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Advanced low-swelling chitosan/graphite oxide-based biosorbents

George Z. Kyzas [a,b,c,*], Dimitrios N. Bikiaris [a], Eleni A. Deliyanni [b]

[a] *Laboratory of Polymer Chemistry & Technology, Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*
[b] *Laboratory of General & Inorganic Chemical Technology, Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*
[c] *Department of Petroleum and Natural Gas Technology, Technological Educational Institute of Kavala, GR-65404 Kavala, Greece*

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ABSTRACT

The effect of graphite oxide (GO) addition on cross-linked chitosan (CSG) and its grafted with carboxyl groups derivative (CSGA) was examined in the present study, mainly in the swelling behavior of the biopolymers. The achieved equilibrium and kinetic experiments presented differences in swelling results, supporting the advantage of GO addition to CS, suggesting a possible application in adsorption columns. Characterization techniques were additionally applied in order to examine the morphology of the reaction product. XRD patterns revealed the GO exfoliation upon reacting with carboxyl-modified CSG.

1. Introduction

Chitosan (CS) is a multifunctional polymer, which has primary and secondary hydroxyl groups, as well as highly reactive amino groups. It has been extensively used as an environmental-friendly biosorbent material for removal of heavy metals, dyes, pharmaceutics and other contaminants from wastewaters [1–3]. However, CS and its derivatives present a high swelling percentage, which is undesirable when these are used for industrial applications in columns. If a potential biosorbent presents a high swelling degree, it will be practically useless for real industrial-scale application despite its "hypothetical" high adsorption capacity. For this reason, in the present study low-swelling neat and grafted with carboxyl groups chitosan was prepared, appropriate as biosorbents and followed by the functionalization with GO layers. GO has multiple oxygen-containing functional groups (carboxyl, hydroxyl, epoxy) which could be covalently attached to its layers resulting in a negatively charged surface [4]. Based on the above concept and given the known problem of high swelling degrees of chitosan polymers [2,5], the effect of GO addition on cross-linked chitosan (CSG) and its carboxyl-grafted derivative (CSGA) was investigated in the present study in order to prepare low swelling materials.

2. Experimental section

Materials: Commercial chitosan (CS) of high molecular weight (3.55×10^5 g/mol), degree of deacetylation 82 wt% and glutaraldehyde (GLA) as the cross-linking agent (50 wt% in water) were purchased from Sigma-Aldrich. The grafting agent used was acrylic acid and the initiator for the polymerization was potassium persulfate (supplied from Merck).

Materials synthesis: The synthesis of GO was done according to the modified Hummers method [6], while the synthesis of CSGA was described by Lazaridis et al. [2]. For the GO addition to the grafted and cross-linked chitosan (final product abbreviated as CSGA-add-GO), after the step of grafting reactions [2], GLA was added (0.05 M) and mixed with the help of a magnetic stirrer at a concentration of 1 wt% (at 25 °C for 24 h), followed by the addition of 0.3 g of GO to the solution prepared. The mixed system was stirred continuously for 90 min in a water bath at 50 °C at pH 10 and kept in water bath for further 60 min at 80 °C. The final product was washed with ethanol and distilled water in turn and dried in a vacuum oven at 50 °C. For comparison purposes, GO was also added to neat chitosan which was cross-linked with GLA and this material was denoted as CSG-add-GO. The content (mass) of GO used for the preparation of biosorbents composites (CSG-add-GO and CSGA-add-GO) was just equal to that of chitosan (CSG and CSGA).

All prepared products were ground to fine powders and finally had particle size of 95–125 μm after sieving. The final grafting percentage (GP, %) of carboxyl groups in both CSGA (~76%) and CSGA-add-GO (~71%) was determined on the basis of the

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[*] Corresponding author at: Laboratory of Polymer Chemistry & Technology, Division of Chemical Technology, Department of Chemistry,
Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece.
Tel.: +30 2310 997812; fax: +30 2310 997859.
E-mail address: georgekyzas@gmail.com (G.Z. Kyzas).

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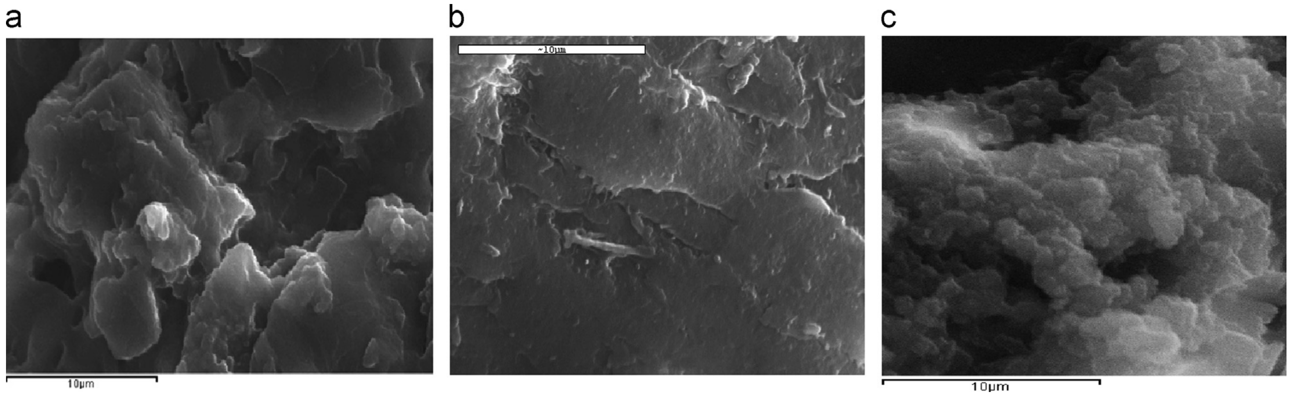

