



Research article

Use of biomass sericin as matrices in functionalized graphene/sericin nanocomposites for the removal of phenolic compounds

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ABSTRACT

The removal of phenolic compounds, a group of environmental pollution even at low concentrations, by the adsorption process has attracted considerable attention around the world. Still, the choice of an adsorbent has proved to be a challenge. As a result, for the first time, functionalized graphene (FG)/sericin nanocomposites to be applied as an adsorbent to remove phenolic compounds from aquatic systems. Sericin, the by-product of the silk process, was naturally benign and economically available matrices, which used to preparation of FG/sericin nanocomposites. The FG was prepared with the reaction between graphite and maleimide, then sericin attached to FG sheets by the amidation reaction. Because of the abundance of chemically active functional groups on the surface of these FG/sericin nanocomposites have been found to be excellent for decontamination of water for phenolic compound removal applications.

1. Introduction

Biomass resources are all forms of organic materials such as plant matter, both living and in waste form, as well as animal matter and their waste products. Biomass resources are mostly classified as waste materials and dedicated energy crops. Waste material can be any urban and industrial waste material that represents a potential pollutant to the environment. Waste materials that would qualify as a biorenewable resource include agricultural residues, yard and garden waste, municipal solid waste, food processing waste, animal manure, etc. Sericin consist of 18 amino acids with active polar side groups, including hydroxyl, carboxyl, and amino groups was produced by silkworms and one of the by-products of the silk process. Furthermore, the amino acids serine and aspartic acid comprise about 33.4% and 16.7% of sericin, respectively [1]. Hence, considerable efforts have been focused on sericin for use in cosmetics, membranes, supplementary food, medical materials, and functional fibers based on the low fabrication cost and environmentally friendly [2, 3]. Thus, sericin can be used in the production of vast variety of biocomposites.

Functionalized graphene (FG) have gained considerable attentions in the field of nanotechnology. Particularly, the FG served as a momentous improver and performance increasing material in composites, also because of its high surface area, π - π interactions, excellent chemical

durability, and large scale production, can be used as a sorbent for remove environmental pollution. Based on the incorporated benefits of both the components in the nanocomposites as active materials in order to improve the sorption performance and potential, a verity of strategies has been investigated for fabricating nanocomposites of graphene materials [4].

In particular, phenolic compounds were considered as being one of the more hazardous for health risks to humans, animals, and aquatic systems. Discharge from industrial processes, some of which include oil refining, petrochemicals, pharmaceuticals, coking operations, resin manufacturing, plastics, paint, pulp, paper, and wood products, have been concerned as the significant origin of phenolic compounds in the environment. Therefore, there is essential to treat wastewater affected by phenolic compounds before release [5, 6]. Currently, several treatment approaches have been adopted to remove toxic phenolic compounds from aqueous solutions, including chemical and electrochemical degradation [7, 8], biological degradation [8], and adsorption [9]. Of the methodologies, as mentioned above, adsorption was a useful technique for the removal of phenolic compounds from aqueous medium [10, 11, 12, 13].

To the best of our knowledge, research on the preparation of the nanocomposites by FG and sericin as matrices have not been utilized. This current work was discussed in preparing a functionalized graphene

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with maleimide/sericin, abundant surface active functional groups, which were able to remove phenolic compounds that the chemical/physical interactions between sericin and functional groups of graphene contribute significantly to the adsorption of pollutants. We propose that using sericin biomass as cheap metrics for large scale production. The effect of the adsorbent dosage on the adsorption performance of the phenolic compounds was investigated. Besides, adsorption of the different phenolic compounds was evaluated. Also, the morphological, structural characteristics of nanocomposites were studied by Fourier transform infrared spectroscopy (FT-IR), field-emission scanning electron microscopy (FE-SEM), and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

L-phenylalanine (Riedel-deHaen AG, Germany), Graphite (Graphite fine powder extra pure, Merck Chemical Co), *N,N'*-Dicyclohexylcarbodiimide (Aldrich, 99%, DCC), 4-dimethylaminopyridine (Aldrich, 99%, DMAP), and all other chemical reagents and materials were supplied by Merck Chemical Co. (Germany).

