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The Usage of Modified Chitosan for the Removal of Hexavalent Chromium from Waste Water

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Abstract

This study presents the results of chromate adsorption upon chitosan modified with thiourea, glutaraldehyde. Firstly modified chitosan was synthesized by using thiourea, glutaraldehyde and chitosan at different molar ratios and adsorption capacities were compared to the original chitosan. The modified chitosan showed higher Cr (VI) retention performance than the original chitosan. While the original chitosan had a percent removal of 32% at an initial concentration of 50 ppm, the percentage of chitosan removal improved to 99.9%. Kinetic and thermodynamic constants are determined at appropriate ambient conditions and adsorption is defined by appropriate adsorption isotherms. Langmuir isotherms were found to be suitable for characterizing the adsorption of chitosan with the modified Cr (VI) ions. Under appropriate experimental conditions, percentages of removal in Cr (VI) removal studies by adsorption using modified chitosan reached 99% and adsorption capacity of 442 mg/g was observed.Characterization of the modified chitosan and original chitosan were characterized by FTIR (Fourier Transform Infrared Spectroscopy), TGA (Thermal Gravimetric Analysis), XRD (X-ray Diffraction) and DSC (Differential Scanning Calorimetry).

Key words

Adsorption, Chitosan, Chromium(VI), Wastewater Treatmant

1. INTRODUCTION

The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. Heavy metals have a harmful effect on human physiology and other biological systems when they are found above the tolerance levels [1]. The presence of trivalent and hexavalent chromium in the environment is the cause of many well documented toxic effects. The maximum levels permitted in wastewater are 5 mg/L for trivalent and 0.05 mg/L for hexavalent chromium [2].

Chromium is a transition element which is located to Group VI-B of the periodical table and its toxic effect has been proven. Chromium exists in environment both as trivalent Cr(III) and hexavalent Cr(VI) forms. Hexavalent chromium is toxic and carcinogenic, while trivalent is relatively harmless [3]. High concentrations of Cr (VI) are present in the wastewater of leather, textile, mining and metal industries. These high concentration must be reduced below the permissible limits before Cr(VI) is discharged into the receiving enviroment [4]. Activated carbon is the world's most widely used adsorbent for heavy metal removal from waste water. Despite its efficient use, active carbon is expensive. Due to the disadvantage, research interest into the production of alternative adsorbents to replace the costly activated carbon. Because of their low cost, natural materials such as chitosan, zeolites, clay and fly ash are classified as low-cost adsorbents [5].

In recent years, studies on the use of chitosan as an adsorbent in heavy metal removal have been investigated. Chitosan is a polymer with polysaccharide structure obtained by alkali deacetylation of chitin. Chitin is the second most common biopolymer after cellulose in nature.It is highly reactive as an adsorbent due to the inclusion of amine and hydroxyl groups in the structure [6]. The degree of deacetylation is one of the most important chemical properties that can affect chitosan performance in many applications. The degree of deacetylation, which determines the content of free amino groups in polysaccharides, can be used to differentiate between chitin and chitosan. FTIR analysis was used to determine the degree of deacetylation of chitosan [7]. Various techniques have been employed for the treatment of heavy metals, including chemical precipitation, mebran processes, ion-exchange and adsorption. Adsorption technique is economically suitable and technically practicable to remove hexavalent chromium from waste water as it requires less operative controls [8].

Briefly, the aim of this study was to investigate the Cr(VI) adsorption performance of chitosan modified with thiourea, glutaraldehyde.

2. MATERIALS AND METHODS

All the chemicals used were of analytical grade. A stock solution of chromium (VI) (100 mg/L) was prepared by dissolving 3.73 g of $K_2Cr_2O_4$ in 1000 mL distilled water. Desired concentrations were obtained by diluting the stock solution with distilled water. Chitosan was obtained from Sigma and and classified to average particle diameterof 0.125–0.250 mm.

2.1. Degree of Chitosan Deacetylation

The degree of deacetylation is one of the most important chemical properties that can effect chitosan performance in many applications. The degree of deacetylation, which determines the content of free amino groups in polysaccharides, can be used to differentiate between chitin and chitosan. To determine the deacetylation degree of chitosan, 1 g of chitosan 100 mL of 5% acetic acid solution was added. It was mixed at a speed of 150 rpm at a temperature of 30º for 6 hours to dissolve. At the end of the process a viscous solution was obtained and analyzed by FTIR (Fourier Transform Infrared) spectrometer. It is expected that the structure will be modified with thiourea in addition to the amine groups and the sulphide will have a positive effect on chromium removal [9].

