Utility of newly modified chitosan in the removal of heavy metal ions from aqueous medium: ion selectivity, XPS and TGA

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Abstract. The purpose of this study is to evaluate the newly prepared modified chitosan, a new environmentally friendly adsorbent, in the field of wastewater treatment. Chitosan (CS) reacted with 3-chloro-2,4-pentanedione to give CS derivatives, CS-CPD. Modified CS with O–O and N–O chelating centres was treated with aqueous solution containing different metal ions to investigate its metal uptake and selectivity. The concentration of metal ions in aqueous solution was measured by inductively coupled plasma-optical emission spectrometry. The structure of the complex was identified by elemental analysis, infrared and solid-nuclear magnetic resonance. In addition, the chelating centres were determined by X-ray photoelectron spectroscopy. The morphology of the modified polymer and its metal complexes was studied to show a dramatic change in cases of the CS-CPD–Pb, CS-CPD–Hg, CS-CPD–Cr and CS-CPD–Co complexes.

Keywords. Chitosan; metal removal; ion selectivity; XPS; TGA.

1. Introduction

Modifications of chitosan (CS) to increase its efficiency as a ligand have received considerable attention in the past few decades [1–6]. On the other hand, CS–metal complexes have attracted great interest due to their potential use in environmental treatment, agriculture, medicine and food industries [7–17]. Industrial and mining wastewater is important sources of pollution of heavy metals [18]. The polluting and toxic heavy metals in wastewater from different sources, such as industrial effluents, mine waters, water supplies and their removal have received much attention recently. The heavy metal sources to the environment have a serious threat to the environment [19,20]. Heavy metals, as well known, are not biodegradable and accumulate in living organisms causing different diseases and disorder. It has been reported that the presence of heavy elements in drinking water causing many diseases such as bladder, skin lesions, lung cancers, cardiovascular effects and anemia [21]. Metal ions, such as Hg(II), Cr(III), Pb(II), Cd(II), Cu(II) and Ni(II) ions are toxic to the aquatic systems. The removal of Cr(VI) using acid-catalysed chemical reduction to Cr³⁺ and then precipitation as hydroxide under alkaline conditions using either lime or caustic soda was reported [22]. The removal of Cu using CS and precipitation as copper hydroxide by liming was also reported [23,24]. Recently, the production of CS–gelatin hydrogel effectively removed Pb(II), Cd(II), Hg(II) and Cr(III) contaminated in wastewater [25]. The effect of reaction parameters, such as temperature, solvent and reaction time on Zn(II) complexation with the Schiff base, ligand

synthesized from salicylaldehyde and CS was reported [26]. The capacity of CS for the metal uptake of different metal ions was reported with different ratios. Sandhya and Tonni [27] had reported in their review article that CS showed high-adsorption capacities of Hg(II), Cr(VI) and Cd(II) with 815, 273 and 250 mg g^{−1}, respectively.

This work is aimed at modifying CS in increasing the capacity and metal uptake selectivity. To the best of our knowledge, this is the first method to prepare these newly synthesized CS derivatives.

2. Experimental

2.1 Materials

3-chloro-2,4-pentanedione was used as received. All chemicals and metal salts were reagent grade and used without further purification.

Elemental analysis was investigated on LECO CHNS-932, at Analab, Faculty of Science, Kuwait University. Infrared (IR) spectra were recorded on a Perkin-Elmer System 2000

FTIR spectrophotometer (Kyoto, Japan). Scanning electron microscopy was carried out at room temperature in a model JSM 6300 JEOL scanning electron microscope (Akishima, Japan) at 20 kV. Thermal analysis (TG) was carried out on a Shimadzu thermal system 50 consisting of TGA-50 and DTA-50 with a heating rate of $10^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere and a temperature range up to 800°C . X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250 Xi using monochromatic $\text{AlK}\alpha$ radiation (1486.6 eV) with a spot size of $850\text{ }\mu\text{m}$.