Sericin powder prepared from silk industry wastewater material was obtained from Kiashahr Silk Company, Iran.

2.2. Pretreatment of sericin

Sericin protein from cocoons of *A. mylitta* silkworm was extracted as defined elsewhere. In a typical process, cocoon pieces were dispersed in 0.02 M Na₂CO₃ solution and boiled for an hour. Then, the obtained sericin proteins solution was dialyzed against water for 2 days by a cellulose membrane [14].

2.3. Preparation of functionalized graphene with maleimide

To synthesize maleimide, a formerly explained process was used [15]. Also, functionalized graphene with maleimide was prepared according to our previously described paper [16], for preparation of maleimide functionalized graphene (MG), 1.0 g of pristine graphite, and 1.0 g of maleimide (MI) was dispersed into 20 mL of 1,2-Dichlorobenzene under ultrasonic for 1 h. The resultant mixture was kept at 50 °C and maintained for 5 days. The formed MG were centrifuged, washed, and then Soxhlet extracted with ethylacetate. To prepare maleimide edge-functionalized graphene (MEG), 1.0 g of pristine graphite, 1.0 g of MI, and 500 g of stainless-steel balls were moved into a stainless-steel vessel, which degassed with charge/discharging with the argon gas. Afterward, fixed the vessel in the planetary ball mill machine, disturbed with 400 rpm for 48 h. The obtained product was Soxhlet, extracted, and washed. Then final products were dried in a vacuum oven at 80 °C for 12 h.

2.4. Preparation of S@MG nanocomposites and S@MEG nanocomposites

Prepared functionalized graphene (0.4 g) was dispersed in 20 mL of ethanol by ultrasonic for 30 min. Then DMAP (0.08 g) and DCC (0.12 g) were added to the suspension, followed by heating to 70 °C. After 30 min, the sericin solution dissolved in ethanol/water (90:10, v/v) was added to the reaction mixture, followed by continuous stirring for 3 days at 70 °C. A black precipitate of the product was collected, centrifuged frequently with water and ethanol. After refluxing by ethanol and collected, the product was dried at room temperature.

2.5. Characterization

The morphology of all composites was done by field-emission scanning electron microscopy (FE-SEM: HITACHI S-4160, Japan). X-ray diffraction (XRD) was characterized by using a Bruker, D8 Advanced diffractometer. Fourier transform infrared spectroscopy (FT-IR) spectra

were measured on a Jasco-680 (Japan) spectrometer. Thermogravimetric analysis (TGA) was characterized by a STA503 (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) in nitrogen atmosphere at the heating rate of 10 °C min⁻¹. The identification of phenolic compounds was evaluated by a Chrompack GC Model CP9001 equipped with a Varian capillary column (50 m, 0.25 mm, 0.25 μm) and FID detector. Initial temperature: 150 °C (15 min); ramp: 3 °C/min; final temperature: 290 °C (15 min).

2.6. Phenolic compounds removal

The standard stock solutions of 4-nitrophenol, bisphenol A, 2-chloro-4-nitrophenol and 2,6-dimethylphenol were prepared in 95% ethanol with a concentration of 60 mM and stored in glass-stoppered bottles at 4 °C. For the investigation of adsorbents on the removal of phenol compounds, 5 mg of the prepared adsorbents were dispersed in prepared stock solutions. The mixtures were continuously agitated on a shaker for 2 days at 25 °C. After shaking, the precipitated adsorbents were removed by centrifuge and filtration. Then, 1 μL of filtered analytes were injected into the GC inlet for analysis. For optimization of method, 10 mg, 1.0 mg, and 0.5 mg of adsorbents added to phenol stock solution with 60 mM concentration, and also phenol stock solution with 30 mM and 100 mM concentration was prepared.