Considering these situations, the strategy of modification has been determined. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity.

2.2. Chitosan Modification

Chitosan is soluble in dilute mineral acids except sulfuric acid. For this reason, chemical stability should be increased by chemical treatments such as glutaraldehyde cross-linking for application in a chemical acidic environment. The process creates new bonds between the chains of chitosan, ensuring that the polymer is resistant to dissolution even in strong solutions such as hydrochloric acid solution [10]. In addition, the presence of chitosan amine groups is an important influence on the absorption of a good absorbent. It is possible to increase the adsorption capacity by increasing the amine groups [9].

Considering these situations, the strategy of modification has been determined. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity. The thiourea and glutaraldehyde were reacted in 20 mL distilled water for 8 hours at 20 ºC [9]. Then, 1 g of chitosan was added and reacted for 72 hours. Modified chitosan filtration and washed several times with distilled water. Then, it was dried at 50 ºC for 24 hours. Dried chitosan samples are stored in a desiccator [9]. Different amounts of thiourea and glutaraldehyde were studied to investigate the effect of thiourea and glutaraldehyde content on the adsorption capacity. The contents of the modified chitosan samples produced are listed in Table 1.

Table 1. Contents of Modified Chitosan Samples

Sample	**Chitosan (g)**	**Glutaraldehyde (mL)**	**Thioürea (g)**
KGT.1	1	1	-
KGT.2	1	2	-
KGT.3	1	4	-
KGT.4	1	8	-
KGT.5	1	1	1
KGT.6	1	2	1
KGT.7	1	4	1
KGT.8	1	8	1
KGT.9	1	1	2
KGT.10	1	2	2
KGT.11	1	4	2
KGT.12	1	8	2
KGT.13	1	1	4
KGT.14	1	2	4
KGT.15	1	4	4
KGT.16	1	8	4

2.3. Cr(VI) Adsorption Experiments

Stock solution of K_2CrO_4 (1000 ppm) was prepared and diluted as necessary to be used in batch adsorption experiments. The concentration of Cr(VI) was analyzed spectrophotometrically (Shimadzu UV 1240) at 540 nm using 1,5-diphenyl carbazide as the complexing agent [11,12].

The adsorption capacities of original chitosan and modified chitosan samples were determined under the conditions of 50 ppm initial Cr(VI) concentration, pH 2.0 and 1 g L^{-1} adsorbent dose. The removal extent and capacity were calculated from Eq. 1 and Eq. 2, respectively.

$$q_e = \frac{V_i C_i - V_e C_e}{W} \tag{1}$$

$$\text{Adsorption(\%)} = \frac{(A_0 - A)}{A_0} * 100 \tag{2}$$

where C_i and C_e are the initial and equilibrium Cr(VI) concentration of solution (mg L^{-1}), q_e is the equilibrium uptake capacity (mg g^{-1}), V is the volume of solution (L) and W is the mass of adsorbent (g). Where A_0 and A are the initial and final absorbance (nm) of the solution, respectively [13].

The effect of pH was studied within the range pH 1–8.0. Adjustments were made by small additions of 0.1 M HCl or 0.1 M NaOH. Cr(VI) solutions of 50 ppm were contacted with modified chitosan samples (0.4 g L^{-1}) and 250 ppm were contacted with modified chitosan samples (0.6 g L^{-1}) for 24 h. Time to reach equilibrium was investigated for initial concentrations (C_0) of 70 and 160 ppm. Samples were driven out at certain time intervals between 1 and 24 h and analyzed for residual Cr(VI) concentration. The effect of adsorbent dose was investigated within the range of 0.2 – 4 g L^{-1} using Cr(VI) solutions of 100 ppm and 250 ppm. Optimal conditions of pH, contact time and adsorbent dose were applied in isotherm studies. Cr(VI) solutions of different concentrations were treated with modified chitosan samples, and collected data were fitted to Langmuir and Freundlich isotherm models.

