Preparation, Characterization and Properties of a Novel Electrospun Polyamide-6/ Chitosan/Graphene Oxide Composite Nanofiber

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Abstract

Chitosan (CS) is a natural biopolymer that due to its excellent properties such as biocompatibility and biodegradability is suitable for use in many applications. But, dependent on the molecular weight and other properties the electrospinning capability of CS is very weak. To solve this problem, it is recommended to blend it with a second polymer. In this work, CS/polyamide-6 (PA6) composite nanofibers were fabricated by electrospinning technique. Then different weight percentages of graphene oxide (GO) i.e. 0.1, 0.25, and 0.5 wt% were used to improve the mechanical and thermal properties of composite nanofibers. The characterization results showed that uniform nanofibers were formed by electrospinning of the PA6/CS nanocomposites blend, and the addition of GO lead to the formation of spider-web-like morphology with decreasing of nanofibers diameter. Further, the GO can improve Young's modulus and thermal degradation resistance of the PA6/CS nanofibers mat. Finally, the potential of prepared composite nanofibers was investigated for the adsorption of lead ions (Pb²⁺) in a batch system. Kinetic studies revealed that the Pb²⁺ ion adsorption onto PA6/CS/GO nanofibers mat followed pseudo-first-order kinetic, and gave the maximum adsorption capacity of 217.39 mg g⁻¹.

Keywords Electrospinning · Chitosan · Polyamide-6 · Graphene oxide · Nanofibers · Adsorption

Introduction

Polymer nanofibers have a lot of interesting features include flexibility in surface functional groups, excellent mechanical strength, and a high surface area to volume ratio [1]. Therefore, they are used in many applications including drug delivery and enzymes immobilization [2], tissue engineering [3], energy storage such as solar cells [4], water and wastewater treatment [5] such as separation [6], filtration [7], and adsorption [8, 9]. Different methods such as interfacial polymerization, drawing, template synthesis, phase separation, electrospinning [10, 11], are used to fabricate nanofibers.

However, electrospinning is the most common technique to produce nanofibers on a large-scale. It is a simple and inexpensive method to produce highly porous and nano-sized fibers with a high surface area to volume ratio. Generally, the electrospinning setup contains three main parts: a high-voltage power supply to charge the polymer solution, a needle with pumps from which the polymer solution is fed, and a collector where nanofibers are accumulated [12]. Various parameters influence the spinning of the polymer solution, including solution parameters (natural and synthetic polymer, surface tension, viscosity, and conductivity), operation parameters (flow rate, applied voltage, distance between tip and collector), and ambient parameters (humidity, temperature, atmosphere) [10]. Therefore, the properties of nanofibers can be improved by adjusting operational conditions and solution properties.

Chitosan (CS) is one of the natural polyaminosacharids that obtain by chemical or enzymatic de-acetylation of chitin from arthropod shells such as shrimp and crabs [13]. Due to the biocompatibility and biodegradability of this biopolymer, CS nanofibers are used in biological [14], biomedical [15], and agricultural applications [16]. In addition, it has a high potential for water purification by removing and adsorbing contaminants due to the presence of OH and NH₂ functional groups in its molecular structure [17, 18]. However, high molecular weight (HMW) CS has low solubility in most solvents, which limits the its electrospinning ability [19]. Generally, low molecular
weight CS tends to form beads rather than fibers. Whereas, HMW CS gives fibers with a larger average diameter [20]. Geng et al. have evaluated effect of molecular weight onto quality of CS nanofibers. They reported that only medium molecular weight CS can produce continuous and uniform nanofibers [21].

The main problem in the electrospinning of HMW CS may be due to the higher charge density of the CS molecules contains higher amino groups per molecule [22, 23]. Therefore, synthetic polymers such as polyethylene oxide [24], polyvinyl alcohol [25], and PA6 [26] are blended with HMV CS to produce uniform nanofibers. The ability to create hydrogen bonds between hydrophilic polymers and CS is one of the important reasons for choosing these polymers to obtain modified composite nanofibers [27, 28]. Pervez et al. successfully fabricated water-soluble CS (HMV)/polyvinyl alcohol composite nanofiber by electrospinning technique [29]. Also, Nirwan et al. prepared a continuous morphology of hybrid CS/polyethylene oxide nanofibers containing CS of a relatively HMV (200 kDa) [30].