3. Results and discussion

3.1. Characterization of nanocomposites

The general procedure for the preparation of S@MG nanocomposites and S@MEG nanocomposites is given in Figure 1. In the first stage, sericin was prepared by the standard method, which explained elsewhere papers [14]. In the second stage, the functionalized graphene on the surface (MG) and the edge (MEG) were used to preparation of the nanocomposites with sericin. For this purpose, the graphite with maleimide was functionalized using a solvent and a mechanical ball-mill with cycloaddition reaction, which functional groups were placed more on the surface and the edges, respectively. Then, DCC and DMAP were used to activate the carboxylic acid groups on the surface and the edges of the graphene sheets. The activation step reaction was then followed by the amidation reaction of the amino acids of biomass sericin. Finally, the prepared nanocomposites were used to remove phenol compounds.

Figure 2 shows the FT-IR spectra of the prepared materials. In the FT-IR spectra of the MIEG and MIG (A1 and B1 of Figure 2), a new two peaks could be seen around 1700 and 1639 cm⁻¹, which is typical of the C=O stretching groups of carboxylic acid and imide, respectively. Also, there are two peaks around at 3400 and 1200 cm⁻¹ regions attributed to the O-H and C-O stretching vibrations, respectively. This is suggestive of the successful functionalization process of the graphite by MI [16]. For sericin (A2 and B2 of Figure 2), the stretching vibration of C=O, bending vibration of N-H, and bending vibration of C-H are seen at 1654, 1550, and 1457 cm⁻¹, respectively [17]. In the FT-IR spectra of S@MG nanocomposites and S@MEG nanocomposites (Figures 3A3, B3), the prepared nanocomposites materials not only reveal distinctive modified graphene bands but also have the characteristic peaks for sericin. The stretching vibrations of C=O, N-H, and O-H have appeared at the FT-IR spectra of nanocomposites. These data approve the formation of the nanocomposites.

The XRD patterns for graphite, MG, MEG, S@MG nanocomposites, and S@MEG nanocomposites are presented in Figure 3. Two diffraction peaks at 26° and 10.5° are seen in the XRD pattern of MG, which could be 8.18, and 10.18 Å graphitic interlayer space, respectively, and these are characteristic of the increasing the layers' distance some of the graphite flakes (Figure 3A2). For MEG, the diffraction peak at 26° resultant to a graphitic interlayer space of 8.18 Å show a 70% reduction in its intensity compared to pristine graphite upon modification, indicating that the grafting of the functional groups at edges had an effect on the edge-expansion during ball-milling (Figure 3B2). The XRD pattern of silk

