



Synthesis, characterization and applications of novel modified chitosan materials for water treatment.

El-Refaie Kenawy¹, M. A. Abu Saied^{2*}, A. A. Saafan¹, S. I. Salem¹



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¹Department of Chemistry, Polymer Research Group, Faculty of Science, Tanta University, Tanta 31527, Egypt.

²Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, City of Scientific Research and Technological Applications (SRTA-City), Borg El-Arab New City, 21934, Alexandria, Egypt.

Abstract

Five modified-chitosan based materials have been prepared and characterized. These materials comprise cross-linked, aminated, sulfated, carboxylated and sulfated-carboxylated chitosan. They were applied for both the adsorption of some heavy metals and for some anionic and cationic dyes. The extent of adsorption depends on the selectivity between the modified materials and the desired metal ion. Ag(I) was the most preferable metal ion by all modified materials whereas Cu(II) was preferable by carboxylated- sulfated chitosan. For dye adsorption, the maximum adsorption capacity depended strongly on the chemical nature of the modified material. The crosslinked and aminated materials were found to be more selective for anionic dyes whereas the sulfated, carboxylated and carboxylated-sulfated materials were more selective for cationic dyes.

Keywords: Chitosan; Modified chitosan; Heavy metals removal; Dyes removal

Introduction

Chitosan is considered a fine natural polymer that has been widely studied in several types of modifications and used for several environmental applications e. g. heavy metal removal, dye removal, and microbiological activities[1-5]. Chitosan modified with 3,4- dimethoxybenzaldehyde derivatives were used for Cd(II) removal and the highest removal efficiency was obtained in the 6.5 – 7.0 pH range[1]. On the other hand, ethylene-1,2-diamine-6-deoxy-*N*-phthaloylchitosan (PtCtsEn) and ethylene-1,2-diamine-6-deoxy-chitosan (CtsEn) modifications were tested in removal of Cu(II), Pb(II), and Zn(II) [2]. Chitosan modified graphene oxide, tetraethylenepentamine (TEPA), histidine, thioglyceraldehyde Schiff's base, polyamidoamine, diethylenetriamine (DETA), tetraethylenepentamine (TEPA) and ethylenediaminetetraetic acid (EDTA) were used for the removal of many metal ions [3, 4]. Moreover, chitosan modified montmorillonite (CTS-MMT), triethylene-tetramine modified magnetic chitosan (TETA-MCS) and diethylenetriamine-functionalized magnetic chitosan were prepared and applied for Th(IV) and U(VI) removal respectively[5-8]. The aldehyde-modified chitosan derivatives were synthesized, and the polymer efficiency for the uptake

of metal ions for both crosslinked and uncrosslinked derivatives revealed that crosslinked derivatives have a significantly larger capacity than uncrosslinked derivatives [9]. In contrast, another study revealed the crosslinked chitosan with glutaraldehyde modification has a much lower adsorption capacity than normal chitosan[10]. Chitosan modified polyvinyl amine and polyacrylonitrile-graft with diethylenetriamine were applied for the adsorption of Co(II), Ni(II) and Cr(III)[13, 14]. Pb(II), Cd(II), and Zn(II) ions were removed from aqueous solutions using the final copolymer (APANCS) [12].

Besides, chitosan and its modifications were used in dye removal from industrial wastewater. The experiments carried out for the adsorption of methylene blue dye (MB) by chitosan/ β -cyclodextrin showed that the highest MB removal was in 4–6 pH range[13, 14]. Chitosan / glutaraldehyde composite resin was prepared and cross-linked with epichlorohydrin [17]. The resultant resin was further modified with 3-amino-1,2,4 triazole,5-thiol and used for removing a Brilliant Blue R250 dye from aqueous media. Moreover, chitosan grafted with poly(methyl methacrylate) was used successfully for the anionic dye (RB19) removal[16] whereas chitosan modified bentonite, chitosan-hexadecyl trimethyl ammonium

*Corresponding author e-mail: dr.sarahsalem87@gmail.com; (Sarah Salem).

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bromide modified bentonite and chitosan-modified palygorskite were used for the removal of some other anionic dyes [17, 18].

In this work, five chitosan derivatives; crosslinked chitosan which is modified with epichlorohydrin (CS-E), sulfated chitosan (CS-S), aminated chitosan (CS-I), carboxylated chitosan (CS-MC) and carboxylate sulfated chitosan (CS-MC-S) were synthesized, characterized and used for heavy metal removal, dye removal and in biological purposes.

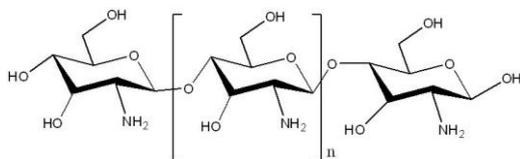
Experimental

Materials and Reagents

Chitosan (CS, M.W. 100000 – 300000), Polyethyleneimine (M.W. 60000, 50 wt% solution) and epichlorohydrin (ECH) were purchased from ACROS Organics™. Ethanol, Isopropanol, Sodium hydroxide free carbonate, acetone and chloroacetic acid were obtained from Barker Analyzed™, Fisher chemicals™ and ACROS Organics™, respectively. Other chemicals were used without further purifications.

Modification of chitosan

Chitosan is soluble in acidic solutions due to the interaction of H^+ and NH_2 , but it is insoluble at higher pH levels. It has a low solubility in organic solvents as well. Chemical modification provides a wide range of new chitosan derivatives to solve the challenges mentioned above. Graft copolymerization is an appealing strategy for modifying the chemical and physical characteristics of chitosan among the different techniques of modification. Grafting chitosan facilitates the synthesis of functional derivatives by covalently attaching a molecule, the graft, to the backbone of the chitosan. Chitosan has two types of reactive groups, scheme 1, that can be grafted: free amino groups and hydroxyl groups. [19-21].



Scheme 1. Structure of chitosan polymer.

In this work, chitosan (CS) was first treated with epichlorohydrin (ECH) as a crosslinking agent in acidic medium. The crosslinked product (CS-E) was then divided in two parts, scheme 2. The first part was treated with sodium sulphite producing sulphated chitosan (CS-S) and the second one was treated with polyethyleneimine (PEI) to increase the number of amine group producing aminated chitosan (CS-I). This was then treated with monochloroacetic acid to produce carboxylated chitosan (CS-MC). The latter

was then treated again with sodium sulphite producing carboxylated sulphated chitosan (CS-MC-S).

Synthesis of epichlorohydrin grafted chitosan, CS-E.

Four grams of CS powder was suspended in 140 ml isopropanol. Fifteen ml of epichlorohydrin dissolved in 100ml of acetone /water mixture (50ml water/50ml acetone) were then added to chitosan solution. The above mixture was stirred under reflux at 70°C for 24h. and the solid product, CS-E, was filtered off and then washed with both distilled water then ethanol respectively.

