure in (2.5.1) and the stirring time was chosen from the experimental results of the contact time.

**Effect of pH**

One of the important controlling parameters in adsorption is pH. the effect of pH on the sorption of Ni<sup>+2</sup>and Co<sup>+2</sup>ions onto authorship

The removal efficiency R% was Calculated as in equation (1-2), while the adsorption capacity (q<sub>e</sub>) was Calculated according to equation (1-2).

$$q_e = \frac{(C_i - C_e) \times v}{w} \dots\dots\dots (1-2)$$

Where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations (mg/L) of metal

ions, respectively.  $V$  is the total volume of solution (L), and  $W$  is the polymer weight (g).

**Table 3: Show the effect of pH of adsorption the  $Ni^{+2}$  and  $Co^{+2}$  ions on the synthesized polymer [3]**

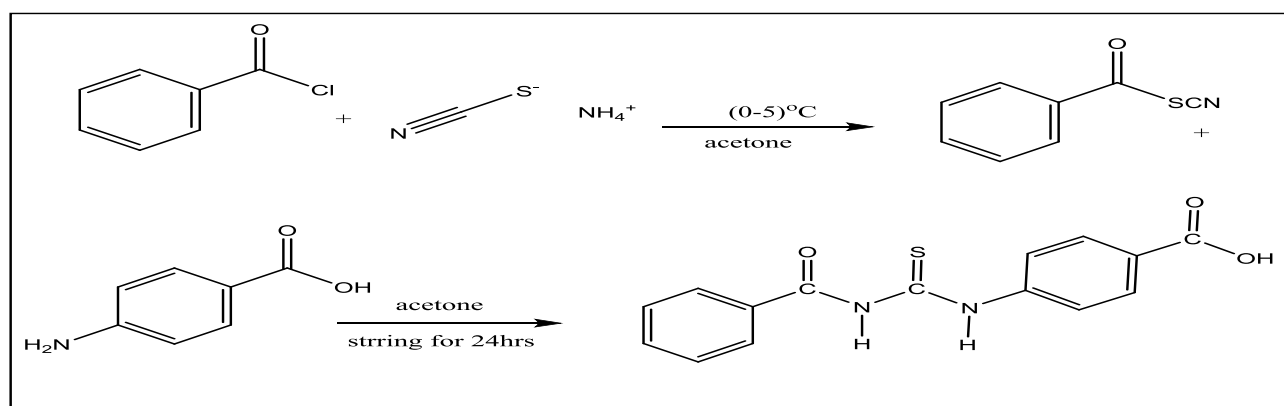
Metal ion	Contact time(min)	pH	$C_e$ mg/L	R%	$q_e$ mg/g
$Co^{+2}$	5	4	17	96	83.9
		7	46	89	78.1
		10	0.056	99.9	87.2
$Ni^{+2}$	10	4	43.8	90	81
		7	16.9	96	86.3
		10	0.182	99.9	89.7

## Results & Discussion

### Preparation and Characterization of 4-(3-benzoylthioureido) Benzoic Acid [1]

Compound [1] was prepared by using many sequence steps as in scheme Fig. (4). The reaction of benzoyl chloride with ammonium

