Proceedings of The Canadian Society for Mechanical Engineering International Congress 2018
CSME International Congress 2018
May 27-30, 2018, Toronto, On, Canada

PREPARATION AND CHARACTERIZATION OF GRAPHENE OXIDE CROSS-LINKED COMPOSITES

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Abstract— Graphene oxide (GO)-based materials have been studied for applications in adsorption and water treatment. Experimental results revealed that GO is a promising adsorbent due to its low-cost production, large surface area, and strong interaction with a wide range of dyes in an aqueous phase. GO chemical structure has the potential to be tuned using chemical methods such as cross-linking to produce a framework material. Therefore, in this study, cross-linking of GO structure using chitosan biopolymer as a cross-linker agent was investigated. Cross-linked GO composites were prepared through a green solution-based chemistry approach. Chemical structural, morphological and thermal changes in the cross-linked GO composites were investigated using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). Also, adsorption properties of samples were obtained using methylene blue (MB) as a cationic probe, in solution phase. According to the spectroscopy results, cross-linked composites suggested interaction between the GO sheets with chitosan through the formation of amide linkages. SEM results showed irregular layer shapes connected to each other with higher surface roughness and porosity in cross-linked samples. Changes in the thermal stability of cross-linked samples can be ascribed to the cross-linking effect. Kinetic adsorption studies indicated higher sorption capacity of cross-linked samples toward MB in aqueous phase compare to pure GO and chitosan.

Keywords ; graphene oxide, chitosan, cross-link, composite.

I. INTRODUCTION

Removal of dyes and organic contaminants originating from printing, food and pharmaceutical industries throughout the world has greatly impacted materials engineering and chemistry. Many of the dye molecules are known to be carcinogenic and can affect air and water quality resulting in various undesirable human and ecosystem health issues [1]. Among the processes used for removal of dyes and contaminants, using the method of adsorption by solid adsorbents is considered as an efficient remediation technique due to its simplicity, low-cost and possibility of recycling of the adsorbent in the adsorption process [2].

Recently, graphene and graphene oxide (GO)-based materials have been investigated as potential adsorbents for applications in wastewater treatment [3]. Graphene comprises of sp^2-hybridized carbon atoms arranged in a two-dimensional honeycomb lattice. Compared to graphene, which has a low aqueous solubility, GO is highly dispersible in organic solvents due to the presence of different oxygenated functional groups on its structure. The highly negative charge density of GO in aqueous solutions serves as an effective adsorption site for cationic dyes [3]. Thus, this material could be valuable for adsorption applications targeting cationic species in aqueous phases (such as methylene blue (MB) cation) and gas (such as N_2) capturing applications [4]. Furthermore, the chemical structure and properties of GO can be further tuned using chemical methods [5]. Fabrication of framework structures from individual GO sheets was studied using chemical interactions to fabricate GO self-assembled structures [6]. Therefore, developing a stable framework from interconnected GO layers is attractive for the successful and practical use of these materials which remains the main challenge. It was found that a GO framework structure can be achieved by cross-linking GO sheets through covalent or non-covalent bond using bio-polymers such as chitosan as a cross-linker [7]. Due to the presence of amino groups, chitosan is considered as a positively charged polysaccharide, which can strongly attract GO sheets with a negative charge through electrostatic interactions. In addition, chitosan amino groups can covalently bond to the carboxyl groups of GO to form a homogenous and well-dispersed GO composite [7]. Therefore, chitosan is an efficient cross-linker which promotes the formation of the GO composite.

This study investigates the use of chitosan as a bio-polymer to produce green GO-chitosan cross-linked composite materials. The aim of this work was to develop a GO framework material with enhanced structural and thermal stability and to evaluate the chemical structure, morphology, thermal stability, and MB adsorption properties of GO cross-linked composites with chitosan for wastewater treatment and adsorption applications.