Preparation of aminated chitosan, CS-I.

The solid product, CS-E, suspended in 100 mL ethanol/water mixture was then treated with 10 ml PEI. The mixture was stirred and refluxed at 60°C for 12h. The product, CS-I, was then washed with both water and ethanol respectively.

Reaction between monochloroacetic acid and CS-I. (CS-MC)

Four grams of CS-I were immersed into 30mL of dimethylsulfoxide and vigorously stirred at 30°C for one hour to swell. The solution was then alkalinized by adding 40mL of 5 M NaOH dropwise to the mixture while stirring for 2 hours. Then, dropwise, 12 grams of mono chloroacetic acid (dissolved in 30 ml dimethyl sulfoxide) were progressively added. The CS-MC product was filtered and washed with water and ethanol, respectively.

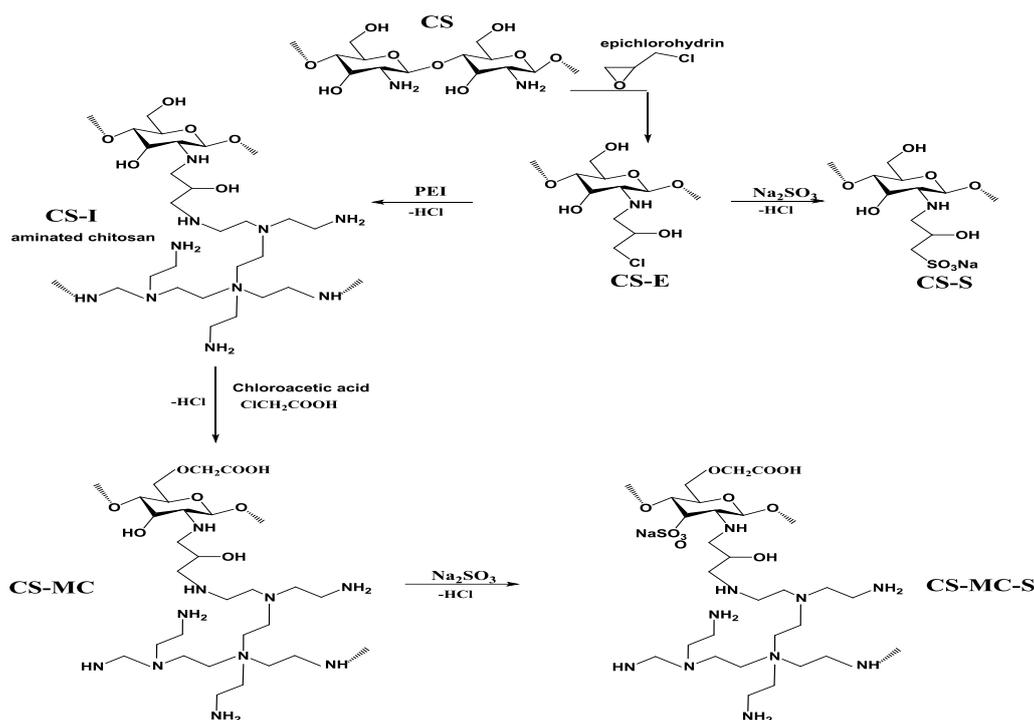
Preparation of sulphonated chitosan, CS-S and carboxylated sulphated chitosan, CS-MC-S.

Two grams of CS-E was immersed in a solution composed of 12g sodium sulphite dissolved in 200 mL water and few sulphuric acid drops were then added to the mixture. The reaction mixture was then stirred under reflux at 80°C for 4h. The product, CS-S, was filtered washed several times with both water and ethanol respectively.

On the other hand, two grams of carboxylated chitosan, CS-MC, was immersed in a solution of 12 g sodium sulphite dissolved in 200 mL water and few sulfuric acid drops were then added to the mixture. The reaction mixture was stirred and refluxed at 80°C for 4h. The carboxylated sulphated chitosan product, CS-MC-S, was then filtered and washed several times with water and ethanol respectively. The modified materials were characterised by physical tools and some physical properties are listed in table 1.

Table 1. Some physical properties for chitosan and its modifications.

Compound	Color	pH	MP °C	DP °C	IR spectra(cm ⁻¹)	Elemental analysis			
						%N	%C	%H	%S
CS	Pale yellow	7.0	220	245	3455(OH), 2877 (-CH ₂), 1645 (N-H), 1384 and 1428 (methylene).	3.49	50.13	8.32	0
CS-E	Pale yellow	4.6	200	230	3434(OH), 2877 (-CH ₃), 1384 (C-O-C), 629(C-Cl).	3.66	49.58	7.74	0
CS-S	Pale yellow	5.6	190	233	3424(OH), 2867 (C-H), 1314-1159 (S-O), 1025 (S=O)	3.97	34.94	7.65	5.45
CS-I	Pale yellow	6.5	203	250	3433(OH), 2897 (C- H),1073(C-N), 1429(amino groups)	12.61	58.72	9.94	0
CS-MC	White	7.3	223	255	3455(OH), 2878 (C- H),1420(C-H), 1617(-COOH)	14.21	59.86	13.5	0
CS-MC-S	Pale yellow	7.62	170	221	3435(OH), 2878 (C- H),600 (S=O) Stretching.	12.97	53.77	9.12	2.2



Scheme 2: Modification of chitosan derivatives

Devices and Instrumentations

Using the AD1030 professional pH-ORP-TEMP Bench Meter, the pH of the synthesized materials was controlled. The melting points and decomposition points of these improved materials were recorded with the digital melting point equipment MPS10. The modified compounds were characterized using an FT-

IR Bruker Tensor 27 IR in the region of 4000-400 cm⁻¹. APD 2000 PRO diffractometer was used to perform X ray diffraction (XRD) patterns. The CuKα (λ = 1.5405Å) X-ray beam was nickel-filtered and operated at 40 kV and 30 mA. With a rate of 2.4°/min, the scanning range was adjusted from 2θ = 2° to 30°. On the other hand, TGA analysis were recorded on

Simultaneous Thermal Analyzer (STA) 6000. SEM images were recorded by JEOL JSM-6360 LA scanning electron microscopy whereas TEM images were recorded by JEOL TEM 2100. The elemental analysis measurements were done using Elemental Analyzer (Mod.: CHNOS Elemental Analyzer ,vario MICRO, Germany). Energy-dispersive X-ray (EDX) analysis were done at acceleration volt of 15 kV.

Heavy metal adsorption

Stock solutions of [Ag(I), Cd(II), Cu(II), Ni(II), Cr(III) and Mn(II)] were prepared by dilution using deionized water from BDH grade, ICP-MULTI ELEMENT standard solution IV 1000 mg/l. The metal uptake was followed using INDUCTIVITY COUPLED PLASMA "ICP" PERKIN ELMER – OPTIMA 7000 DV. Six ml stock solution was diluted to 120 ml deionized water. Twenty ml of this solution was mixed with 25 mg of the desired adsorbent (modified chitosan's) in six different experiments for the different modifications. The adsorbed metal ions were recorded at least six times intervals[22].