2.4. Adsorbent Characterization

Identification of the crystalline species or impurities in original chitosan and the change in crystalline structure after modification with surfactant were provided by X-ray diffraction analysis. Thermalgravimetric analysis of original chitosan and modified chitosan samples was carried out by Perkin Elmer, Diamond TG/DTA in air atmosphere, within the temperature range of 30-1000 ºC with a heating rate of 10 ºC min^{-1}. The FTIR spectra of samples were recorded with Perkin Elmer Spectrum One Spectrophotometer within 4000–450 cm^{-1} as an average of four scans.

3. RESULT AND DISCUSSION

3.1. Chromium Removal with Chitosan and Modified Chitosan

3.1.1. Comparison of Original Chitosan and Modified Chitosan in Cr(VI) Removal

Firstly modified chitosan was synthesized by using thiourea, glutaraldehyde and chitosan at different molar ratios and adsorption capacities compared to the original chitosan were compared. The modified chitosan showed higher Cr (VI) retention performance than the original chitosan. While the original chitosan had a percent removal of 32% at an initial concentration of 50 ppm, the percentage of chitosan removal improved to 99.9%. The chrome Cr (VI) holding capacities and removal percentage of the original chitosan and modified chitosan are shown in Table 2.

Table 2: The Cr (VI) holding capacities and removal percentage of the original chitosan and modified chitosan

Sample Name	Amount of Retention (mg/g)	Removal Percentages (%)
KGT.1	46.62	89.24
KGT.2	45.36	90.73
KGT.3	48.45	96.91
KGT.4	49.94	99.88
KGT.5	47.22	94.44
KGT.6	47.47	94.93
KGT.7	48.45	96.91
KGT.8	47.59	95.18
KGT.9	44.37	88.75
KGT.10	48.45	96.91
KGT.11	47.09	94.19
KGT.12	48.95	97.90
KGT.13	47.34	94.69
KGT.14	46.97	93.95
KGT.15	49.97	99.95
KGT.16	49.32	98.64
Original Chitosan	16.43	32.85

The modified chitosan No. KGT.15 was synthesized to be used as an absorbent when the appropriate conditions for Cr (VI) removal were determined using the results.

3.1.2. Effect of pH on Cr(VI) Removal

pH is one of the important parameters affecting the adsorption capacity due to its influence on the surface properties of adsorbent and metal ionization. The results of experiments conveyed at different pH levels are shown in Fig.1.

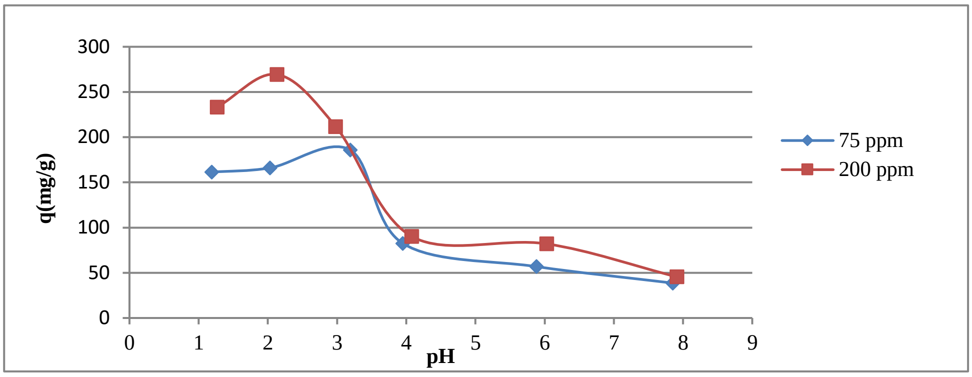

Figure 1.Determination of the appropriate pH range for adsorption of Cr (VI) ions on modified chitosan; t = 24 hours, T = 293 K

3.1.3 Effect of Contact Time on Cr(VI) Removal

The effect of contact time was examined in the range of 1h to 24 h for 70 and 160 ppm initial Cr(VI) concentrations, and the results are shown in Figure 2.