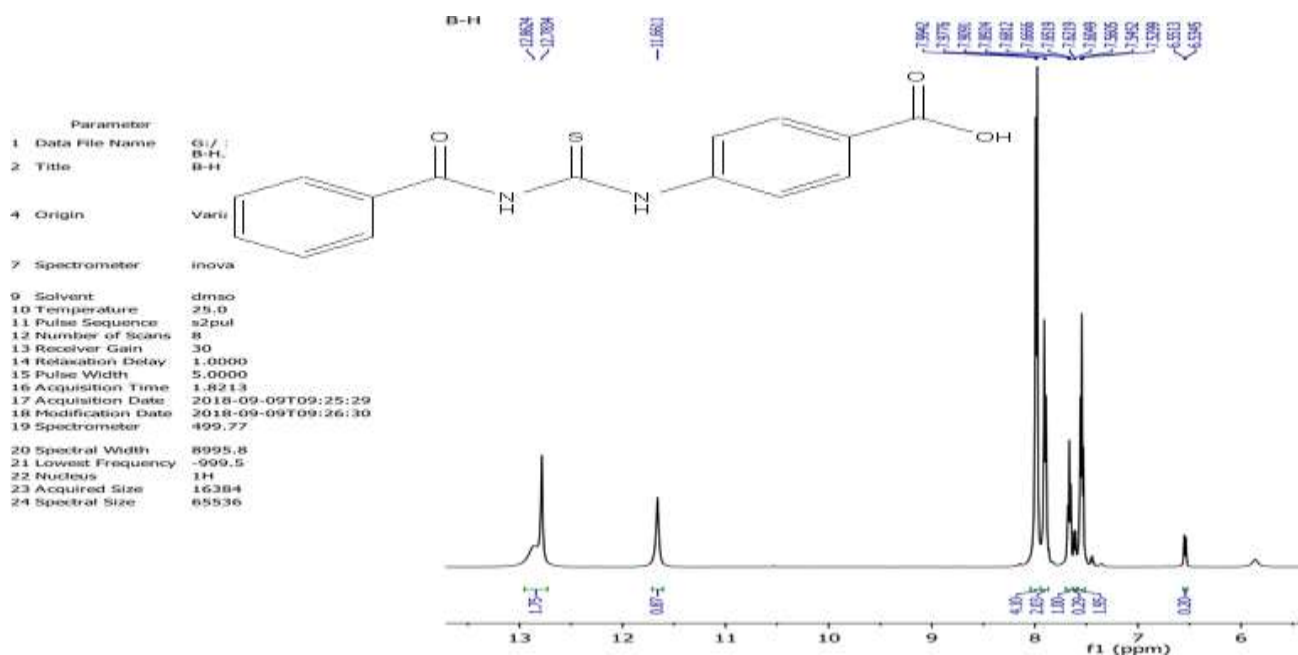
thiocyanate in acetone at  $(0-5)^{\circ}C$  to yield benzoic cyanic thioanhydrid which react with 4-amino benzoic acid yielded 4-(3-benzoylthioureido) benzoyl chloride compound [1] that identified the fusion point (246-248) and  $^1H$ MNR spectrum .Scheme (3-1).



**Fig. 4: Scheme : Preparation path of compound [1]**

Figure (5) displays the following characteristic chemical shifts in (DMSO- $d_6$ ) ppm the : multiplet peaks at  $\delta(7.52-7.99)$  ppm for two ring aromatic protons , the singlet peak at  $\delta(11.66)$  ppm for (1H, NH) present

between (C=O and C=S) groups ,a singlet peak at  $\delta(12.78)$  ppm for (1H, NH) present between (C=S and Ph) groups, a singlet peak at  $\delta(12.86)$  ppm for carboxylic acid (1H, OH).



**Figure 5:  $^1H$ -NMR spectrum of compound [1]**

### Preparation and Characterization of 4-(3-benzoylthioureido) benzoyl Chloride [2]

Compound [2] was prepared to literature through the condensation of compound [1] with thionyl chloride  $\text{SOCl}_2$  in dry benzene Scheme (6) compound [2] were characterized by melting point (196-198) °C and FTIR spectra. The FTIR spectrum of this

compound Figure (7) showed the shift of stretching bond of (C=O) group from (1687)  $\text{cm}^{-1}$  to (1751)  $\text{cm}^{-1}$  give a good evidence formation acid chloride the figure exhibits a bond (1678) $\text{cm}^{-1}$  which assigned to the  $\nu(\text{C}=\text{O})$  stretching vibration, the bond at (1253.7) $\text{cm}^{-1}$  due to the (C=S) stretching vibration and bonds at (1587) $\text{cm}^{-1}$  and (1533) $\text{cm}^{-1}$  are assigned to the  $\nu(\text{C}=\text{C})$  aromatic stretching vibration. Scheme Fig. (6).