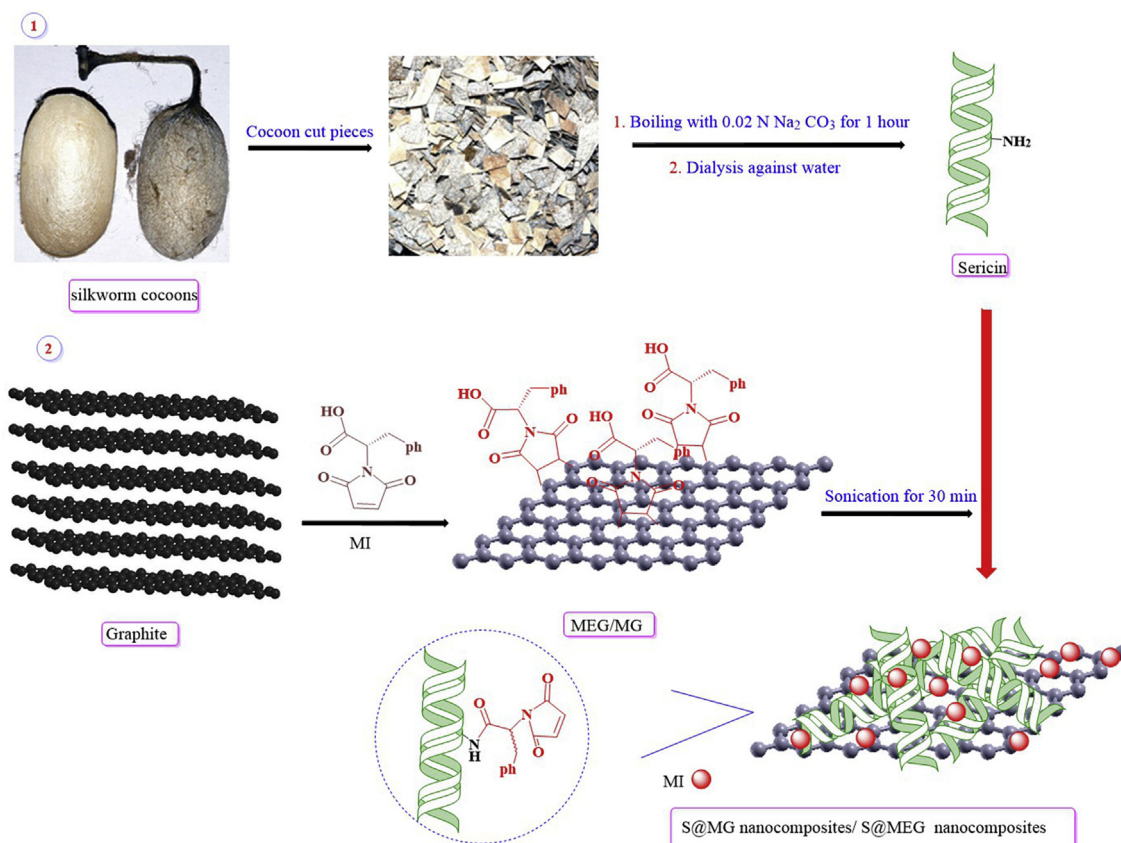


Figure 1. Schematic illustration of the formation of the S@MG nanocomposites/S@MEG nanocomposites.

sericin reveals a diffraction peak at $2\theta = 16$ and the highest diffraction peak at $2\theta = 19.2$ [18]. From the XRD patterns of S@MG nanocomposites and S@MEG nanocomposites, the peak at 26° shifted to a lower angle, which assume that grafting of sericin and increasing in the interlayer spacing of functionalized graphene, seemingly owing to π - π the stacking interaction between the aromatic ring of sericin and aromatic skeleton of

functionalized graphene and also amidation reaction between the amino acids of sericin and functionalized graphene (Figure 3A3, B3).

Figure 4 displays FE-SEM images of the MG and MEG. For the MG, layer-like morphology can also be observed (Figure 4a, b). The functionalization of graphite at the edge and surface graphene sheets led to an increase in the layer spacing of graphene sheets. According to the FE-SEM