2.2 Synthesis of CS-CPD: reaction of CS with 3-chloro-2,4-pentanedione

3-chloro-2,4-pentanedione (0.01 mol) was added to 100 ml of toluene containing a CS film ($5 \times 5\text{ cm}$) and sodium carbonate (1.5 g). The reaction mixture was refluxed for 8 h. The produced modified CS derivative films were refluxed in

ethanol for 1 h. Elemental analysis of CS-CPD: C%: 40.14, H%: 6.88, N%: 5.90; IR (KBr, ν_{max} , cm^{-1}): 3389 (OH), 3286, 3159 (NH), 2887, 2887 (CH-aliphatic), 1726, 1651 (CO).

2.3 Synthesis of N-pyrazolylchitosan: reaction of CS-CPD with hydrazine hydrate

The CS-CPD film ($5 \times 5\text{ cm}$) was added to 100 ml DMF containing hydrazine hydrate (0.01 mol) and then, heated under reflux for 8 h. The pyrazolylchitosan derivatives obtained were refluxed in ethanol for 1 h. Elemental analysis: C%: 44.01, H%: 7.21, N%: 10.69; IR (KBr, ν_{max} , cm^{-1}): 3364, 3290, 3158 (OH and NH), 2887, 2887 (CH-aliphatic), 1651 (CO).

2.4 Metal complexation

The CS-CPD film ($5 \times 5\text{ cm}$) was submerged in a hot solution of metal nitrate salts (0.01 mol) in DMF and then, heated

Figure 1. FTIR of CS and CS-CPD.

Figure 2. Solid NMR of CS and CS-CPD.

Scheme 1. Modification of CS with 3-chloro-2,4-pentanedione.

Figure 3. XPS data of the CS-CPD-Fe complex: (A) Fe peaks; (B) nitrogen peaks; (C) carbon peaks and (D) oxygen peaks.

under reflux for 5 h. The obtained metallopolymer complex films were purified by heating in ethanol for 1 h.

CS-CPD-Pb complex: elemental analysis: C%: 40.62, H%: 7.03, N%: 6.67; IR (KBr, $\nu_{\max}$, cm^{-1}): br. 3550 (OH and NH), 2911 (aliphatic-CH), 1727, 1559 (CO). CS-CPD-Hg complex: elemental analysis: C%: 42.28, H%: 8.02, N%: 7.04; IR (KBr, $\nu_{\max}$, cm^{-1}): br. 3536 (OH and NH), 2975 (aliphatic-CH), 1721, 1635 (CO). CS-CPD-Ca complex: elemental analysis: C%: 39.26, H%: 6.75, N%: 6.97; IR (KBr, $\nu_{\max}$, cm^{-1}): 3598 (OH and NH), 2822 (aliphatic-CH), br. 1651–1622 (CO). CS-CPD-Co complex: elemental analysis: C%: 27.70, H%: 5.54, N%: 8.62; IR (KBr, $\nu_{\max}$, cm^{-1}): 3546, 3375, 3307, 3260, 3205 (OH and NH), 2869 (aliphatic-CH),

Scheme 2. Suggested complex structures with different metal ions: (A) complex with chelating centre N–O and (B) complex with chelating centre O–O.

1633 (CO). CS-CPD-Cr complex: elemental analysis: C%: 32.35, H%: 6.14, N%: 8.60; IR (KBr, $\nu_{\max}$, cm^{-1}): br. 3500 (OH and NH), 1725, 1561 (CO). CS-CPD-Fe complex: elemental analysis: C%: 33.60, H%: 6.30, N%: 9.10; IR (KBr, $\nu_{\max}$, cm^{-1}): 3449, 3384, 3322, 3235, 3138 (OH and NH), 2976 (aliphatic-CH), 1725, 1620 (CO). CS-CPD-Ni complex: elemental analysis: C%: 24.23, H%: 5.16, N%: 8.04; IR (KBr, $\nu_{\max}$, cm^{-1}): br. 3557 (OH and NH), 1675 (CO).

2.5 Ion selectivity

A modified CS film (5×5 cm) was added to aqueous solution containing (0.01 mol) a metal nitrate mixture ($M = \text{Pb}^{2+}$, Hg^{2+} , Ca^{2+} , Co^{2+} , Cr^{3+} , Fe^{3+} or Ni^{2+}) [28]. The mixture was stirred for 24 h. Then, the reaction product were filtered, and the concentration of the metal ion and the blank solution were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement.