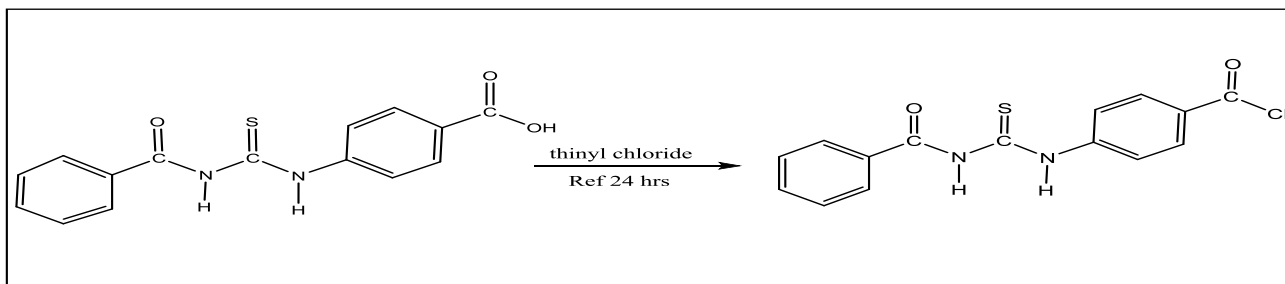


Fig. 6: Scheme: Preparation path of compound [2]

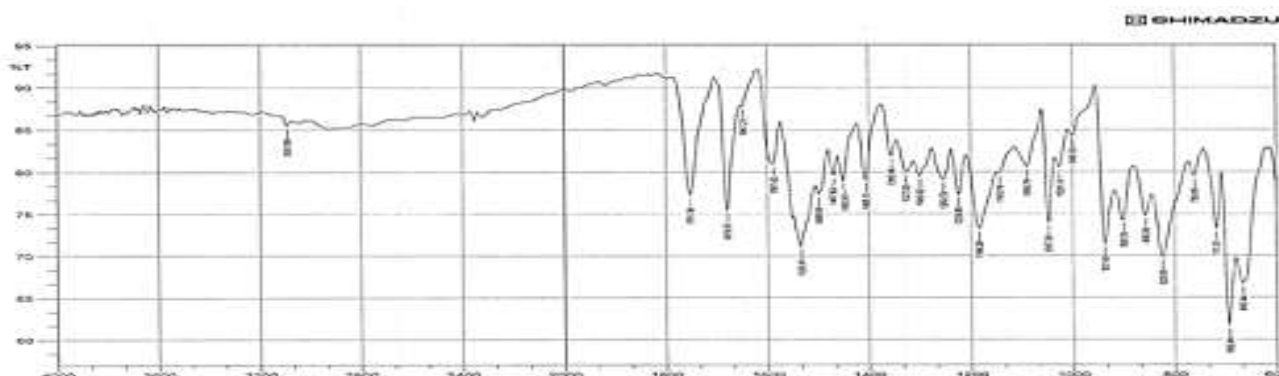


Figure 7: FTIR spectrum of compound [2]

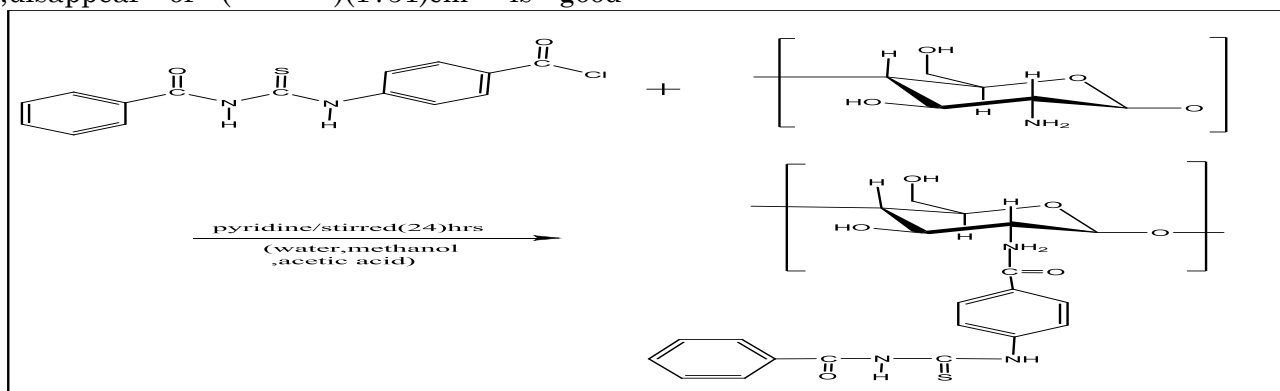
### Characterization and Preparation N-(4-(3-benzoyl thiourido)) benzamide chitosan [3]