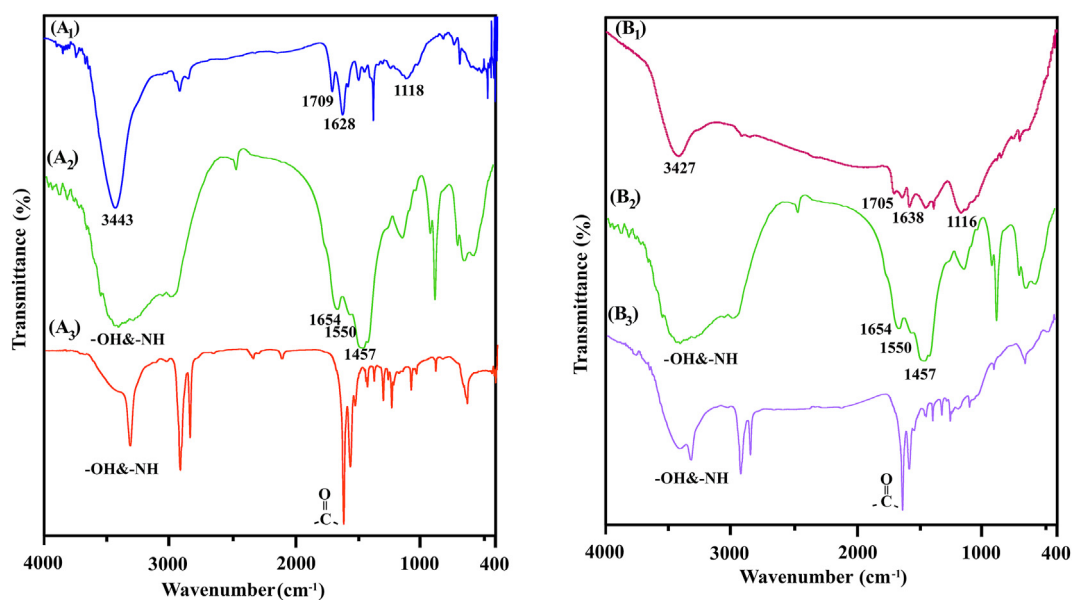


Figure 2. FT-IR spectra of (A1) MG, (A2) sericin, (A3) S@MG nanocomposites, (B1) MEG, (B2) sericin, (B3) S@MEG nanocomposites.

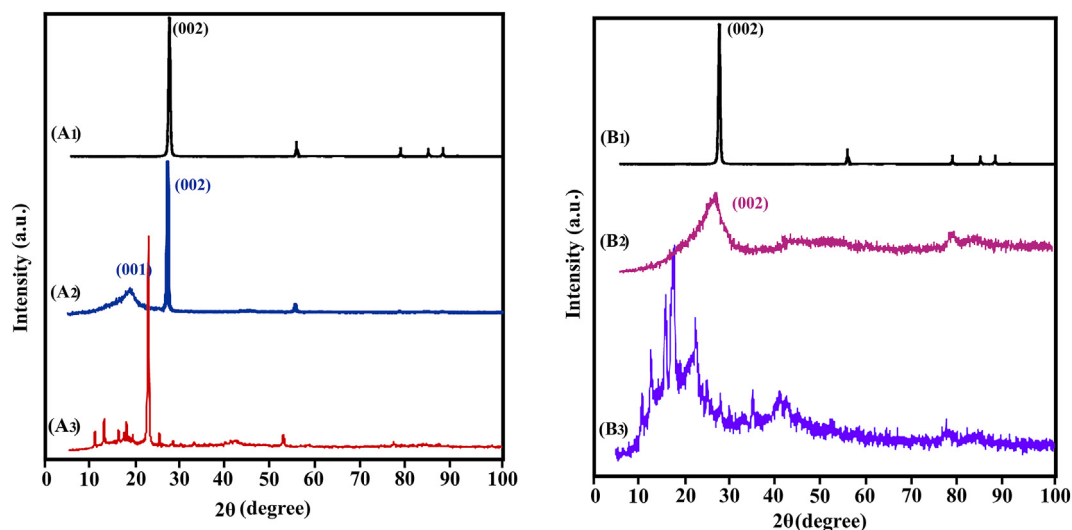


Figure 3. XRD patterns of (A1) graphite, (A2) MG, (A3) S@MG nanocomposites, (B1) graphite, (B2) MEG, (B3) S@MEG nanocomposites.

images, the grain size of MEG is mainly in the range of 0.4–0.7 μm (Figure 5a, b). After ball-milling and, as a result, edge-functionalization, decrease in the sizes of the graphene sheets. The FE-SEM images of the S@MG nanocomposites and S@MEG nanocomposites are presented in Figures 4c, d, and 5c, d, respectively. The surface morphologies of the S@MG nanocomposites and S@MEG nanocomposites show the difference from those of MG and MEG. In the case of S@MG nanocomposites, the leaf-like of sericin on the layer of graphene sheets can be clearly perceived. The FE-SEM images of S@MEG nanocomposites show that the sericin with rod-like morphology dispersed in the nanocomposites [19], may be attributed to different morphology of functionalized graphene sheets.