Dye adsorption

Ten dyes, anionic and cationic, were chosen to test the activity of these modified chitosan as dye adsorbent. These dyes were Quinaldine Red (QR), Acid Alizarin Violet N (AAV), Sunset Yellow FCF (SY), Indigo Carmen (IC), Acid Green 25 (AG), Acid Blue 40 (AB), Methyl Violet (MV)-(2B), Acid Black B (ABK), Chromotrope 2R (C2R) and Neutral Red (NR).

Standard dye solutions of these dyes were prepared and diluted to the desired concentrations using bidistilled water. Three ml of the dye solution was placed in a three ml quartz cell and then mixed with 0.1g of the parent and modified chitosan. The absorbance was recorded using UV-Vis spectrometer were recorded on SHIMADZU-UV-1700-020 linked to an electronic temperature controller (TCC-260). The adsorption profile was recorded at different time intervals, A_t and the absorption infinity (A_∞) were recorded after 24 hours whereas the initial absorbance (A_0) was recorded in absence of the solid material[23-26].

Results and discussion

Polymer characterization

Fourier transform infrared (FTIR) spectroscopy

According to the literature survey, the absorption bands in figure 1a for the used parent chitosan agrees well with that previously reported [27-29].

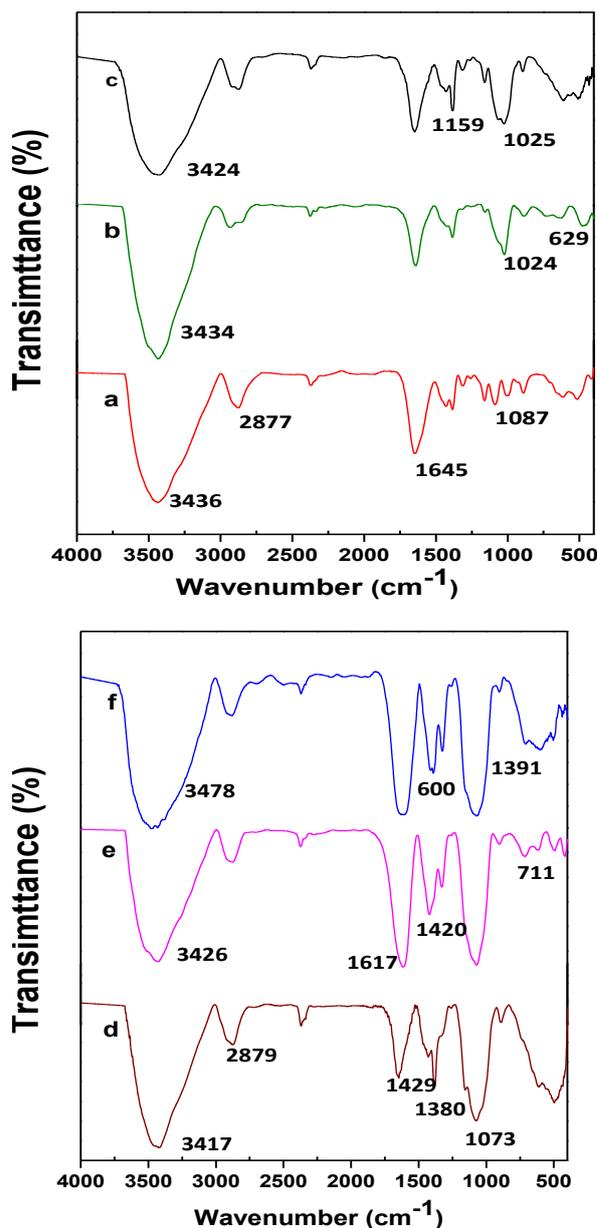


Figure 1. FTIR analysis for (a) CS (b) CS-E (c) CS-S (d) CS-I (e) CS-MC (f) CS-MC-S.

The existence of OH and NH₂ groups is indicated by broad and strong bands extending from 3200 to 3600 cm⁻¹ in Figure 1b for the crosslinking of chitosan with epichlorohydrin, which is compatible with the peaks at 1024 and 1152 cm⁻¹ assigned to alcoholic C-O and C-N stretching vibration. Asymmetric and symmetric CH₂ groups can be attributed to the peaks at 2918 and 2873 cm⁻¹. The peak at 1638 is a good example of amine deformation. The C-N stretching is represented by the peak at 1384 cm⁻¹, while the C-O-C stretching is represented by the peak at 1258 cm⁻¹. [30]. New

bands appear in the ranges of 1261–1266, 1226–1228, 1065–1074, 1001–1005, 941, 805–813, and 580–582 cm^{-1} when comparing the spectra of sulfated chitosan with Epi-chitosan (figure 1c). Asymmetric stretching of SO_2 is represented by the signals at 1261–1266, 1226–1228 cm^{-1} , while the symmetric vibration is represented by the band at near to 1070 cm^{-1} . The C-O-S stretching vibration is responsible for the band around 800 cm^{-1} , while SO_2 deformation appears around 580–582 cm^{-1} [31]. Many authors have noticed a band at 1000 cm^{-1} in the spectra of chitosan sulphate they have prepared.[31-33] It doesn't matter if the replacement is in carbon or nitrogen. A sulphate group can be assigned to this band. Figure 1d shows the emergence of new absorption bands at 1073, 1380, and 1428 cm^{-1} , as well as the sharpness of the band at 2880 cm^{-1} , when comparing FTIR spectra of CS-I and CS-E. This information could be attributed to the formation of more amino groups on the modified polymer which was missing on CS-E polymer. The disappearance of the (C-Cl) peak absorption band shows clearly that the macromolecules of PEI have been introduced to the structure of CS-E forming CS-I.

Figure 1e clearly demonstrates the appearance of new bands at 711 cm^{-1} and 1306 cm^{-1} as well as the disappearance of an absorption band at 1380 cm^{-1} . The band at 1420 cm^{-1} assigned for the O-H stretching vibration whereas C-H bending vibration represented at 711 cm^{-1} . The stretched and the sharper band at 1617 cm^{-1} represents clearly the formation of carboxylated chitosan, (CS-MC). Figure 1f represents the sulfonation of the latter compound. The C-O-S stretching vibration is responsible for the band around 800 cm^{-1} , whereas SO_2 deformation is visible around 580–582 cm^{-1} . [31].

Thermal gravimetric analysis, TGA

Table 2. Thermal degradation (remained weight %) of chitosan and its modified products.