Chemical modification of chitosan were obtained by reaction of chitosan polymer with compound [2]. The modified polymer  $\text{MC}_1$  identified by FTIR spectrum. FTIR spectrum as show in Figure (3-3) illustrated the presence following absorption bonds (3200)

$\text{cm}^{-1}$  assigned to the  $\nu$  (O-H) stretching

,disappear of  $(-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl})$ (1751) $\text{cm}^{-1}$  is good

indication that the  $(-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl})$  converted to (N-C=O) ,(1627)  $\text{cm}^{-1}$  to (C=O) of amide group due to inter-hydrogen bonding ,and weak bond for (C=S) at (1255) $\text{cm}^{-1}$  due to conjugated (-N=C-) and intra H-bonding. Scheme Fig. (8).



Scheme 8: Preparation path of compound [3]

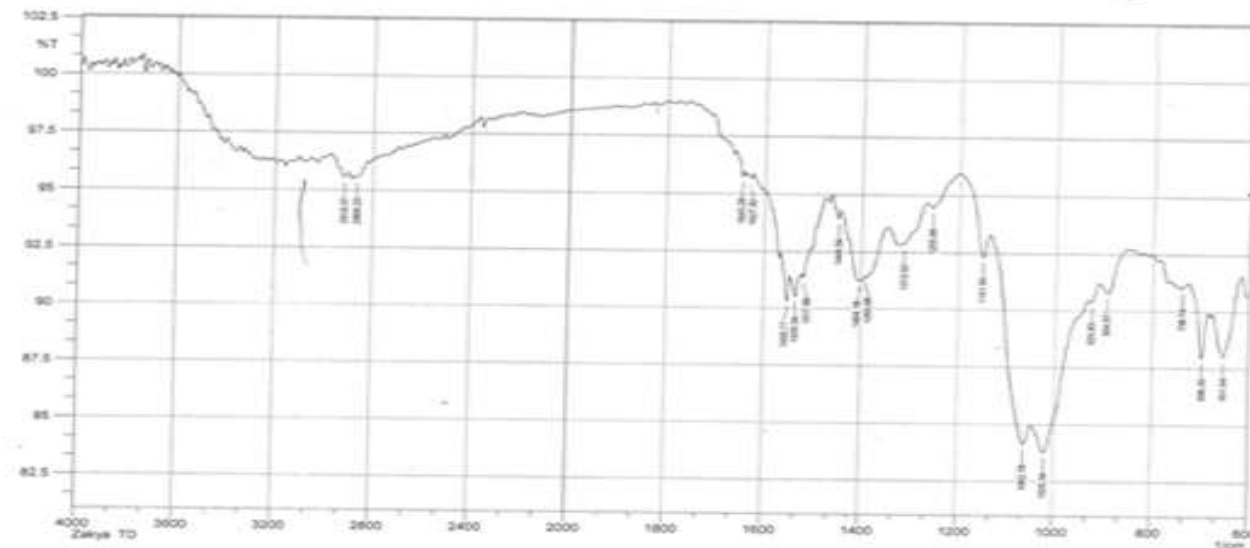


Figure 9: FTIR spectrum of compound [3]

### Heavy Metal Adsorption using Modified Chitosan Polymers as Adsorbents

In order to examine the efficiency of the modified chitosan polymer [3] as adsorbents to various heavy metals. A series of experiments were studied under various factors such as contact time, pH, and adsorbent weight. The metal ions  $\text{Ni}^{+2}$  and  $\text{Co}^{+2}$  were used as examples of heavy metals. The removal process strongly depended on the ion exchange and chelating properties of adsorbents, which are linked further with the network composition and most important factor determination of adsorption capacity [6].

### Effect of Contact Time onto Metal ion Adsorption

The contact time was evaluated as one of the most important factors affecting the adsorption efficiency. The amount of the adsorbed heavy metal ions increased with increasing of the time and after equilibrium time adsorption attain equilibrium [7]. The percentage removal of mentioned metal ions were measured by using atomic adsorption technique and the results drawn as a function of contact time. Figure (10).