The TG curve for graphite, MG, MEG, S@MG nanocomposites, and S@MEG nanocomposites are shown in Figures 6 and 7. Graphite exhibited a small weight loss (6 wt%) from room temperature to 800 $^{\circ}\text{C}$, due to the removal of the introduced oxygenated species, while after modification with maleimide, this amount for MG and MEG were increased to be 30 wt% and 22 wt%, respectively. This weight losses offer

suggestion for the thermal decomposition of functional groups. A weight loss at about 250 $^{\circ}\text{C}$, which observed in the thermogram of S@MG nanocomposites and S@MEG nanocomposites, can be ascribed to the destruction of functional groups of modified graphene and thermal degradation of grafted sericin on the graphene sheets [20].

3.2. Phenolic compound removal

3.2.1. Influence of adsorbent dosage

The effect of the adsorbent dosage effect on the phenolic compound removal efficiency by the different quantities of the nanocomposites to 30 mM of phenol solution was investigated. The result showed that the removal efficiency of phenol improved when nanocomposites dosage was increased. As shown in Table 1, the maximal adsorption is attained at 0.01 g of adsorbent dosage, but the difference in adsorption for 0.01 g and 0.005 g is not significant. Consequently, the 0.005 g of adsorbent dosage was preferred as optimal conditions for the following experiments.

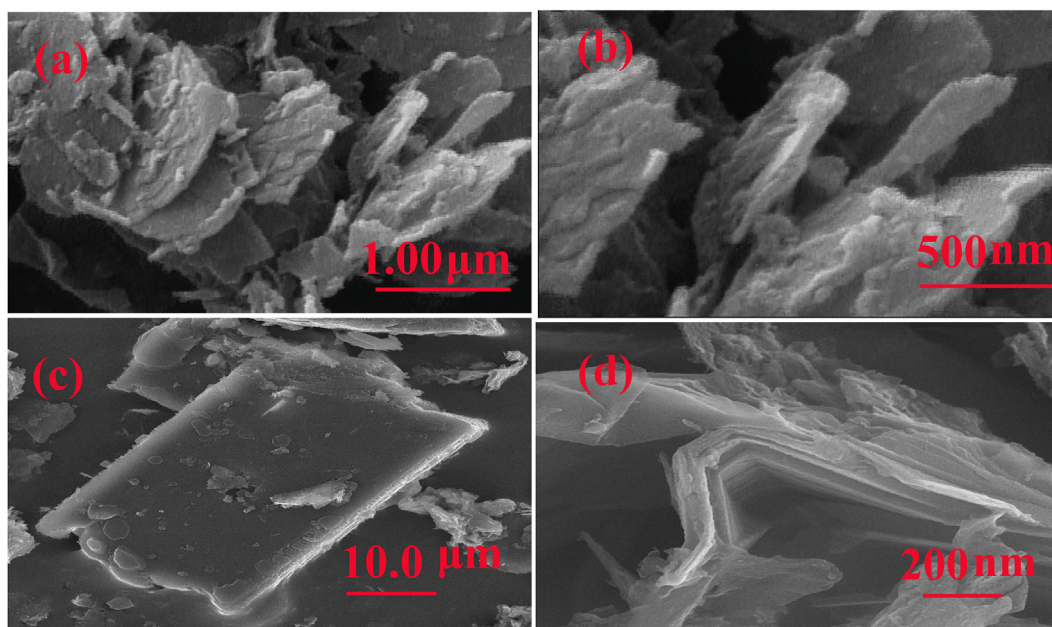


Figure 4. FE-SEM images of (a, b) MG, (c, d) S@MG nanocomposites.