PA6 is one of the most common polymers that used in fibers, films, and injectable engineering plastics [31]. The blending of PA6 with other polymers leads to improve the physical and mechanical properties due to the presence of amine and carboxyl groups [32]. Many research has been conducted on fabrication of the PA6/CS nanofiber composites [33, 34]. But the major disadvantages of synthesis/natural composite nanofiber are their low thermal and mechanical properties when blended [35]. To overcome these limitations, various reinforcing nanofillers such as GO and carbon nanotubes are used in composite nanofiber scaffolds [36–38].

GO has high surface area and oxygen-functional groups including hydroxyl, carboxyl, and epoxy groups at its sheet corners [39, 40]. Also it is noteworthy to mention that the incorporation of GO nanosheets into electrospun nanofibers increases the hydrophilicity of nanofibers and thus leads to an increase in the adsorption performance of nanofibers [41, 42]. Therefore, the content of GO in the nanofiber composite matrix could be a considerable element that determines the properties of nanofibers [43–45].

Recently, Feng et al. [46] reported the preparation of porous polyacrylonitrile/GO nanofibers by a simple one-step electrospinning process for efficient adsorption of Cr₆⁺ ions from aqueous solutions. Najafabadi et al. [47] examined the adsorption behaviors of Cu²⁺, Pb²⁺ and Cr₆⁺ metal ions from aqueous solutions using chitosan/GO composite nanofibers. In another study, Nylon-6, 6/GO nanofibers fabricated through the electrospun method and the adsorption behavior of Cr₆⁺ was investigated [48]. These studies have explored the use of GO nanofiller plays an important role in adsorption capacity of nanocomposite adsorbent in the wastewater treatment process.

In this study, PA6/CS composite nanofiber was fabricated by electrospinning method, with the aim to investigate the effect of CS content on morphological properties of nanofibrous structures. Furthermore, effects of adding GO on the mechanical properties and thermal stability of resulted composite nanofiber was studied. Moreover, the ability of nanofiber mat was investigated in the batch adsorption process of Pb²⁺ ions from aqueous medium.

**Experimental**

**Materials and Methods**

Hydrogen peroxide (35%), sulfuric acid (98%), hydrochloric acid (37%), acetic acid (99%), potassium permanganate (99%), graphite powder, and potassium nitrate (99%) were purchased from Merck. Formic acid and lead nitrate were provided from Fluka. CS powder (HMW: 310,000–375,000 Da, > 75% deacetylated) was purchased from Sigma-Aldrich. PA6 was obtained from Tehran Aliaf Company. All chemicals were in analytical-reagent grade and were used without further purification.

**Synthesis of GO**

At first, graphite is converted to graphite oxide using the modified Hummer method [49]. The amount of 0.7 g was added to 115 mL of concentrated sulfuric acid gradually. This solution stirred intensely in the ice bath. Then, 2.1 g of potassium permanganate was added slowly over a period of 45 to 60 min. The ice bath was removed, and then 230 mL of water was added to it gradually after a half hour. Afterwards, 50 mL of hydrogen peroxide was added into the solution to obtain a yellow solution. In order to neutralization, the solution was filtered and washed with water and acid. The precipitate which is known as graphite oxide was dried in the oven at 50 °C. To preparation of GO nanosheets, the prepared graphite oxide was added to distilled water, and sonicated in ultrasonic bath for 60 min.

**Preparation of Electrospinning Solutions**

CS powder was dissolved in the concentrated acetic acid gradually over several steps to provide 7 wt% CS, and then stirred for 24 h at room temperature. Then the specific amount of PA6 pellets were dissolved in the formic acid and CS solution was added to the prepared PA6 solution to obtain different weight percent (2, 4, 8, 12, 16, and 20) of CS to PA6. Thereafter, the resulting solution was stirred for 1 h at room temperature. Next step, certain amounts of ultrasonicated GO were added to the PA6/CS solution to be formed 0.1, 0.25, and 0.5 wt% of GO in the final mixture.
The final mixture was sonicated for 10 min to obtain homogeneous solutions before electrospinning.