II. EXPERIMENTAL

A. Materials

Medium molecular weight chitosan (Mw=95,0000-310,000~95% deacetylation), sodium nitride ($NaNO_3$), potassium permanganate ($KMnO_4$), sulfuric acid (98%, ACS grade), methylene blue (high purity, biological stain), hydrogen peroxide (30% v/v) were obtained from Sigma-Aldrich Canada Ltd. Graphite flake, natural, -325 mesh, 99.8% (metals basis) were obtained from Alfa Aesar Thermo Fisher Scientific.

B. Synthesis of Graphene Oxide

GO was synthesized from graphite flakes using the modified Hummer's method [8]. Briefly, 100 mL of concentrated H_2SO_4 was added into a 500 mL flask filled with 4 g of graphite in an ice bath, followed by the addition of 2 g of $NaNO_3$ and stirred for 4 h. Then, 12 g of $KMnO_4$ was gradually added while the mixture was stirred for 2 h. The ice-bath was then removed, and the system was heated at 35°C for another 30 minutes. Subsequently, 240 mL distilled water was slowly added to the system and continued to stir for another 30 minutes. Then 160 mL of water and 30% v/v H_2O_2 were added to terminate the reaction. The solution was stirred overnight and purified using multiple washing with millipore water, HCl (30 %) and ethanol until it reached pH~7. After multiple washings, the solid GO was vacuum-dried at 40°C to obtain completely dried GO powder.

C. GO-Chitosan Cross-Linked Composite Preparation

Preparing of the GO-chitosan composite materials was carried out by preparing the GO solution with a concentration of 1 mg/mL. Also, 1% w/v chitosan solution was prepared by dissolving 5 g of chitosan in 500 mL of 1% v/v glacial acetic acid. The resulting chitosan solution was added dropwise to the GO solution with continuous stirring for about 4 h. The mixture was neutralized to pH~ 7 followed by stirring for 12 h. The precipitate was separated from the supernatant via medium-speed centrifuge (5000 rpm) followed by washing with millipore water and drying at ambient temperature for 48 h. Separately, pure GO solution with concentration of 3 mg/mL was also prepared for comparison purposes. The resulting composites were ground in a mortar and pestle followed by sieving through a 40-mesh sieve. An outline of the experimental procedure is illustrated in Fig. 1.

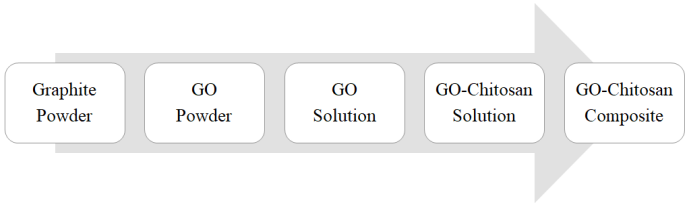

Figure 1. S*ynthetic procedure for GO-based composite materials.*

D. Measurements and Characterization

Fourier transform infrared (FTIR) spectra were obtained to confirm successful oxidation of graphite by observing the appearance of different functional groups and to monitor changes in these functional groups upon cross-linking. A Bio-RAD FTS-40 IR spectrophotometer was used to obtain the IR spectra of the composite materials. The sample powder was mixed with pure spectroscopic grade KBr (weight ratio: 1:10). The FTIR spectra was obtained in reflectance mode with a resolution of 4 cm^{-1} over the spectral range of 500-4000 cm^{-1} using 71 kHz SPINAL-64 decoupling during acquisition with external reference to adamantane at δ=38.48 ppm. The surface morphology and surface topography of non-cross-linked and cross-linked composite materials were studied using scanning electron microscopy (SEM) (Hitachi Model SU8010). Images from samples were collected under accelerating voltage (3 kV). Thermal stability and decomposition temperature of the obtained composite materials were measured using a TA Instruments Q50000IR thermal gravimetric analysis (TGA) system which was operated from room temperature to 500°C at a heating rate of 5°C min^{-1} under nitrogen atmosphere.