2.6 Treatment of Gulf water samples

The real Gulf water sample (5 l) was pre-concentrated to a final volume of 150 ml. The metal ion concentration was determined by ICP-OES. The pre-concentrated sample was divided into three portions of 50 ml, followed by treating with the modified CS film under a shaking rate of 350 rpm for 24 h. The mixture was filtered and the polymer film was washed several times with double-distilled water. The results of ICP-OES measurements before and after treatment and the percentage of the metal uptake were estimated according to the following equation [29]:

$$\text{Adsorption\%} = \frac{C_i - C_f}{C_i} \times 100, \quad (1)$$

where C_i and C_f are the initial and final concentrations of the metal ion (mg l^{-1} or $\mu\text{g l}^{-1}$) before and after treatment, respectively. The results are the average of three measurements and precise to $\pm 1.25\%$.

Figure 4. XPS data of the modified CS complex: (A) CS-CPD-Pb; (B) CS-CPD-Hg and (C) CS-CPD-Cr complexes.

3. Results and discussion

3.1 Modification and characterization of CS

CS alkylated with 3-chloro-2,4-pentanedione in the presence of sodium carbonate to give *N*-alkylated products CS-CPD. The reaction product was determined based on the

Figure 5. XPS data of the modified CS complex: (A) CS-CPD-Ca; (B) CS-CPD-Ni and (C) CS-CPD-Co complexes.

Fourier transform infrared (FTIR) spectrum (figure 1) which displayed two carbonyl bands at 1736 and 1651 cm⁻¹. Furthermore, solid nuclear magnetic resonance (NMR) revealed the presence of the carbonyl group at δ 245.38 ppm and the amide carbonyl group at δ 178.03 ppm (figure 2).

Table 1. Ion selectivity (ICP) of different metal ions from aqueous solution by CS-CPD.

Metal ion	C_i (mg l ⁻¹)	C_f (mg l ⁻¹)	$(C_i - C_f)$	Sorption (%)
Hg	165,398	13,400.80	151,997.2	91.89
Co	1836.00	151.84	1684.16	91.73
Pb	3315.10	284.11	3030.99	91.43
Ca	1642.5	164.25	1478.25	90.00
Ni	2366.80	331.35	2035.45	86.00
Fe	2420.56	359.21	2061.35	85.16
Cr	2382.60	889.91	1492.69	62.65

Table 2. ICP-OES results of the Gulf ocean water sample before and after treatment with the chelating polymer CS-CPD.

Metal ion	C_i	C_f	% of metal uptake
Na ⁺ a	16,427.550	2506.550	84.742
K ⁺ a	763.900	178.260	76.664
Mg ²⁺ a	1611.400	164.580	89.787
Ca ²⁺ a	509.500	16.870	96.689
Co ²⁺ b	2.540	0.273	89.252
Ni ²⁺ b	13.750	0.173	98.737
Cu ²⁺ b	13.700	0.154	98.876
Cd ²⁺ b	BDL	ND	ND
Pb ²⁺ b	74.200	25.148	66.108
Fe ³⁺ b	1.070	0.014	98.692
Hg ²⁺ b	15.100	0.885	94.139

^a C_i in mg l⁻¹; ^b C_i in µg l⁻¹; ND, not detected; and BDL, below detection limit.

In addition, other carbons are present at 106.26, 85.30, 78.76, 64.69, 60.88 and 27.64 ppm. Moreover, the structure was confirmed via reaction of the polymeric derivative, CS-CPD with hydrazine hydrate to give pyrazolylchitosan derivatives (CS-PY) (scheme 1). The reaction is self-catalysed by hydrazine hydrate. Thus, the reaction is believed to proceed *via* nucleophilic attack of the nitrogen lone pair to the carbonyl carbon to give non-isolated intermediates **1**, followed by the loss of water molecules to give intermediate **2**, further attack by the second nitrogen atom to the second carbonyl carbon and the loss of another water molecule leading to the formation of the final isolated compound CS-PY. The structure determined based on IR which revealed the absence of the carbonyl group at 1736 cm⁻¹.

3.2 Formation of complexes

The modified CS was refluxed with a metal salt solution in a suitable solvent to give the corresponding complexes. The structures of the obtained complexes were determined based on elemental analysis, FTIR and XPS data. XPS of

Table 3. TGA of CS-CPD and its metal complexes.