**Electrospinning Process**

The composite nanofiber was fabricated by electrospinning machine (Fanavar Nanomeghias, Iran). To this end, all samples were loaded into a plastic syringe (steel needle, G20). The injecting rate of solutions was 0.6 mL h\(^{-1}\), and the voltage was adjusted at 25 kV. The distance between the syringe needle and the aluminum collector was 16 cm.

Thermogravimetric Analysis (TGA-DTA STA504 BAHR, Germany), was performed at a temperature range of 25–600 °C with rate of 10 °C/min in air atmosphere. The functional groups corresponding to the samples were analyzed by Fourier Transform Infrared (FTIR, Bruker spectrometer model 22 Vector, Germany). The Scanning Electron Microscope (SEM, KYKY EM 3200, China) was used for the characterization and investigation of morphological of prepared nanofibers. The average diameter and diameter distribution of nanofibers were obtained with an image analyzer (Digimizer image processing). The mechanical properties were evaluated using tensile test (SANTAM, Iran), and the point of zero charge (pH\(_{PZC}\)) was determined using the solid addition method [50].

**Adsorption Study**

The metal adsorption capacity of composite nanofibers was determined in batch experiments. Pb\(^{2+}\) ion solutions were prepared by dissolving lead nitrate in distilled water at room temperature. Adsorption experiments were performed by changing the adsorbent dosage (0.01–0.1 g), solution pH (2–7), and constant initial Pb\(^{2+}\) concentration 50 mg L\(^{-1}\), to determine the optimal adsorption conditions for Pb\(^{2+}\) adsorption. The composite nanofibers were immersed in ion solutions and all samples were continuously shacked on a shaker for 60 min. Furthermore, the adsorption isotherm and the kinetic studies were established using the various initial concentrations of Pb\(^{2+}\) (25–150 mg L\(^{-1}\)) and different contact times (5–120 min). The Pb\(^{2+}\) ion concentrations were measured using atomic absorption spectrophotometer (novAA-400 Analytic Jena, Germany). The percentage sorption and the equilibrium adsorption capacity (\(q_e\)) of Pb\(^{2+}\) were calculated using the following equations

\[
\%\text{Sorption} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

\[
q_e = \frac{C_0 - C_e}{m} \times V
\]

where \(C_0\) is the initial metal ion concentration (mg L\(^{-1}\)), and \(C_e\) is the equilibrium Pb\(^{2+}\) ion concentration (mg L\(^{-1}\)). \(V\) is the liquid volume (L) and \(m\) is the weight of adsorbent nanofibers (mg) (Fig. 1).