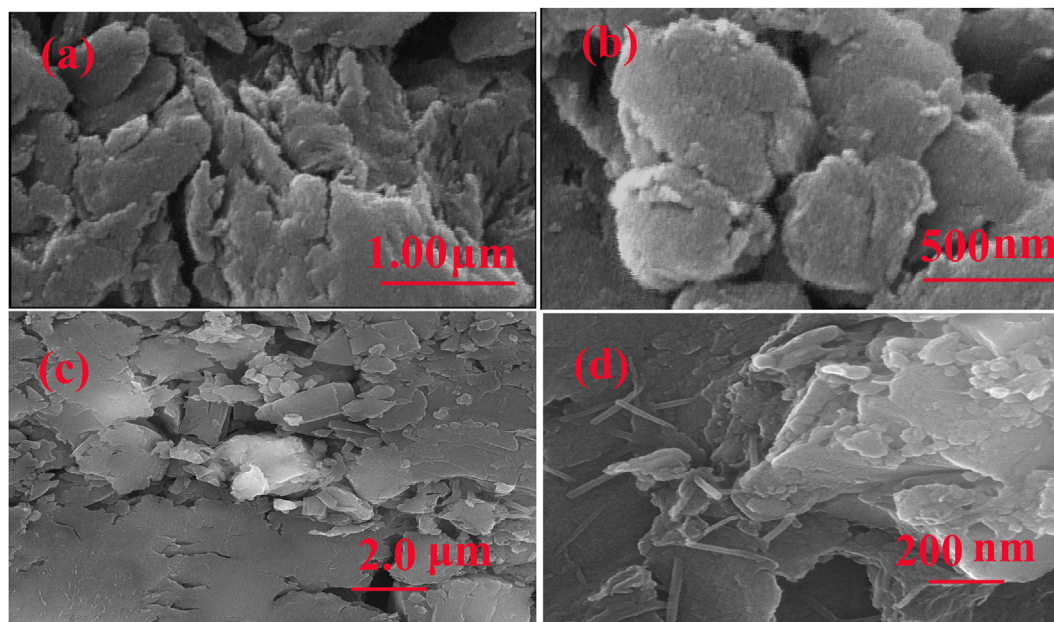


Figure 5. FE-SEM images of (a, b) MEG, (c, d) S@MEG nanocomposites.

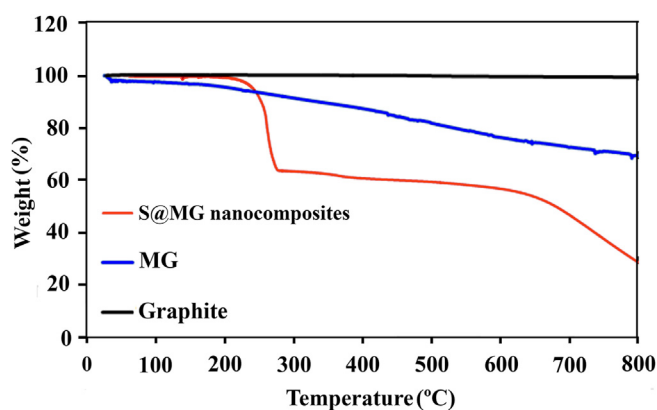


Figure 6. TGA thermograms of graphite, MG, and S@MG nanocomposites.

3.2.2. Influence of phenol concentration

To obtain effect of phenol concentration on removal efficiency, the different concentrations of phenol solution by 0.005 g of adsorbents were examined. According to Table 2, phenol sorption capacity values for 100 mM concentration of phenol was decreased. Hence, 60 mM of phenol

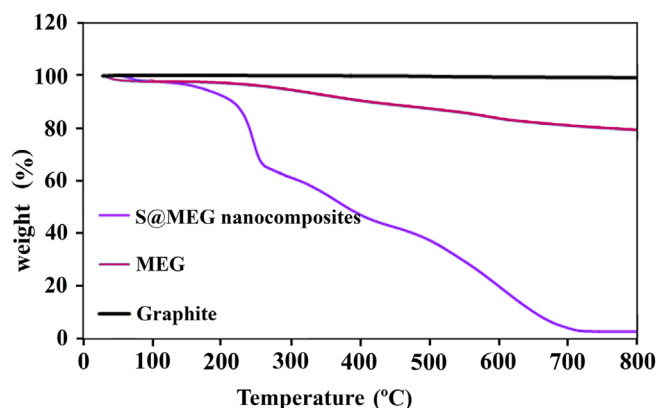


Figure 7. TGA thermograms of graphite, MEG, and S@MEG nanocomposites.

concentration was applied as an optimal state for the following experiments.