Compound	Temp. (°C)	Weight loss (%)	Residue % (metal nitride)	Compound	Temp. (°C)	Weight loss (%)	Residue % (metal nitride)
CS-CPD	82.66	13.446	0.00	CS-CPD-Co	60.67	8.106	23.15
	275.22	46.622			242.04	47.624	
	641.36	37.924			525.56	2.851	
CS-CPD-Pb	207.93	76.421	17.50	CS-CPD-Cr	596.44	3.881	6.64
	432.83	2.911			732.66	14.150	
	800.00	3.168			60.49	9.489	
CS-CPD-Hg	67.38	10.197	33.14	CS-CPD-Ca	182.87	44.161	4.66
	246.25	43.648			313.56	18.798	
	552.45	2.280			460.10	8.359	
CS-CPD-Fe	615.90	1.907	4.81	CS-CPD-Ni	800.00	12.546	3.94
	800.00	8.828			172.31	88.403	
	82.48	7.413			473.65	1.173	
	189.55	45.451			800.00	5.766	
	302.18	19.667			199.47	84.147	
	511.98	14.701			457.28	4.882	
	688.85	7.874			800.00	7.033	
	800.00	0.088					

the metallopolymer confirmed the presence of metal and it refers to the centre of chelation, through studying the binding energy.

3.3 XPS

XPS was used to analyse the elemental states and contents in the sample. Figure 3A–D shows the survey spectra of Fe, N, C and O in the modified polymer CS-CPD. The XPS spectra of Fe are shown in figure 3A, the peaks at 711 and 724.3 eV are assigned to $\text{Fe(III)}2p_{3/2}$ and $\text{Fe(III)}2p_{1/2}$, respectively, denoting a band for Fe–O. The peak at a binding energy of 709.08 denoted a band for Fe–N bond. The band of the CS complex at 399.5 eV was attributed to the amino groups that were involved in the hydrogen bond ($\text{NH}_2\text{--O}$) (figure 3B). The CS–Fe complex denoted a band for N1s at around 402 eV (figure 3B). This band was assigned to the chelation

Figure 6. TGA curves of CS-CPD; CS-CPD–Cr; CS-CPD–Fe and CS-CPD–Pb.

Figure 7. TGA curves of CS-CPD–Ca; CS-CPD–Cd; CS-CPD–Co; CS-CPD–Hg and CS-CPD–Ni.

between the amino groups and iron ions ($\text{NH}_2\text{--Fe}$). Figure 3C shows the C1s peak of the CS-complex, main peak at 284.4 eV, which is ascribed to the presence of $\text{C}=\text{C}/\text{C}\text{--C}$ sp^2 carbon atoms in the framework. The peaks at 286.5 and 287.6 eV correlate with the carbon in C–O and the carbonyl carbon in $\text{C}=\text{O}$, respectively. The O1s peaks at 531.6 eV (figure 3D) was assigned to N–C–O chemical bindings in *N*-acetylated-glucosamine units. The peaks at 531.5 eV corresponded to free hydroxyl groups of CS. In light of this information, structure (A) (scheme 2) can be assigned to the complex structure.

The XPS spectra for all metal complexes with modified CS are presented in figure 4A–C. Figure 4A shows the detailed spectra of Pb peaks, produced from the reaction of CS-CPD with lead nitrate, appearing at 138, 139.23 eV ($\text{Pb } 4f_{7/2}$) and 143.21, 144.07 eV ($\text{Pb } 4f_{5/2}$) assigned to Pb(II)–O . Thus, structure B (scheme 2) was assigned as a reaction product.

Figure 4B shows XPS spectra produced from the reaction of modified polymer CS-CPD with Hg(II) . The high-resolution spectra of Hg(II) (figure 4B) exhibited two peaks at 101.08 and 105.14 eV assigned to $\text{Hg } 4f_{7/2}$ and $\text{Hg } 4f_{5/2}$, respectively (Hg^{2+}). This may indicate that the Hg is embedded in the polymeric chain.