**Results and Discussion**

**Characterization of Electrospun Nanofibers**

**FTIR Results**

Figure 2 illustrates the various FTIR spectra of nanofibers; (a) pure PA6, (b) pure CS, (c) composite nanofibers of PA6/CS, (d) GO, and (e) composite nanofibers of PA6/CS/GO which was investigated in the range of 400–4000 cm\(^{-1}\). In the spectra of PA6 nanofibers, two branches broad peaks appear to represent the second type of −NH functional group in the range of 3200–3500 cm\(^{-1}\). Also, the peak in the 2945 cm\(^{-1}\) demonstrates the C–H methylene bond in its structure. Other peaks appear in 1571 and 1639 cm\(^{-1}\) which are related to C=O stretching and N–H vibration bonds in the PA6 structure [51]. In the spectrum of CS, the broad band in 1419 cm\(^{-1}\) belongs to −NH and −OH stretching bonds which this expansion continues from 3200 to 3600 cm\(^{-1}\). The peak in 2923 cm\(^{-1}\) is referred to stretching CH\(_2\) group. Moreover, the bands in 1570 and 1647 cm\(^{-1}\) are assigned to the first and second types of the amino groups binding of CS.
Furthermore, the FTIR spectrum of PA6/CS nanocomposites exhibits the characteristic bands at 1549 and 1645 cm\(^{-1}\). These peaks show the shift of index peaks of C=O stretching and N–H vibration bonds in the PA6 and amine peaks of CS. This displacement indicates the hydrogen bond created by the interaction of hydroxyl and amine hydrogens in the structure of both polymers [52]. Finally, the FTIR spectrum of PA6/CS nanocomposites is illustrated by interaction between these two polymers in the formation of weak covalent and intermolecular hydrogen bonds. The FTIR spectra of synthesized GO shows several functional groups. The broadband in the range of 3000 to 3500 cm\(^{-1}\) is related to the hydroxyl functional group which appears 3427 cm\(^{-1}\) that confirms the presence of trapped water molecules in the GO structure. As well as the peak at about 2924 cm\(^{-1}\) is related to the stretch vibration of \(-\text{CH}\) with sp\(^2\) hybridization. The peaks at 1742 cm\(^{-1}\) is corresponding to the carbonyl functional group. In addition, a sharp peak appears in 1629 cm\(^{-1}\) which belongs to the C=C bond of GO structure that probably overlaps with the -OH group water and appears more intensely. The peaks at 1007 cm\(^{-1}\) and 1069 cm\(^{-1}\) in the synthetic sample range confirmed the presence of stretching and bending of the C–O and C–O–C bonds. The characteristic peak at 1171 cm\(^{-1}\) indicates the stretch vibration of C=O of the alkoxy or epoxy functional groups. The presence of a sharp peak at 1286 cm\(^{-1}\) indicates the presence of a C–OH bond in the sample [53, 54]. The presence of these functional groups at the surface of GO nanosheets can increase the interaction between GO with PA6/CS in the composite matrix and can be a good reason for sufficient mechanical properties in the final product.

The peak intensity at 3400 cm\(^{-1}\) in PA6/CS/GO increased in the comparison with pristine CS spectrum. In addition, the peaks in 2937, 1643, and 1553 cm\(^{-1}\) demonstrate the vibration of C–H, C=O, and N–H related to PA6 in the nanocomposite. These displacement to the low-frequency can be attributed to the hydrogen bond between these functional groups in PA6 with CS hexagonal ring and the functional groups of GO. Another shift due to hydrogen bonding formation, belong to stretching vibration of C=O of the alkoxy or epoxy functional groups in GO from 1171 to 1169 cm\(^{-1}\) [38, 55, 56].

**SEM Analysis Results**

The SEM was employed to analyze the s morphology of nanofibers. The statistical calculations were performed by selecting 100 points in each image using Digimizer image processing software. The SEM images of 7 wt% CS solution in acetic acid are given in Fig. 3. Accordingly, only
more regular CS nanoparticles were obtained, and it is not possible to produce nanofibers by electrospinning of pure CS solution. The reason behind this is the high molecular weight of CS that affected on the viscosity, conductivity, and surface tension [21].

According to the SEM images given in the Fig. 4, nanofibers can be produced by electrospinning of the PA6/CS blend in weight percentages of 2 to 20 wt% of CS in PA6, with the common solvent (formic acid). The weight percentages of more than 20% were investigated.
experimentally. However, it was observed that by increasing the of CS, the viscosity of the polymer solution prevented its continuous flow in the electrospinning syringe and leads to the difficulty to spinning up to 30 wt% [57].

According to the SEM images in all the examined percentages, fibers with nano-sized dimensions without beads and fractures were fabricated. Therefore, statistical analysis was used in order to more accurate study. Statistical analysis can be used to determine the fiber size distribution and the evaluation of arithmetic weighted mean of fiber diameter and dispersion [58]. The calculations were carried out with help of the histogram diagram for each specimen presented in Fig. 4 and the diameter of the fibers was measured in nanometer (nm).