Fig. 1. SEM images of (a) GO; (b) CSGA; (c) CSGA-add-GO.

percentage mass increase of the final product relative to the initial mass of chitosan (M_{in} and M_{fin} denote the mass of CS before and after grafting reaction, respectively):

$$GP = \left(\frac{M_{fin} - M_{in}}{M_{in}}\right) 100\% \tag{1}$$

Characterization techniques: X-ray powder diffraction (XRD) patterns were recorded at an XRD-diffractometer (model Richard Seifert 3003TT, Ahrensburg, Germany) with a CuKα radiation for crystalline phase identification ($\lambda = 0.15405$ nm for CuKα). Scanning electron microscopy (SEM) images were performed with an electron microscope (model Zeiss Supra 55 VP, Jena, Germany). The accelerating voltage was 15.00 kV and the scanning was performed in situ on a sample powder. Swelling experiments (effect of contact time on swelling) were performed at pH 3. 1 g of each material was immersed in deionized water in order to be swollen for 24 h. The particles were left to be swollen, collected and measured at fixed time-intervals. The swollen samples were weighted and the swelling percentage (SP, %) was calculated by Eq. (2) (where M_t (g) is the mass of the swollen sample at time *t*, and M_0 (g) is the initial mass of the sample before swelling):

$$SP = \left(\frac{M_t - M_0}{M_0}\right) 100\% \tag{2}$$

3. Results and discussion

SEM and XRD: SEM images of the biosorbents were presented in Fig. 1. GO presented the sheet-like structure, while it showed a rougher surface after the reaction with CSGA, revealing that CSGA had been assembled on the surface of GO layers with a high density causing the GO exfoliation. CSGA clearly demonstrated a smoother morphology with some random wavy surface points. It was observed that the drying method during synthesis caused the collapse of any possible porous microstructure of CSGA, possibly due to hydrophilic interactions between water molecules and carboxyl, hydroxyl and amino groups of chitosan [2].

The XRD patterns of materials were presented in Fig. 2. In the diffraction pattern of GO, the characteristic XRD peak of GO was appeared at $2\theta = 10.9°$. The interlayer distance between the carbon layers, as determined by Bragg's law, was increased clearly from 3.36 Å for graphite to 8.11 Å due to the large amount of polar groups generated between the layers of graphite during oxidation [7], which caused an increase in the graphite's crystal lattice length along axis *c*.

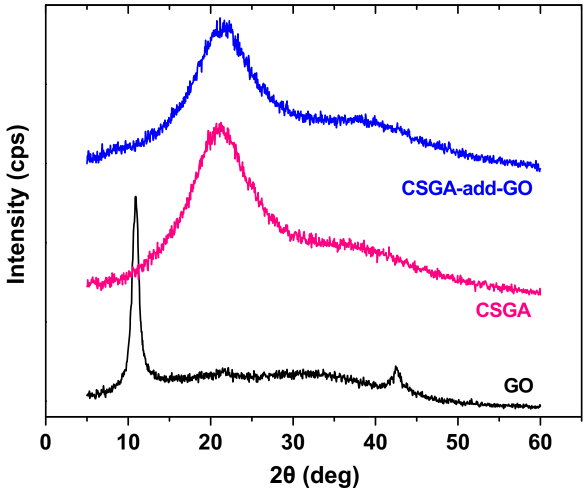

Fig. 2. XRD patterns of GO, CSGA, CSGA-add-GO.

The X-ray pattern of CSGA biopolymer exhibited one broad peak at around $2\theta = 21°$, while the crystalline peak of CS at $2\theta = 11°$ disappeared (probably attributed to the weakening of hydrogen bonding interactions between hydroxyl and amino groups of CS as a result of stereochemical hindrance of the side chains). So, it was believed that the grafting reactions were initiated. After the addition of GO to CSGA, the XRD pattern obtained a broad peak at $2\theta = 20.2°$ attributed to the amorphous state of chitosan, indicating that the amorphous-like structure of CSGA was not changed after the reaction. The presence of GO was not demonstrated. The XRD results indicated that a significant fraction of the amino groups of CS were inserted between GO layers and after an amino nucleophilic substitution reaction with mainly epoxy groups of GO [8], caused its reduction and, hence, the destruction of the layered structure. Changes in the basal spacing and exfoliation of the layered structure of GO have also been documented upon the preparation of a composite of magnetic CS and GO [9].

Swelling analysis. Equilibrium: The most interesting finding of this study was the effect of GO addition on SP of chitosan derivatives. In order to achieve biosorbents for adsorptive column-design, the SP is necessary to be low. In particular, the non-grafted cross-linked chitosan (CSG) presented SP equal to 88%. Grafting the above material with carboxyl-groups, SP was reduced to 75%, which could be explained by the existence of more functional groups (carboxyl) on the chitosan backbone, limiting/inhibiting the free entrance of water molecules into a polymeric network. The addition of GO to CSG (formation of CSG-add-GO) made a more intense reduction of SP from 88% to 58%, which