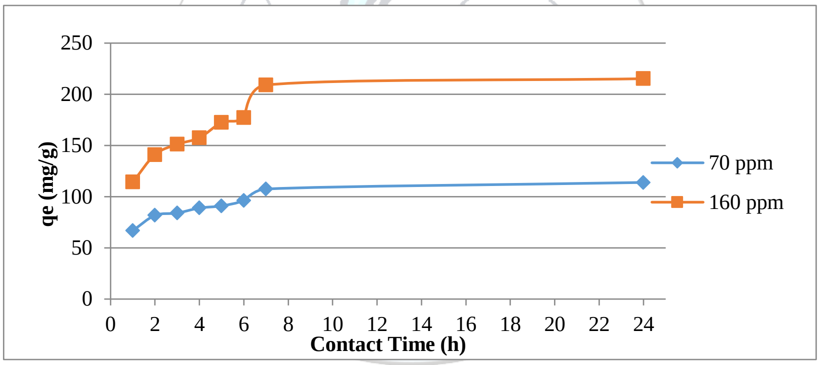

Figure 2. Determination of the equilibrium time of adsorption of Cr (VI) ions on modified chitosan; t = 24 hours, m = 0.03 g T = 293 K.

Figure 2 shows that the duration of the equilibrium is independent in the initial concentration. It was observed that the amount of retention increased at negligible level after the first seven hours. For this reason, it can be said that the seven hour contact period of Cr (VI) ions is sufficient for adsorption with modified chitosan.

3.1.4. Effect of Absorbent Dose on Cr(VI) Removal

Determination of the appropriate adsorbent dose is important for the efficiency and cost of the adsorption process. In the experiments, the effects on adsorption were investigated by changing the adsorbed dose at two different initial concentrations.The effect of the adsorbent dose on the amount of retention and percentages of removal is shown in Table 3 and Table 4.

Table 3. The effect of the adsorbent dose on the amount of retention and percentages of removal at C_0= 100 ppm

Adsoebent Dose (g/50mL)	Amount of Retention (mg/g)	Removal Percentages (%)
0.03	126.4	75.83
0.04	114.3	91.41
0.05	98.0	97.96
0.07	69.8	97.59
0.10	49.8	99.44
0.15	33.3	99.81
0.20	25.0	99.94

Table 4. The effect of the adsorbent dose on the amount of retention and percentages of removal at C_0= 250 ppm.

Adsoebent Dose (g/50mL)	Amount of Retention (mg/g)	Removal Percentages (%)
0.03	227.2	54.52
0.04	203.9	65.25
0.05	172.1	68.86
0.07	145.0	81.23
0.10	112.7	90.13
0.15	79.9	95.82
0.20	62.4	99.93

The difference between the percentages of removal increases with each step from 0.01 g to 0.07 g to the adsorbent dose. It is seen that the difference between the percentages of elimination in adsorbent dose increases after 0.07 g is negligible. It has been decided that the appropriate adsorbent dose should be between 0.07 g / 50 mL and 0.1 g / 50 mL.

3.2. Adsorption Isotherm Studies

As a result of the studies, the optimum environment conditions for hexavalent chromium removal from waste water with modified chitosan were determined as solution pH 1-3, adsorbent dose 1.4 (g / L) and contact time 7 hours. After selection of optimal operating conditions, isotherm studies were conducted to characterize the adsorption of Cr(VI) upon modified chitosan. It was studied with different initial concentrations at constant temperature to obtain isotherm graphs. Relationship between the adsorbate concentration of the equilibrium solution and the amount of adsorbent material per unit adsorbent should be established. It should be determined again by changing the temperature to determine the effect of the change with temperature. For this purpose, five different

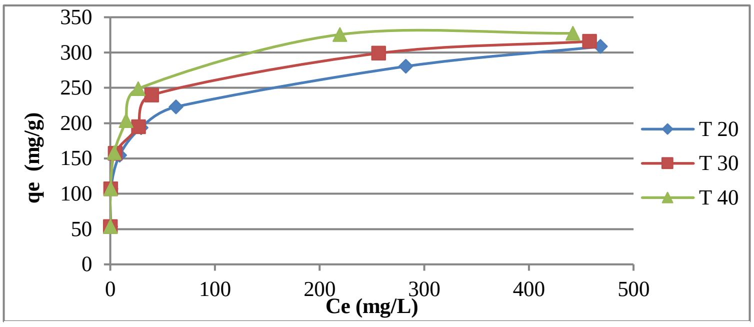

Figure 3: Determination of adsorption capacities at different temperatures; (C0) = 75, 150, 225, 300, 375, 675, 900 ppm.

initial concentrations and three different temperatures were used. The relationship between the amount of retention and the concentration of solution in equilibrium is shown in Figure 3.