Arithmetic weighted mean ($\lambda_w$) and weighted standard deviation ($S_w$) are calculated as follow:

$$\lambda_w = \lambda_0 + \frac{h}{N} \sum_{j=1}^{m} u_j FC_j$$  \hspace{1cm} (3)

$$S_w = \sqrt{\left(\frac{1}{N} \sum_{j=1}^{m} (u_j^2 FC_j) - \left(\frac{1}{N} \sum_{j=1}^{m} (u_j FC_j)^2\right)\right) h^2}$$  \hspace{1cm} (4)

which $m$ is number of bins and $h$ is bin width that calculated by Eq. 5. $FC$ and $N$ is frequency count and number of statistical samples, respectively. As well as $u$ is the defined variable of Eq. 6 which in that $\lambda_C$ is the bin characteristic or bin center, and $\lambda_0$ is the dominant characteristic of the statistical
set that corresponds to the highest peak. Finally, \( Y \) is the quality loss function which briefly defines as the identifier of the second-order effect of both the weighted arithmetic mean and standard deviation as a response for optimization has been considered, is defined as Eq. 7; where the low value of \( Y \) is favorable. In other words, the lower quantity of \( Y \) is due to the smaller diameter mean and the narrower distribution of the fiber diameter [59].

\[
Y = \frac{\lambda_{\text{max}} - \lambda_{\text{min}}}{m} \tag{5}
\]

\[
u = \frac{(\lambda c - \lambda_0)}{h} \tag{6}
\]

\[
Y = \lambda_w^2 + S_w^2 \tag{7}
\]

The obtained results of the statistical calculations for each SEM image are presented in Table 1. According to this table, the diameter of nanofibers increases with increasing weight percentage of CS until 8 wt% in the PA6 matrix. As well as, in the histogram diagram the growth in the nanofibers diameter from 140 nm in pristine PA6 to 461 nm in 8 wt% CS sample along with an increasing in the nanofibers diameter distribution is observed. In Fig. 4a and f, shows the SEM images of pristine PA6 and PA6/CS 16%. As shown the thinner nanofibers with more uniformity is obtained. Further, Fig. 4c and d are corresponded to PA6/CS with 4 wt% and 8 wt% respectively, which adhesion and shrinkage in the nanofibers structure is observed. According to Table 1 and the results obtained in the range of 2–8 wt% of CS in composite nanofiber the mean diameter of the nanofibers, \( \lambda_w \) and \( S_w \) has also increased. The \( Y \) function also became larger with increasing values of \( \lambda_w \) and \( S_w \). Furthermore, The presence of CS in the solution causes the solution to be more resistant to stretching in the electric filed, and this is a reason for increasing the diameter of nanofibers [58, 60].

The diameter of nanofibers fabricated by electrospinning solution containing 12 wt% and 16 wt% of CS is reduced. According to the Fig. 4e and 3f a narrow distribution of fiber diameters is visible and consequently low values of \( \lambda_w \) and \( S_w \) were observed in Table 1. The corresponding average diameter for these mats were calculated 369 nm and 297 nm respectively. The reason behind these observations can be related to the increased conductivity of the spinning solution which overcomes the viscosity in the high CS concentration.

In this condition, with augmenting electrical conductivity the elongation of the solution increases and the fiber with less diameter is produced [61].

Figures 4g and h show that the average diameter of produced nanofibers reached to 429 nm and as well as the regular and uniform structure of them was started to be changed by further increasing in CS concentration up to 24%. While the values of \( \lambda_w \) are less than those samples with the same mean diameters (4 wt% and 8 wt%). These results indicate a better (narrow) distribution of the diameter of the nanofibers. In other words nanofibers were produced with a uniform diameter but with a high average diameter. This phenomenon can be attributed to the increase in the density of surface charge of composed jet during electrospinning with increasing CS concentration as an ionic polyelectric [57].

Based on the results PA6/CS nanofibers with 2 wt% and 16 wt% CS have good statistical characteristic. Therefore, they are suitable to selection for adding GO to fabricate PA6/CS/GO composite nanofiber. The high concentration of CS (16 wt%) was selected for further studies.