	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	T _{1/2} /°C
CS	98%	92%	79%	43%	36%	30%	23%	17%	363
CS-E	97%	95%	58%	42%	33%	28%	25%	22%	354
CS-S	97%	95%	68%	50%	44%	38%	32%	25%	413
CS-I	97%	95%	68%	49%	42%	37%	30%	23%	400
CS-MC	97%	92%	73%	53%	44%	31%	19%	10%	434
CS-MC-S	98%	95%	79%	63%	57%	49%	39%	31%	592

Scanning electron microscopy (SEM)

One of the most effective techniques for studying surface phenomena of prepared materials is the scanning electron microscope (SEM). Figure 3 shows the SEM images recorded for chitosan and its modified materials. Inspection of these images clearly reveals

Both figure 2 and table 2 represent the curves and values of thermal degradation of chitosan and its modified products recorded from 50°C to 800°C at heating rate of 10°C/min. According to these results chitosan and its modified products showed few different thermal degradation patterns in each case. The degradation of all samples revealed that the degradation mechanism on nitrogen is so simple and mostly it is a one or two step reaction [34]. For example, the first step starts at 50°C with a weight loss of 8% whereas the second stage starts at 280°C and reaches a maximum at 390°C with a weight loss of 38%. [35]. Other values can be easily shown on table 2. Regarding these results, it was clear that the modified polymer, CS-MC-S, has a greater thermal stability compared to the other modified products as well as the parent polymer where the order of thermal stability can be arranged as follows; CS-MC-S > CS-MC > CS-S > CS-I > CS > CS-E. By calculating the T_{1/2} of these polymers clearly approves that the modification is slightly increased the thermal stability comparing to the parent polymer chitosan, Table 2.

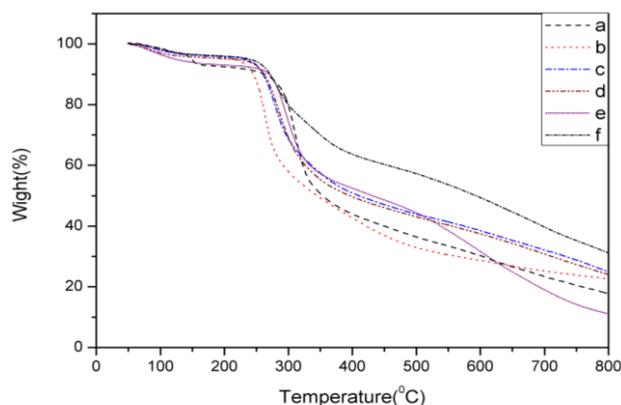


Figure 2. TGA analysis for (a) CS (b) CS-E (c) CS-S (d) CS-I (e) CS-MC (f) CS-MC-S.

that the morphology of chitosan changed upon treatments. Chitosan, figure 3a, that showed a smooth surface in homogeneous shape of scales (like in fishes) with some dark and bright area is changed to a smoother wider surface with the disappearance of scales when treated with epichlorohydrin, figure 3b. In addition, the compound CS-S showed the appearance of a folded cracking surface, figure 3c. On comparing,

figures 3 b with 3d, a very soft silky layers in spinning shape were observed. For the carboxylated chitosan (CS-MC), figure 3e, a different morphology was obtained with more layered and smoother shape as well as small cracks in the middle were appeared. The carboxylated sulphated compound, CS-MC-S, become

much more homogeneous and much smoother with appearance of small bright scales, figure 3f. Therefore, the changes in morphology upon chemical modifications generally means new compounds were formed.

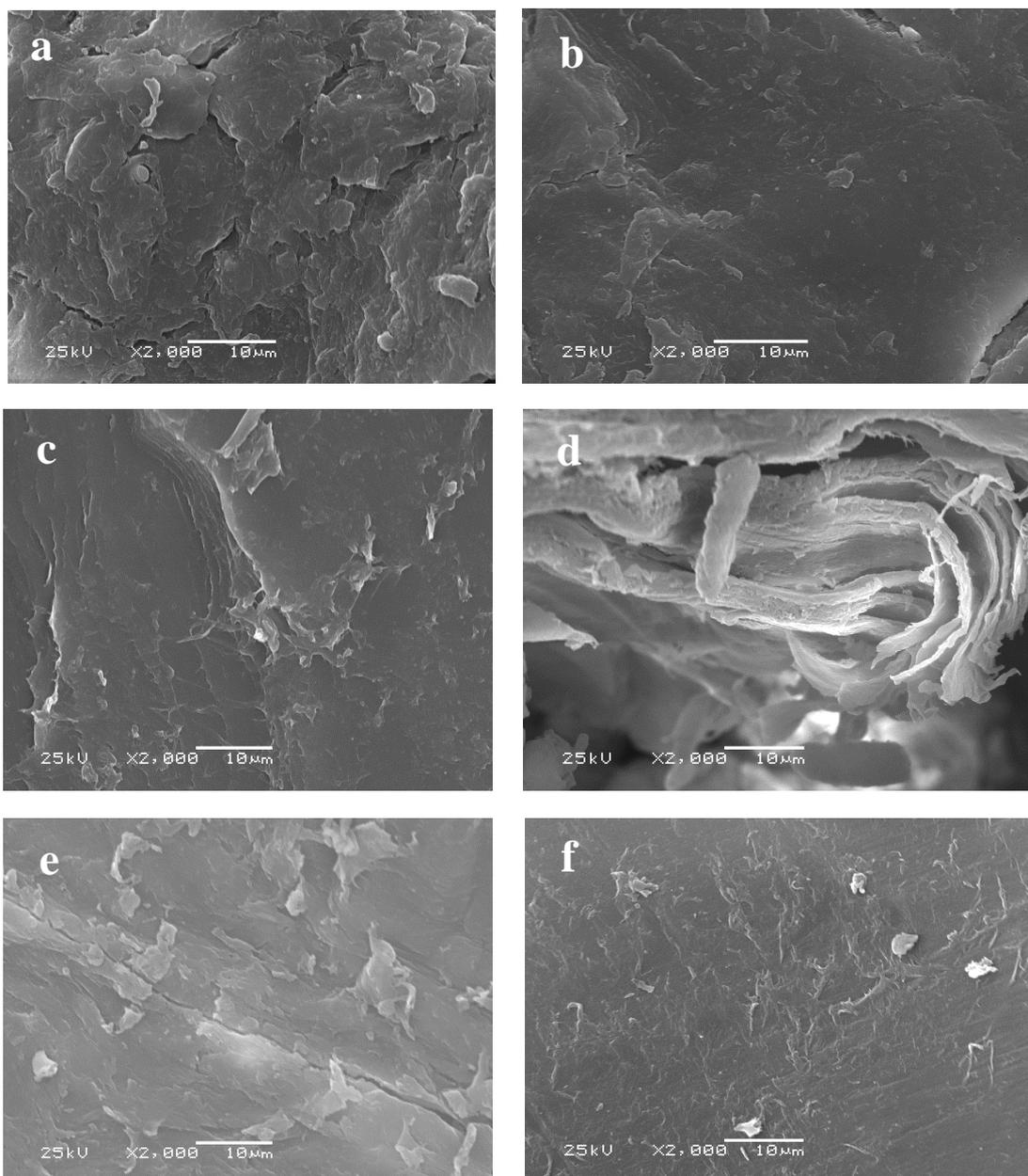


Figure 3. SEM micrographs for chitosan polymer and its modifications (a) CS (b) CS-E (c) CS-S (d) CS-I (e) CS-MC (f) CS-MC-S.