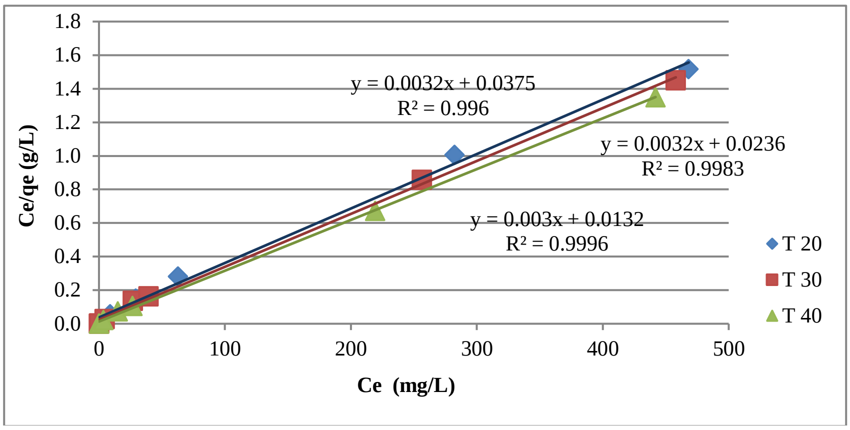

Figure 4. Langmuir constants for different temperatures in the adsorption of Cr (VI) ions with modified chitosan

To determine whether the obtained data correspond to Langmuir isotherms, a graph of C_e / q_e values versus C_e values was drawn. This is shown in Figure 4.

The correlation constant in the three different temperatures being greater than 0.96 indicates that the Langmuir isotherm is suitable for characterizing the adsorption of the Cr (VI) ions with the modified chitosan. Data were fitted to linearized forms of isotherm models and results are given in Table 5.

Table 5. Langmuir Constant

Sıcaklık	**Sabitler**				
	K_L (L/g)	a_L (L/mg)	q_m (mg/g)	R^2	Dağılma sabiti R_L
293	26.66	0.085	308.4	0.996	0.012
303	42.37	0.135	315.7	0.998	0.008
313	75.75	0.227	327.2	0.999	0.004

3.3. Characterization of Chitosan and Modified Chitosan

3.3.1. X-Ray Diffraction Analysis

X-ray diffraction of the original chitosan and modified chitosan is shown in Figures 5 and 6.

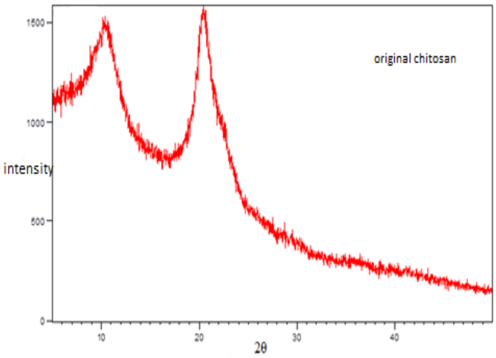

Figure 5. Original chitosan XRD pattern

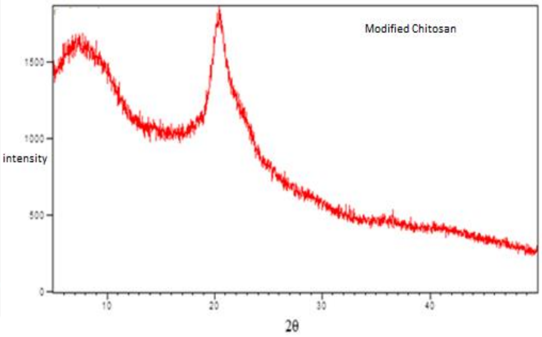

Figure 6. Modified chitosan XRD pattern

XRD analysis was also made for the proof of modification. The modification of chitosan with glutaraldehyde and thiourea showed a peak flattening at 11 ° with the resultant original chitosan, indicating a significant decrease in crystallinity as a result of chitosan cross-linking with glutaraldehyde. The crystallinity of the chitosan polymer may play a limiting role in metal retention capacity. The crystallinity parameter of chitosan is an important parameter of accessibility to the inner region for both water and metal ions. Many studies have shown that reducing the crystallinity results in an improvement in metal ion retention properties [14,15].

3.3.2.Thermal Gravimetric Analysis of Adsorbents

Figure 7 shows the mass change graph due to the temperature obtained at 25 - 1000 ºC temperature by Thermal Gravimetric Analysis (TGA) method of chitosan and modified chitosan. In order to examine the thermal behavior of chitosan and modified chitosan in detail, differential thermogravimetric (DTG) curves of the materials are given in Figure 8.