Figure 5 shows the SEM images of PA6/CS/GO electrospun nanofibers with 0.1%, 0.25% and 0.5% weight percentage of GO. Furthermore, the average diameter of nanofibers and other statistical parameters were given in Table 2. Results show that the addition of GO led to decreasing of nanofibers diameter. Further, according to the Fig. 5, it can be seen a dual morphology appears in the nanofibers when the GO concentration is increased in the polymer matrix. This morphology named spider-web-like that was reported in the electrospinning of PA6 in the presence of GO and carbon nanotubes [62, 63]. The formation of this morphology attributed to the fast solvent degradation of polymer chains caused by well dispersed GO nano sheets through the electrospinning process [63]. It can be suggested that adding the GO to the polymer matrix enhances the electrical conductivity and the instability of the Taylor cone. In these situation, due to high applied voltage, the production of electrostatic forces will be larger and jet stretching will be happen for the optimal formation of nanoweb [64]. As shown in Fig. 5a, the spider-web-like morphology and beads was observed in the nanofibers in the concentration of 0.1 wt% of GO in the polymer matrix. Furthermore, the spider-web-like morphology was enhanced by increasing the concentration of GO from 0.1 wt% to 0.25 and 0.5 wt%.

| Sample | CS (wt%) | Mean(nm) | \( \lambda_w \)(nm) | \( S_w \)(nm) | \( Y \)(nm^2) × 10^{-3} |
|--------|---------|----------|----------------|-------------|---------------------|
| A      | 0       | 140      | 142            | 31          | 21.13               |
| B      | 2       | 259      | 261            | 49          | 70.9                |
| C      | 4       | 416      | 413            | 146         | 192.3               |
| D      | 8       | 461      | 462            | 143         | 234.6               |
| E      | 12      | 369      | 370            | 99          | 146.8               |
| F      | 16      | 297      | 294            | 57          | 90                  |
| G      | 20      | 382      | 380            | 96          | 154                 |
| H      | 24      | 429      | 406            | 98          | 175                 |

Table 1 The results of the statistical analysis and calculation of the distribution of the diameter of the PA6/CS/GO composite nanofibers with different weight percent of CS
Thermal Analysis Results

TGA was used to investigate the thermal decomposition and thermal properties of electrospun nanofibers and the impact of GO on this property was investigated. The TGA thermograms of pristine PA6 nanofibers and CS, PA6/CS and PA6/CS/GO electrospun nanofibers are given in Fig. 6(1). The differential thermal analysis (DTA) also shown in Fig. 6(2). As seen as in Fig. 6(1), at first, all plot exhibits a same descending pattern between 25 and 130 °C, which is attributed to the loss of the surface-bound water adsorbed of moisture in the samples. The moisture content of the material is lost as the temperature increases, the adsorbed water is reduced, and the sample is dried. It is clear that the plot (a) correspond to PA6 nanofiber exhibits very good thermal resistance and are completely stable to the temperature range of 190 °C. After this temperature the major mass reductions are started and the nanofiber displayed a loss of weight about 10% to the temperature of about 360 °C. The subsequent step at 470 °C, 82% of the total mass is lost corresponded to decomposition of PA6’s chain. According to Fig. 6–1, 2(c), CS shows a lower thermal stability and the sample destruction started at the temperature range of about 167 °C. The subsequent step at 470 °C, 82% of the total mass is lost corresponded to decomposition of CS’s chain. The major chain degradation situated at 560 °C. After this temperature the major mass reductions are started and the nanofiber displayed a loss of weight about 10% to the temperature of about 360 °C. The subsequent step at 470 °C, 82% of the total mass is lost corresponded to decomposition of PA6’s chain. The major chain degradation situated at 560 °C. According to Fig. 6–1, 2(c), CS shows a lower thermal stability and the sample destruction started at the temperature range of 167 °C. Also, the large amount of the CS mass is completely decomposed to temperature of 370 °C. It is necessary to note that about 30% of the CS remained after the heating cycle. The TGA plots of composite nanofibers shows different behavior. Decomposition of PA6/CS composite nanofiber starts at range of 187–350 °C. Afterward, major mass loss is observed up to 480 °C and more than 85% of nanofiber is destroyed.
While, the remainder left after decomposition in this sample is about 7%. Also what is obvious is the increase in PA6/CS thermal resistance compared to the CS and the peak temperature for composite nanofibers shifted up, due to the interaction of CS with PA6.