Figure 4C shows the XPS spectra produced from the reaction of modified polymer CS-CPD with Cr(III) . Two peaks for Cr (figure 4C) centred at 577.28 and 586.95 eV were resolved for the $\text{Cr } 2p_{3/2}$ and $\text{Cr } 2p_{1/2}$ peaks, respectively, and assigned to the Cr(III)–O bond. Thus, structure B (scheme 2) was assigned as the complex product.

Figure 5A shows the high-resolution XPS spectra of the Ca 2p core levels. Two peaks were seen, identified as Ca $2p_{1/2}$ and Ca $2p_{3/2}$, in the order of increasing binding energy. Ca $2p_{3/2}$ at 347.3 is a typical binding energy of the Ca^{2+} ion. The narrow and sharp peaks indicate that Ca is connected with O [30,31]. Structure B (scheme 2) was assigned as a reaction product.

The Ni 2p region (figure 5B) has complex multiple split peaks. The Ni $2p_{3/2}$ main peak and its satellite at 855.6 and 862.5 eV, and the Ni $2p_{1/2}$ main peak and its satellite at 874 and 880, respectively, are assigned to the Ni–O bond. Structure B (scheme 2) was assigned as a reaction product.

The Co 2p peak (figure 5C) has significantly split spin-orbit components. The presence of Co–O could demonstrate two peaks located at binding energies of 781 ($\text{Co } 2p_{3/2}$) and 796.6 ($\text{Co } 2p_{1/2}$) eV. Two-satellite Co–O peaks are observed at binding energies of 804.6 eV for $\text{Co } 2p_{3/2}$ and 796.7 eV for $\text{Co } 2p_{1/2}$. The peak at a binding energy of 802 eV may be assigned to the Co–N bond [32]. Structure A (scheme 2) was assigned as a reaction product.

3.4 Ion selectivity

A mixture of nine metal salts was treated with modified polymer films. The ICP-OES measurements for the blank

Figure 8. SEM images with 10,000 magnification: (A) CS-CPD; (B) CS-CPD-Pb; (C) CS-CPD-Hg; (D) CS-CPD-Cr; (E) CS-CPD-Ca and (F) CS-CPD-Fe complexes.

solution and the solution after 24 h treatment with different films were carried out. The differences refer to the metal uptake value. The ICP-OES measurements before and after treatment and the percentage of the metal uptake are shown in table 1 and are computed according to equation (1). Atomic absorption measurements for a mixture of the modified polymers, CS-CPD with a mixture of metal nitrate, $M = Pb^{2+}, Hg^{2+}, Ca^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}$ or Ni^{2+} before and after treating with the polymer are also presented in

table 1. The polymer selectivity order of the modified polymer, CS-CPD can be arranged as follows:

$$Hg > Co > Pb > Ca > Ni > Fe > Cr.$$

It is clear from the data that the highly selected ions by CS-CPD are Hg^{2+} (91.89%), Co^{2+} (91.73%), Pb^{2+} (91.43%) and Ca^{2+} (90%). The high selectivity of the Hg ion may be due to the fitting of the Hg ion with the chelating centre. In a

Figure 9. SEM images with 10,000 magnification: (A) CS-CPD-Ni and (B) CS-CPD-Co.

comparative study, the metal uptake of the modified CS showed more uptake than that of CS in the case of Hg, Pb, Co and Ca. A little difference was observed in the case of Ni, Fe and Cr about 1–1.5% more.

3.5 Metal ions determination in Gulf water

The use of the modified polymer for the Gulf ocean water analysis showed that the CS-CPD could uptake various metal ions (such as Na, K, Mg, Ca, Co, Ni, Cu, Cd, Pb, Fe and Hg) from the Gulf ocean water. The Cu, Ni, Fe, Hg and Co ions were measured in $\mu\text{g l}^{-1}$, while Na, K, Mg and Ca ions were measured in mg l^{-1} . The ICP-OES measurements before and after treatment and the sorption percentage of the chelating polymer are presented in table 2 and are calculated according to equation (1).