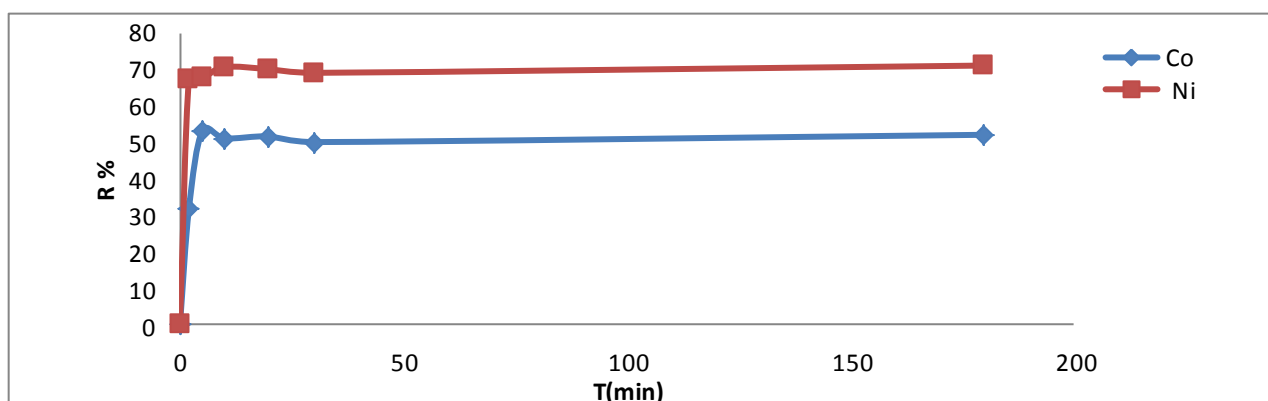


Figure 10: Effect of the contact time on metal ions removal by polymer [3]

### Effect of the pH on metal ions adsorption

The influence of pH on ion adsorption from solutions of  $\text{Ni}^{+2}$ , and  $\text{Co}^{+2}$  by polymer [3] (0.05 gm), cation exchange membrane, was studied in the pH values (4, 7, 10) at  $25^{\circ}\text{C}$ , under continuous stirring. Figure (3-5) show the impact of pH on  $\text{Ni}^{+2}$  and  $\text{Co}^{+2}$  ion

removal efficiencies. It can be see that metal ions removal percentage by polymer [3] generally increased with the increasing pH value. The pH of aqueous solution in an important parameter that may influence the uptake of the adsorbate. The chemical characteristics of both adsorbent and adsorbate vary with pH, the pH of solution

affects the degree of ionization and speciation of various metal ions, which leads to a change

in the reaction kinetics and equilibrium characteristics of the adsorption process [8].

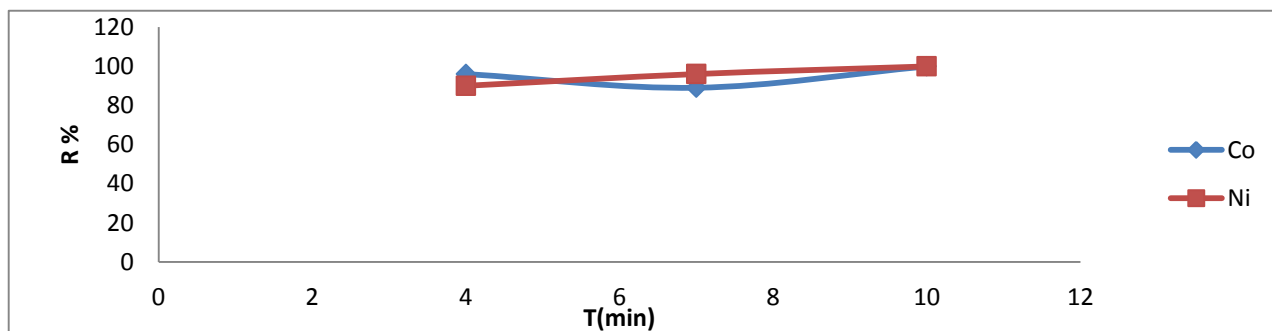


Figure 11: Impact of pH of solution on metal ions removal by polymer [3]

## Conclusion

Adsorption experiments were conducted for nickel ions and cobalt. This study showed that the modified chitosan compounds have a good adsorption capacity for the this

elements. From the experimental results, the contact time found to :  $\text{Co}^{+2}$  (5 minutes) and  $\text{Ni}^{+2}$  (10minutes) for polymer [1].The removal ratio is increasing with increase the pH.

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