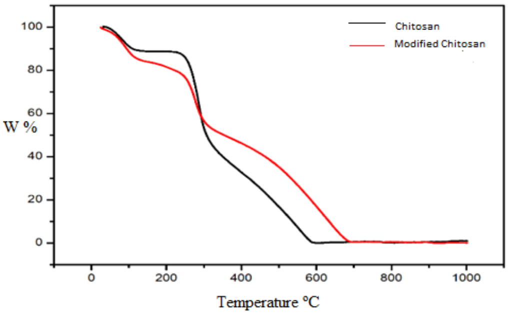

Figure 7. Chitosan and Modified Chitosan TGA Curve

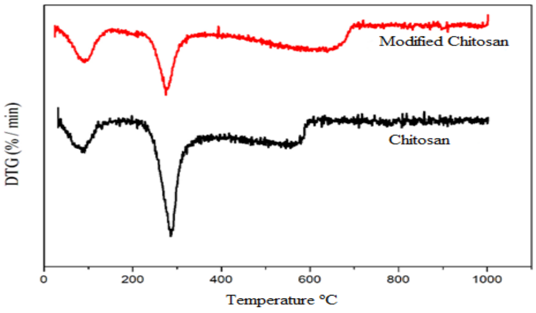

Figure 8. Chitosan and Modified Chitosan DTG Curve

Both samples showed mass loss at 100 ºC, while at the same time DTG curves both peaks at 100 ° C on both samples. When studies done in the literature are examined, the initial weight loss at about 100 ° C is due to the evaporation of water. The other weight loss at 200-500 ºC is due to the deterioration of the structure of the chitosan molecule [16]. Thermal gravimetric analysis gives information on the composition of chitosan and modified chitosan. On the other hand, information about the connections between the chitosan and the modified chitosan was needed. For this reason, analysis with XRD and FTIR and study with TGA was supported.

3.3.3.FTIR Analysis of Adsorbents

The chemical structures of the chitosan and modified chitosan and the changes in the functional groups of the compounds were investigated by FT-IR spectroscopy and the peak intensities were interpreted in accordance with the literature. The FTIR spectra of the original chitosan and modified chitosan are given in Figure 9.

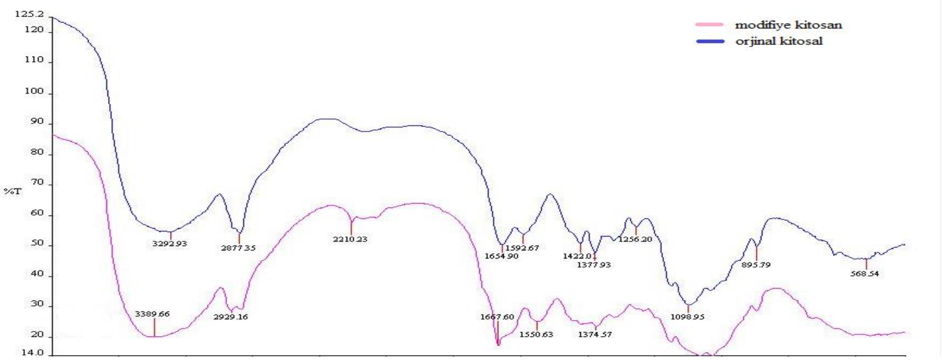

Figure 9. Original chitosan and modified chitosan FTIR spectrum.

The disappearance of the NH_2 band in the cross-linked chitosan as a consequence of the cross-linking mechanism with gulataldehyde at 560 cm $^{-1}$ in the original chitosan is evidence of the cross-linking of chitosan [16].

4. CONCLUSIONS

In this work, chitosan was first modified with glutaraldehyde and thiourea. The modified chitosan showed better performance in chrome removal compared to the original chitosan. The effects of different experimental conditions on the adsorption process were investigated by studying different solution pH, temperature, initial concentration, contact time and adsorbent dose. As a result of the studies, the optimum environment conditions for hexavalent chromium removal from waste water with modified chitosan were determined as solution pH 1-3, adsorbed dose 1.4 (g / L) and contact time 7 hours. Langmuir isotherm has been identified as the most suitable isotherm. Chitosan and modified chitosan are characterized by XRD, FTIR and thermal gravimetric analysis.

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