E. Kinetic Sorption Studies of Methylene Blue

Study of the kinetics of sorption of cross-linked material with chitosan toward MB was carried out by means of the one-pot method [9], where ~100 mg of a powdered sample was added to a folded filter paper with both ends sealed before adding to the sorbate solution. The sealed filter paper was immersed in a fixed volume (250 mL) of a 5 μM MB solution. The MB solution aliquots were pipetted (3 mL) at selected time intervals and the residual supernatant MB concentration estimated by UV–vis absorbance of MB (λmax =664 nm). The kinetic uptake of pure GO, chitosan and its cross-linked composite at each sampling time interval (t) was determined using (1), where C_0 (mM) refers to the initial dye concentration at t=0, C_t (mM) is the residual amount of MB at variable time (t), V (L) is the volume of the MB solution, and m (g) is the weight of the adsorbent. C_o and C_t refer to the dye concentration at t = 0 and variable times.

$$Q_t = \frac{(C_0 - C_t)}{m} V \qquad (1)$$

To show and compare sorption characteristics of GO and its cross-linked form with chitosan the pseudo-second-order (PSO) model was used to obtain sorption parameters (such as Q_e which is the adsorbate quantity in the solid phase (mg/g)) and kinetic parameters (such as K which represents the sorption affinity constant). Kinetic isotherm profiles were obtained by plotting Q_t vs t. The PSO kinetic models (2) was used to evaluate parameters of the isotherm, where Q_e is the amount of solute adsorbed at a pseudo-equilibrium (mg/g) condition, Q_t is the amount of solute adsorbed at time t (mg/g) and K_2 is the rate constant of PSO adsorption model.

$$Q_t = \frac{Q_e^2 K_2 t}{1 + K_2 t Q_e} \qquad (2)$$

III. RESULTS AND DISCUSSION

Various GO samples were cross-linked with chitosan, where GO was obtained from graphite powder as shown in Fig. 2.

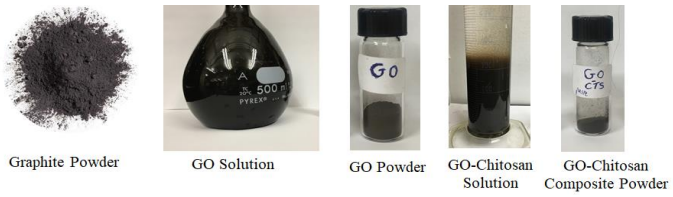

Figure 2. *Image of the produced GO-based cross-linked composite materials*

A. Fourier Transform Infrared (FTIR) Spectroscopy

Fig. 3 shows the FTIR spectra of the cross-linked composite materials versus pure GO and chitosan as precursors. Firstly, the successful GO preparation (oxidation of graphite) was validated using FTIR by the characteristic peaks located at~3200−3700 cm^{-1} ascribed to the stretching of the hydroxyl groups (O-H), ~1680-1730 cm^{-1} and 1550-1650 cm^{-1} as characteristics of the carbonyl groups (C=O) and sp^2-hybridized C=C, and the bands at~1230-1350 cm^{-1} corresponds to epoxy groups. Also, in the spectrum of chitosan, the main characteristic peaks are centred at 1650 cm^{-1} and 1590 cm^{-1}; these correspond to the C=O stretching vibration of NHCO and the N-H bending of NH_2, respectively. The presence of the peak of both precursors (GO and chitosan) are supported by similar spectral features of cross-linked composite materials. However, some bands for the cross-linked GO composites are absent or their intensity increase when compared to similar bands for the non-cross-linked GO. Formation of covalent bonds between GO and chitosan can be demonstrated by elimination of some of the original GO bands and rise of new ones. The absence of a peak at 1730 cm^{-1}, is attributed to C=O in carboxylic acid moieties in GO, and the greater intensity of the peak at 1595 cm^{-1} corresponds to the formation of covalent bond in cross-linked GO composites. This information provides support for the formation of amide linkages between GO and chitosan as the linker and is in agreement with a previous report [10].