Transmission electron microscopy (TEM)

The particle shape and particle size of chitosan samples were determined using a transmission electron microscope, TEM. The graphs recorded for chitosan nanoparticles represent a solid and consistent

structure, and they were spherical with some diagonals in shape with a size ranged between (80nm) and (200 nm) diameter. However, after modifications processes, the modified compounds still showed the nano size molecular structure with some changes in its

size and shape. In addition, some modified compounds showed a much decrease in molecular size compared to the parent chitosan for example CS-MC, figure 4e.

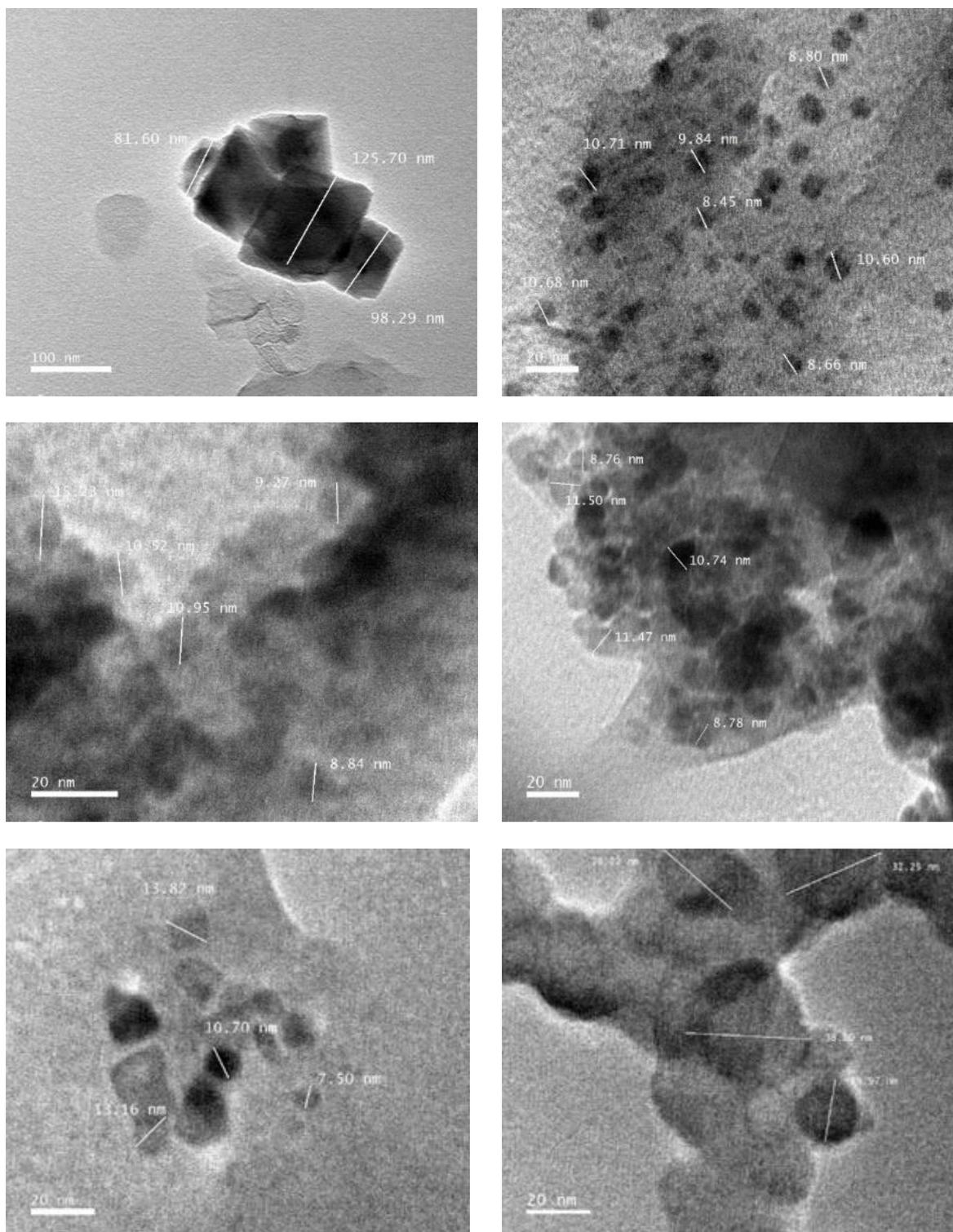


Figure 4. TEM micrographs for (a) CS (b) CS-E (c) CS-S (d) CS-I (e) CS-MC (f) CS-MC-S at (20 nm) magnification.

Elemental analysis

The elemental analysis data listed in table 3, clearly suggest the formation of the new materials. The appearance of sulfur for compounds CS-S and CS-

MC-S confirmed the sulfation processes. Moreover, the increase in the nitrogen content of the last three compounds, on the other hand, confirmed the amination processes.

Table 3. The elemental analysis of chitosan and its modification.

Polymer	N%	C%	H%	O%	S%
CS	3.49	50.13	8.324	37.54	0
CS-E	3.66	49.58	7.747	31.21	0
CS-S	3.97	34.94	7.651	38.11	5.445
CS-I	12.61	58.72	9.948	11.36	0
CS-MC	14.21	59.86	13.54	12.93	0
CS-MC-S	12.97	53.77	9.122	16.48	2.195

Energy Dispersive X-Ray Analysis (EDX)

EDX, is an x-ray technique used to identify the elemental composition of materials [36]. EDX spectrum analysis for Chitosan and its modifications approved the success of the modifications, and the results of the elemental composition are listed in table 4, and plotted in figure 5. Therefore we can easily compare the masses concentration percentages in chitosan and its modifications. The presence of peaks for the following elements: carbon, chloride, nitrogen, oxygen, and sulfur, with varying intensities related to their concentration in chitosan and its modifications, can be seen in the results. However, the sulfur's characteristic peaks emerged exclusively in CS-S and CS-MC-S, showing that the synthesis process was successful.