3.6 TGA analysis

Thermogravimetric analysis (TGA) is an easy method to study the thermal stability or thermal degradation behaviour where the weight loss of the sample is measured continuously, whereas the temperature is changed at a constant rate of $10^{\circ}\text{C min}^{-1}$. Table 3 and figures 6 and 7 show the thermal decomposition temperatures of modified CS and its complexes with different metals. The weight loss percentage for the CS and its metal complexes in the temperature $<200^{\circ}\text{C}$ were due to the loss of absorbed or adsorbed water, in addition to H-bonding in the polymeric material [33]. In the case of modified CS, the maximum loss at 275.22°C was 46.62%. In general, the weight loss increases with an increase in the temperature. The comparison of the maximum weight loss with the temperature between different metallopolymer complexes shows that the Hg-complex is the highest one and the Ca-complex is the lowest one. The remaining metal nitride is

arranged as follows:

$$\text{Hg} > \text{Co} > \text{Pb} > \text{Cr} > \text{Fe} > \text{Ca} > \text{Ni}.$$

The temperature, weight loss and residual percentages are indicated in table 3.

3.7 Morphology and structures

The change in the surface morphology may be due to the introduction of the metal ions in the polymer matrix or CS modification. SEM was carried out to confirm the chelation of the metal ions with the modified polymer, in addition, to study how the change in surface occurred. The morphologies of modified CS and polymer metal complexes with different metal ions are shown in figures 8 and 9 with 10,000 magnifications. CS shows a smooth surface, while CS-CPD-Pb, CS-CPD-Hg and CS-CPD-Cr showed dramatic surface changes. This means that the chelation mostly occurred on the surface of the polymer. On the other hand, the smooth surface may be due to the penetration of the metal ion and stronger embedding of metal ions in the matrix of the polymer than the others. Figure 8A shows the SEM micrograph of CS-CPD. The modification with 3-chloro-2,4-pentanedione makes a little change in the surface as compared to the CS surface. The SEM micrograph of the CS-CPD-Pb complex (figure 8B) shows a dramatic change in the surface as well as after metal complexation was generated which confirms the formation of the metal complex in agreement with the XPS data. The surface has a regular cubic shape. The SEM micrograph of the CS-CPD-Hg complex (figure 8C) seems to be clear as it appears from a non-uniform growth of the complex at different places on the surface. The SEM micrograph of the CS-CPD-Cr complex (figure 8D) shows an extreme change as compared with that of the CS-CPD surface. Magnification at 10,000 is very specific as its shape seems to be like tubes. The SEM micrograph of CS-CPD-Ca shows a uniform surface with a little change

Figure 10. EDS analysis for CS-CPD-Hg, CS-CPD-Cr and CS-CPD-Fe.

as compared to CS-CPD (figure 8E). Figure 8F shows the SEM micrograph of CS-CPD-Fe complex. Black spots which seem to be emitted in addition to white spots surrounded by black shades were observed. The SEM micrograph of CS-CPD-Ni shows a little change (figure 9A), while the SEM micrograph of the CS-CPD-Co complex shows a tube-shaped structure similar to that in the case of the CS-CPD-Cr complex (figure 9B).

3.8 EDX or EDAX analysis

Energy-dispersive X-ray (EDX or EDAX) is an analytical technique used for the chemical characterization of a sample. On the other hand, this technique was used for analysis and it confirms the presence of metal ions. Figure 10 shows the energy-dispersive spectroscopy (EDS) spectra of the metal complexes CS-CPD-Fe, CS-CPD-Hg and CS-CPD-Cr.

Figure 11. EDS analysis for CS-CPD-Ni, CS-CPD-Co and CS-CPD-Ca.

In addition, figure 11 shows the EDS spectra of the metal complexes CS-CPD-Co, CS-CPD-Ni and CS-CPD-Ca. The data obtained confirm the metal uptake and reveal the presence of a metal complex. The uptake of all metal ions by the polymer matrix, in addition to other atoms, was confirmed by EDS spectra.

4. Conclusions

In this study, CS was able to uptake through modification under normal conditions. The modifications carried out by the reaction of 3-chloro-2,4-pentanedione with the amino group as an active site in CS. The use of the modified CS in waste

treatment was investigated. The data showed that the modified CS was selective for some metallic ions depending on the type of chelating centres N–O and O–O. The metal ions Fe and Co preferred the N–O chelating centre, while Pb, Cr, Ni and Ca preferred the O–O chelating centre.

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