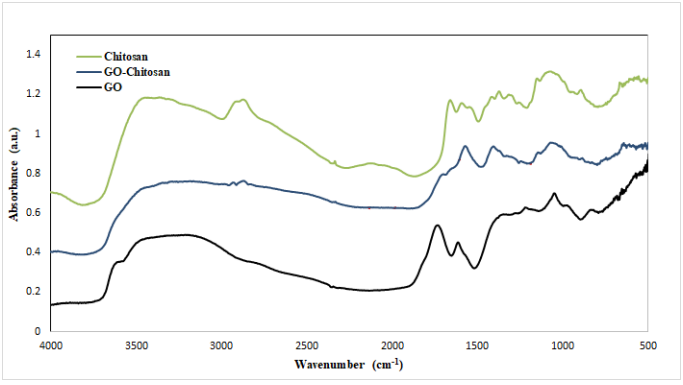

Figure 3. *FTIR spectra of the precursors and GO-based cross-linked composite.*

B. Scanning Electron Microscopy

Fig. 4 shows SEM micrographs of non-cross-linked and cross-linked GO composite materials. Fig. 4 (a) depicts graphite as a starting material, while Fig. 4 (b) is GO both made up of multiple layers stacked on top of each other. By comparison, the cross-linked GO composites Fig. 4 (c) and (d) indicate wrinkled ledges with irregular shape of layers connected to each other. The micrographs revealed that cross-linking of the GO alters its morphology and surface roughness according to the cross-linker type and content. The obtained results herein indicate the composites possess higher surface roughness and porosity when compared with pristine graphite or GO. These variations in morphological and textural changes provide support for the self-assembly cross-linking between GO and chitosan.

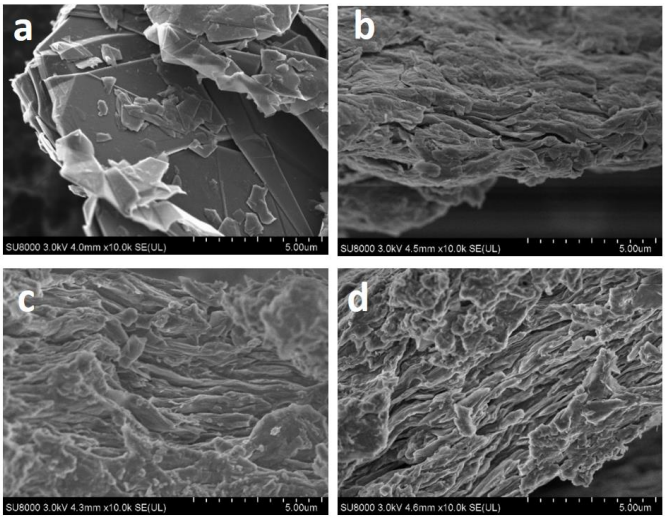

Figure 4. *SEM micrographs of graphite (a), GO (b), GO-based cross-linked composite materials (c) and (d).*

C. Thermal Gravimetric Analysis

The TGA results for the cross-linked GO composite materials are shown in Fig. 5. A rapid thermal decomposition occurred at ~200°C for GO, while the cross-linked GO displayed two thermal events at approximately 250°C, and ~455°C. These thermal events for the GO composites correlate to decomposition of GO oxygen functionalities and its framework structure, respectively. The change in the thermal stability of the cross-linked GO is due to framework effects arising from formation of covalent (amide) linkage and cross-linking with chitosan in agreement with earlier FTIR band result (Fig. 3).