Table 4. Elementary EDX analysis for Chitosan and its modifications

Polymer	C	N	O	S	Cl
CS	53.4	16.2	30.4	-	-
CS-E	54.2	9.4	16	-	20.4
CS-S	47.3	17.5	21.5	13.7	-
CS-I	42.72	14.95	42.33	-	-
CS-MC	36.3	33.1	30.6	-	-
CS-MC-S	40	16	23	21	-

X-ray Diffractometry (XRD) analysis for chitosan and its nanocomposites

The characterization of crystalline material can be determined using X-ray diffraction. XRD of chitosan displays peaks at 2θ around 11.75 and 19.66. The regularity in the CS structure was attributed to presence of NH_2 and OH groups, that formed strong inter and intra molecular interaction. By modification for chitosan no new bands were observed indicating the bands grafting didn't affected the structure, figure

5. By careful inspection we notice that only in case of CS-MC and CS-MC-S the two prominent crystalline beaks are still seen but the beak at 19.66 became more broad indicating less crystallinity state, and that the packing was slightly distracted. It was reported that the ionic crosslinking of CS affected the crystalline structure and the native packing of CS was destructed[37].

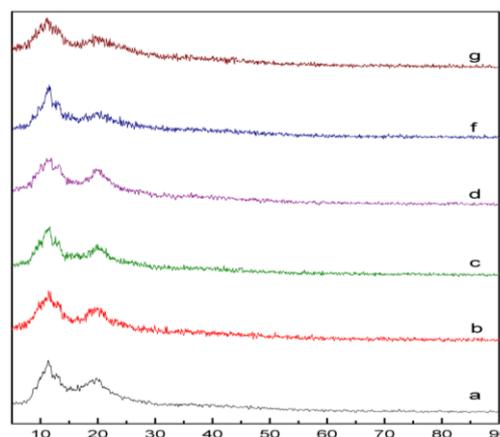


Figure 5. XRD analysis for chitosan and its modifications.

Applications

Two of the water treatment applications have been used and analyzed on this research, heavy metal adsorption and dye adsorption were tested against chitosan and its modifications.

Heavy metals adsorption

Adsorption of metal ions with modified chitosan

Many economic and environmental issues have benefited from the good metal binding characteristics of chitosan derivatives with improved sorption capacity and selectivity [38,39]. With our modified

chitosan materials, the percentage adsorbed vs. time adsorption curves were recorded for Cd(II), Cu(II), Ag(I), Ni(II), Cr(III), and Mn(II) at room temperature using batch method, figure 6.

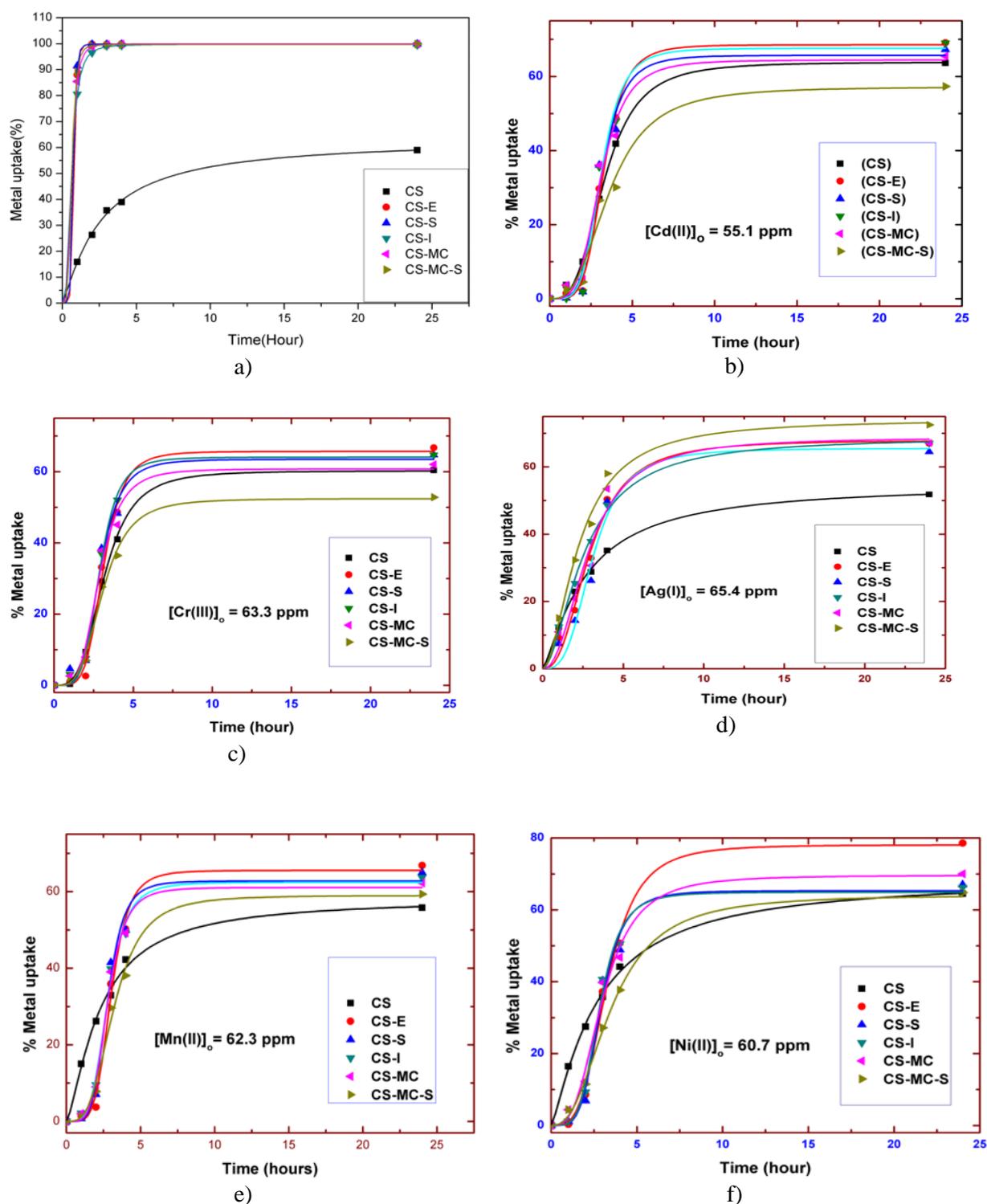


Figure 6. The removal efficiency of some metal ions using chitosan and its modified products.

The maximum adsorption equilibrium for all modified materials was observed for the adsorption of Ag(I)

ions compared to the other materials, table 5. Moreover, the adsorption of Cd(II) ions is preferable by CS-E and CS-I whereas the adsorption of Cu(II) ions is preferable by CS-MC-S which has a lower affinity for adsorption of Cr(III) ions. Cr(III) ions, on the other hand, has almost similar adsorbability power showed by the other four modified materials. This adsorbability is slightly greater than the parent

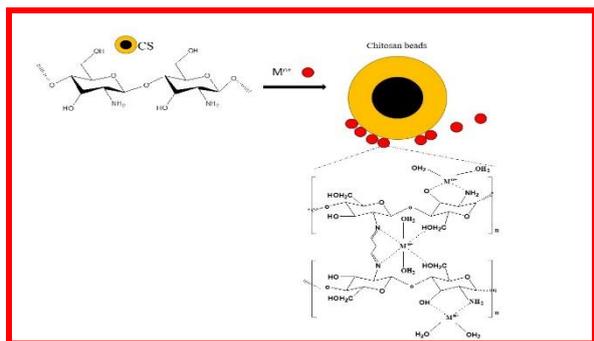
compound, chitosan. Moreover, manganese (II) ions were better adsorbed by all modified materials ranged from 60.5 – 66.9% which was still better than that with chitosan itself. In addition, the adsorption of Ni(II) ions by all modified materials was slightly better compared to Mn(II), Cu(II), Cr(III) and Cd(II) and greater than chitosan except for CS-MS-S which is similar to parent compound.