3.2.3. Adsorption behavior of nanocomposites for phenolic compounds

The capability of the prepared nanocomposites to remove phenolic compounds was examined in an aqueous medium (Table 3). Numerous phenolic compounds were utilized for the elimination of water solution. The whole removal efficiency for the nanocomposites was higher than that of modified graphene with maleimide, as explained in Table 1. The mechanisms by which pollutants are adsorbed onto carbon adsorbents may include physical adsorption, electrostatic interaction, ion exchange, surface complexation, and precipitation [21]. There is an excess of functional polar groups, including hydroxyl, amine, and phenyl, on the surface of the nanocomposites. The above-mentioned functional groups would be to π - π the stacking interaction and hydrogen bonding between the nanocomposites and phenolic compounds, which should significantly assist the adsorption of phenolic compounds on nanocomposites surface. The highest elimination efficiency was found with S@MG nanocomposites; for instance, the Bisphenol- A is two times more effective than S@MEG nanocomposites. The S@MG nanocomposites also displayed a slightly higher elimination efficiency for 4-Nitrophenol, which may be attributed to the existence of nitro groups that able to hydrogen bonding with nanocomposites. For the Bisphenol- A, the two benzene rings able to π - π stacking interaction more than other compounds, suggesting that the surface adsorption could be faster than the other compounds. In addition, the adsorption for S@MG nanocomposites more than of the S@MEG nanocomposites, which relates to the sericin, is

Table 1. Removal efficiency for phenol onto different adsorbents dosage.

Adsorbent	0.01 g	0.005 g	0.001 g
S@MG nanocomposites	99%	94%	85%
S@MEG nanocomposites	86%	56%	43%

Table 2. Removal efficiency onto adsorbents at different concentration phenol.

Adsorbent	30 mM	60 mM	100 mM
S@MG nanocomposites	96%	94%	75%
S@MEG nanocomposites	55%	56%	30%

Table 3. Removal efficiency onto adsorbents for various phenolic compounds.

Samples	S@MG nanocomposites	S@MEG nanocomposites
Phenol	94%	56%
4-Nitrophenol	96%	63%
Bisphenol- A	99%	70%
2-Chloro-4-nitrophenol	88%	56%
Dimethylphenol	43%	38%
Trimethylphenol	40%	32%

more stacked on S@MG nanocomposites in layer-to-layer sheets and increased adsorption efficiency due to coefficient of FG and sericin. These results confirm the FE-SEM analysis.

3.2.4. Regeneration of nanocomposites

To evaluate the action of the prepared nanocomposites for useful practices, the recycled ability of sorbent is an essential property. Afterward, four cycles, the removal efficiency of S@MG nanocomposites for phenol of 98%–95%, was decreased. Subsequently, renewed nanocomposites was a novel reusable sorbent and can be outstandingly employed for the phenolic compound resumption from water and wastewater.

4. Conclusions

Briefly, the sericin biomass was grafted on the surface of functionalized graphene to the preparation of FG/sericin nanocomposites. The sericin on the surface of FG has established with FT-IR, XRD, FE-SEM, and TGA analysis. The prepared nanocomposites were applied as a sorbent for the phenolic compounds from the water solution. The 0.005 g of adsorbent dosage and 60 mM of phenol concentration were preferred as optimal for conditions tests. By employing the S@MG nanocomposites as best adsorbent, 99% of Bisphenol- A removal reached the process. The obtained outcomes showed that the elimination of phenolic compounds was operative, which advocated the good adsorptive ability of nanocomposites due to rich functional groups on the surface. The current work is predictable to open up different chances in using other biomasses with numerous particles for the operative contaminant exclusion from wastewater.

Declarations

Author contribution statement

Manzar Mahmoudian: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Amir Abdolmaleki: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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