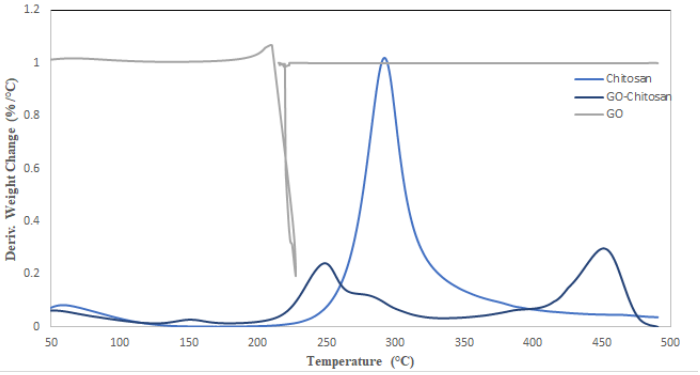

Figure 5. *TGA curves of GO and GO-based cross-linked composite.*

D. Kinetic Uptake Studies of Methylene Blue

Kinetic uptake studies of GO cross-linked chitosan systems can provide valuable insights on the reflection of cross-linking effect on adsorption properties GO composites. The surface functionality and sorption properties are affected by structural changes in the GO cross-linked material [11]. Fig. 6 presents the kinetic adsorption profiles with MB over a 240 minute interval, in which the PSO kinetic model provided reasonable fitting results. According to the obtained kinetic parameters (k and q) as listed in table 1, the GO cross-linked composite displays enhanced uptake capacity for MB which is related to the cross-linking effect. The Q_e and the PSO rate constant values (k and q) for the three sorbent materials increased upon cross-linking: chitosan (4.175) < GO (5.059) < GO-chitosan (5.107) and, chitosan (0.003) < GO (0.006) < GO-chitosan (0.019), respectively. It was shown that the intra-particle diffusion and external diffusion play an important role in the adsorption kinetics [12]. The greater kinetic uptake of the composite material recommends there are more active adsorption sites according to the increasing Q_e values as the GO becomes cross-linked. The decreasing kinetic trend of all sorbent materials suggests diffusion of MB through the pore network of the sorbent materials decreased with increasing contact time between sorbent and MB. This may be related to the decreasing number of available adsorption sites as time increases.

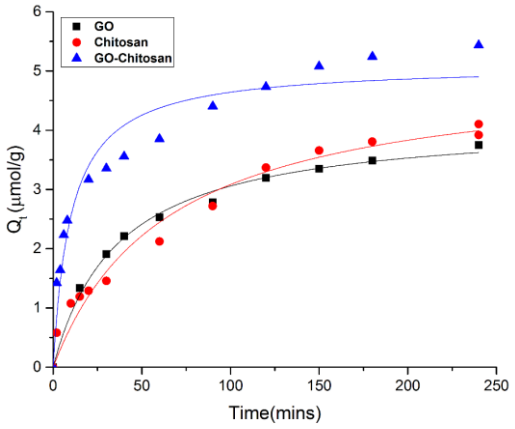

Figure 6. *Uptake kinetic profile of MB by GO and GO-based cross-linked composite material, where the fitted lines are associated to the second-PSO model (see (2)).*

TABLE 1. PSO KINETIC MODEL VALUES FOR, GO, CHITOSAN AND ITS CROSS-LINKED COMPOSITE

model	**pseudo-second order**		
equation	$Q_t = \frac{Q_e^2 K_2 t}{1 + K_2 t Q_e}$		
adj. R-Square	0.99779	0.981663	0.96183
		value	***standard error***
GO	q (mg/g)	4.17552	0.07646
	k (g mg/min)	0.00655	5.21701E-4
chitosan	q (mg/g)	5.05941	0.28235
	k (g mg/min)	0.00308	6. 54771E-4
GO-chitosan	q (mg/g)	5.10796	0.19656
	k (g mg/min)	0.01948	6.64771E-4

CONCLUSIONS AND FUTURE WORK

In this study, GO-based cross-linked composite materials were synthesized with various surface properties and morphologies that arise from cross-linking with chitosan at various compositions. FTIR was conducted on the cross-linked composites and compared to pure GO to support the formation of amide linkages. The greater surface roughness of the GO cross-linked composite materials parallel the variable morphology revealed by SEM. TGA results revealed evidence of cross-linking between GO and chitosan according to changes in the thermal stability of the composite materials. In conclusion, GO-based composites could be used as stable framework structures for potential applications in the removal of dyes and pesticides in wastewater environments.

Future testing to support this study will involve BET nitrogen adsorption to obtain information on gas sorption capacity and estimate the average pore size and surface area of samples using a Micromeritics ASAP 2020 (Norcross, GA) instrument. Also, mechanical properties of GO composite thin films will be measured by Dynamic Mechanical Analyzer (DMA) 2890.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) under the Discovery Grant (418729-2012 RGPIN). We would like to thank support and expert technical assistance of Ms. Leila Dehabadi in performing IR spectroscopy, and TGA analysis.

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