Table 5. The maximum amount adsorbed of metal ions mg / g by the prepared materials.

Sample	Ag(I)	Cd(II)	Cr(III)	Cu(II)	Mn(II)	Ni(II)
CS	34.6	28.0	30.5	27.1	27.8	34.1
CS-E	58.6	30.4	33.3	35	33.5	34.2
CS-S	58.5	29.6	32.7	33.7	33.4	32.2
CS-I	58.2	28.8	32.7	32.9	31.8	32.2
CS-MC	58.5	30.4	31.3	35.1	34.1	32.2
CS-MC-S	58.5	25.2	26.7	37.9	29.6	30.96

Inspection of table 5 demonstrates that the materials treated with epichlorohydrin and sulfated materials are generally having greater adsorbability with all metal ions compared to the parent compound chitosan. Also, aminated materials (treated with polyethyleneimine) and carboxylated one (treated with mono chloric acid) have also the same behavior except for nickel(II) ions. The carboxylated and sulfated chitosan showed a better adsorbability for Ag(I), Cu(II) and Mn(II) ions whereas lower adsorbability for Cd(II), Cr(III) and Ni(II) ions. Therefore, from the data depicted in table 5 it is clear that there is no general trend controlling the order of adsorbability. However, we can conclude that there are some selectivity factors which controlling the interaction between metal ion and the support or in other words between the support and the specific metal ion[38-40]. Silver ions, for example, have a great and almost equal selectivity for all the modified materials compared to the parent compound, chitosan. Cadmium (II) and Cr(III) ions also have similar selectivities with all materials except for carboxylated- sulfated chitosan, CS-MC-S. However, this last material showed a better selectivity for Cr(III) ions over the other materials even chitosan and lower selectivity for Ni(II) ions, Moreover, the chitosan and the first four modified materials showed similar selectivity for Ni(II) ions whereas the last modified materials, CS-MC-S, showed a lower selectivity. Metal ion sorption can occur by one of three mechanisms: ion exchange, metal ion coordination, or reduction, depending on the nature of the metal ion and the structure of the functional substituent in chitosan derivatives.[41,42]. It could be possible that the three mechanisms work whether separately or together with the different materials and different metal ions. Since one of these mechanisms is based on electrostatic interactions between the metal and the modified

materials, so the pH of the solution will affect the sorption process [43,44]. For our modified materials, the solution pH was varied from one material to another, table (1). One of the most important parameters impacting the adsorbability value is the pH of the solution, which determines the degree of protonation. Therefore, lower pH values will increase the competition between metal ions and hydrogen protons for sorption sites[43]. This in turns reduce the efficiency of the sorption process in some cases. The protonation degree of chitosan amino groups and the charge of metal ions dictate the optimal pH value for sorption. [42]. Even so, certain other aspects will play a role. For example, it has been reported that increasing the number of electron donor nitrogen atoms in the macromolecule through crosslinking and increasing sorption capacity and selectivity by introducing more functional moieties will increase the number of electron donor nitrogen atoms in the macromolecule, which will assist the coordination mechanism for sorption in some circumstances.[41,45,46]. Other factors such as ionic radius and the valance state of metal ions could be also effective. The net result for sorption efficiency will be affected by all these factors leading to the variation in adsorbability listed in table 5. Similar results were reported for sorption of some heavy metal with some chitosan derivatives [47,48]. The adsorption processes can be visualized as in scheme 3.



Scheme 3. Schematic representation for the adsorption of metals using chitosan derivatives

Adsorption of dyes with modified chitosan

The adsorption of dyes by chitosan and its modified materials was the subject of many investigations because their hazardous environmental effects [16,49,50]. The adsorption experiments comprise both anionic and cationic dyes. Figure 7 represents the removal efficiency of some dyes used in this study using chitosan and its modified products. The maximum removal efficiencies were calculated after 24 hours and listed in table 6. Inspection of this table reveals that chitosan can adsorb these dyes in a good capacity and in some cases these capacities were greater than 80%. This was due to the high number of functional amines and hydroxyl groups in the compound [51-53].

Dye adsorption

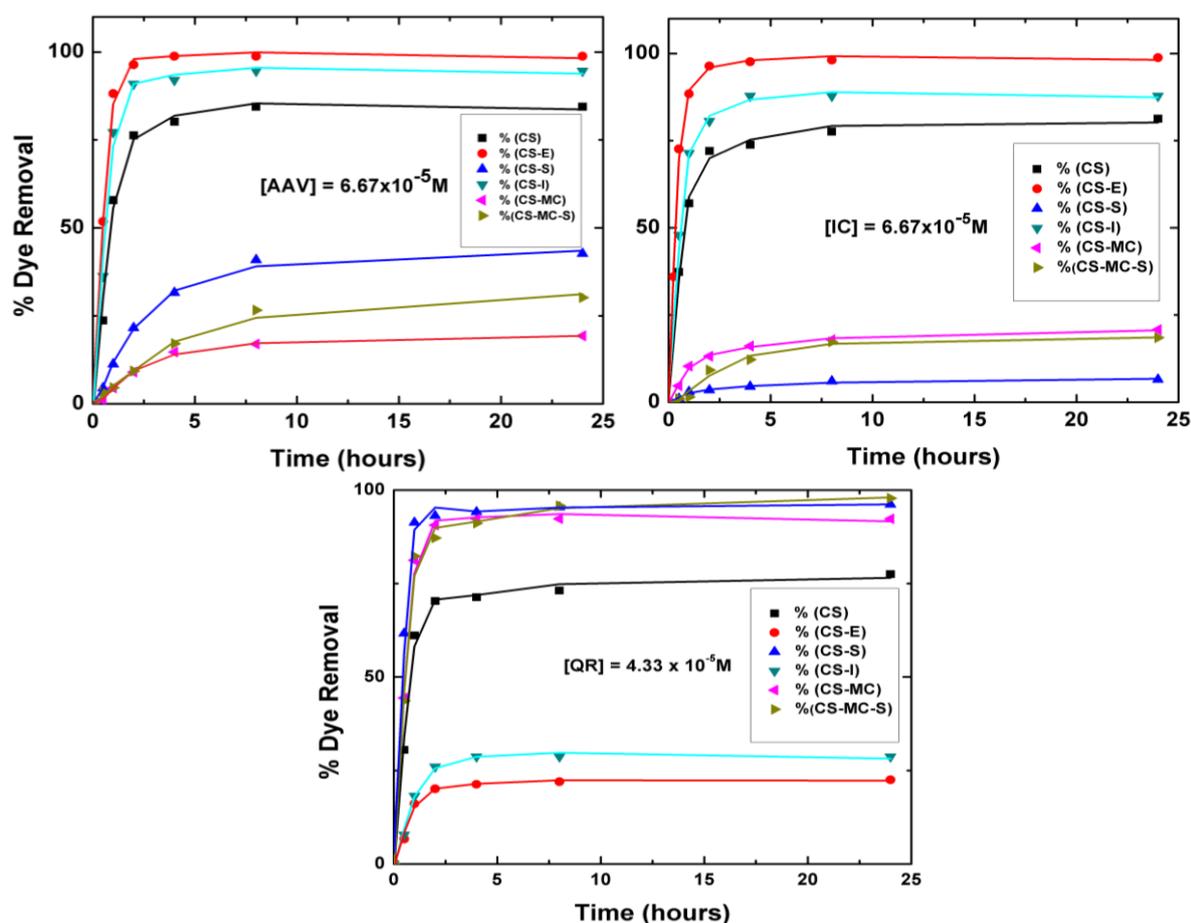


Figure 7. Dye removal percent versus time for the adsorption of Acid Alizarine Violet (AAV), Indigo Carmin (IC) and Quinaldine Red (QR) using chitosan and its modified products at 25°C.

Table (6). Dye removal using chitosan and its modified derivatives

Type	Dye	% Removal					
		CS	CS-E	CS-S	CS-I	CS-MC	CS-MC-S
Anionic dyes	Indigo carmine (IC)	81.1	98.8	6.52	87.8	20.8	18.5
	Acid green (AG)	78.1	96.2	22.82	92.5	26.2	26.9
	Acid alizarine violet (AAV)	84.4	98.8	42.7	92.3	19.3	30.2
	Sunset yellow (SY)	61.2	99.2	7.9	96.1	38.3	41.52
	Acid black (ABK)	82.5	85.7	64.5	91.8	50.1	44.2

	Acid blue (AB)	80.1	94.4	47.12	88.2	20.1	34.3
	Chromotrope 2R (C2R)	57.2	99.8	30.5	97.82	16.6	28.6
Cationic dyes	Quinaldine red (QR)	77.5	22.5	96.16	28.6	92.3	97.8
	Methyl violet (MV)	72.1	34.1	98.1	42.5	94.6	88.2
	Neutral red (NR)	67.2	75.2	87.8	91.8	88.4	92.3
	pH	7.0	4.6	5.6	6.5	7.3	7.62

In addition, results in the same table demonstrate that the adsorption capacities of modified chitosan vary according to the type of adsorbent, type of the dye and the pH of the external solutions. For anionic and anionic azo-dyes, the epichlorohydrin cross-linked chitosan has much better adsorption power compared to the parent polymer. Despite the fact that the crosslinking of chitosan with epichlorohydrin reduces its adsorption power [54], another factor which is the pH of the external solution played a good role. This pH is equal to 4.6 which is acidic and therefore can easily protonate both amino and hydroxyl groups in crosslinked chitosan. This, in turn, will increase its adsorption power through electrostatic interactions between the anionic dyes and protonated adsorbent because the pK of chitosan is 6-7 [14,54]. Aminated chitosan, on the other hand, was found to adsorb anionic dyes strongly compared to chitosan. This can be easily attributed to the increased amino groups due to amination. Besides the slightly acidic solution (pH=6.5) will also facilitated the protonation of amino groups $-^+NH_3$ and therefore the electrostatic attraction with anionic dyes[55]. Contrary to this manner, sulfated, carboxylated and carboxylated sulfated chitosan have much lower adsorption capacities compared to chitosan due to the electrostatic repulsion between negatively charged anions table (6). The result also indicated that cationic dyes were adsorbed successfully by sulfated, carboxylated and carboxylated sulfated chitosan. This can be attributed to the increased electrostatics attraction the negativity charged anions on the adsorbents and cationic dye molecules. For ECH- crosslinked and aminated chitosan, the adsorption power decreased significantly because of electrostatic repulsion between these adsorbents and the dye especially in slightly acidic medium in case of CS-I and to the crosslinkage effect in case of CS-E. The higher adsorption capacities record for neutral red may be attributed to some other kinds of interactions between anthracene based dyes and adsorbents and/or to selectivity factors. The adsorption kinetics were tested for pseudo first order, pseudo second order and intraparticle diffusion and the results correlate very well with pseudo first order kinetics according to the equation, $\ln [Dye]_t = -kt + \ln [Dye]_0$, figure 8. Where $[Dye]_0$ and $[Dye]_t$ are the initial concentration and the concentration at any time t respectively. The pseudo first order rate constants

were evaluated from the slopes of the straight lines and found to be in the range of $(0.8-1.5) 10^{-2} \text{ min}^{-1}$.

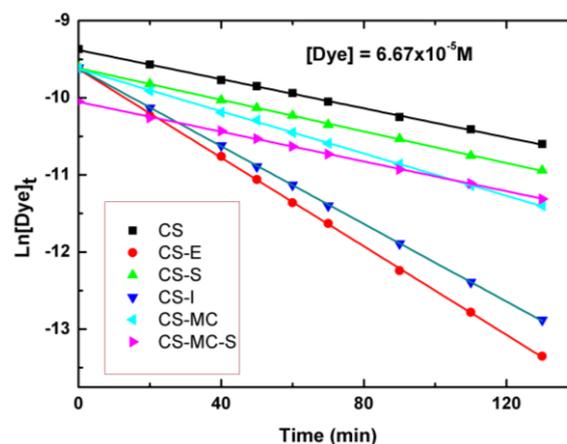


Figure 8. Pseudo first order plot for the adsorption of some organic dyes using chitosan and modified chitosan at 25°C.

Conclusion

In this study, five novel sorbents have been modified from chitosan. The obtained results conclude that CS, CS-E, CS-S, CS-I, CS-MC and CS-MC-S exhibited significant adsorption power for both heavy metals and organic dyes. Also, Ag(I) ions have the strongest sorption capacity by all modified materials compared to other metal ions. Moreover, anionic dyes are strongly adsorbed by CS-E and CS-I whereas cationic dyes are strongly adsorbed by CS-S, CS-MC, and CS-MC-S. The sorption kinetics correlate very well with the pseudo first order kinetics. The advantageous of using these materials as adsorbents are low cost of preparation and low toxicity as well as their good efficiencies.

Conflicts of interest

We would like to declare that there is no conflict of interests regarding this manuscript.

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