With the addition of GO to the PA6/CS matrix, the sample degradation is performed at a higher temperature Fig. 6–1, 2(c). In the PA6/CS/GO composite nanofibers the range of first weight reduction is changed to 204–354 °C. Additionally, 80% of total weight loss at 477 °C and 8% of composite nanofibers remained after the program ended. The reason behind this, it seems the penetration of two-dimensional sheets of sp² GO in the polymer matrix helps to stronger connection between the PA6 and CS chains. Moreover, they act as a barrier against thermal decomposition and increase the degradation temperature [65]. High thermal resistance of composite nanofibers is a good rating for this composition for use in their various applications.

**Mechanical Properties**

The mechanical properties of the fabricated nanocomposite were investigated by tensile test. Tensile strength refers to fracture resistance, and is determined by stretching of a uniformly sized polymer piece. The tensile strength stress is the applied force divided by the cross-sectional area. The strain force, is the variation of the sample length divided by the initial length. The ratio of stress to strain is called Young’s modulus [66].

Investigation of stress–strain curves is one of the methods of detecting fibers from plastics and elastomers. Elastomers have little initial gradient change and change dramatically after elongation. But both plastics and fibers first show a sharp slope (high variations) until they reach the yield point or break point. Before this point, stretching is reversible. Sufficient tension is applied at this point, so the deformation then occurs, until the length becomes irreversible. Eventually the sample breaks. Therefore, by drawing the stress-tension diagram, Young’s modulus is obtained from the slope of the plot.

The stress–strain curves of the electrospun nanofibers PA6, PA6/CS, and PA6/CS/GO with different contents of GO are shown in Fig. 7. The measured mechanical properties including Young’s modulus, tensile strength and elongation at break were provided in Table 3. As can be seen, electrospun PA6 nanofiber presented a high tensile stress of 5.68 MPa, with a tensile strain of 29.94%, and the Young’s modulus of 37.4 MPa. However, the Young’s modulus of 5.3 MPa and tensile strength of 1.04 MPa with an elongation of 11.24% was observed for PA6/CS nanofibers. However,

![Fig. 6 TGA-DTA thermograms of a PA6 electrospun nanofibers, b CS powder, c electrospun composite nanofibers of PA6/CS (16%), and d PA6/CS/GO (0.5%)](image)

![Fig. 7 The stress–strain plot of a PA6 electrospun nanofibers, and the electrospun composite nanofibers of b PA6/CS (16%), c PA6/CS/GO (0.25%), and d PA6/CS/GO(0.5%)](image)

| Sample       | Tensile strength (MPa) | Elongation at break (%) | Young’s modulus (MPa) |
|--------------|------------------------|-------------------------|-----------------------|
| PA6          | 5.68                   | 29.94                   | 37.4                  |
| PA6/CS (16%) | 1.04                   | 11.24                   | 5.3                   |
| PA6/CS/GO (0.25%) | 1.11            | 10.24                   | 5.25                  |
| PA6/CS/GO (0.5%) | 1.27            | 9.67                    | 9.66                  |
Young’s modulus of 5.25 MPa and 9.66 MPa for PA6/CS/GO with 0.25 and 0.5 wt% of GO were obtained, respectively. A similar phenomena was reported in the open literatures [67, 68]. The tensile stress and strain of PA6/CS/GO nanofiber at concentration of 0.5 wt% GO increased to 1.27 MPa and 9.67, due to the high resistivity of GO. To sum up, the mechanical strength of PA6/CS/GO nanofibers was improved by increasing GO concentration in the polymer matrix.

**Batch Adsorption Experiments**

**Effect of Solution pH**

The pH is one of the influential factors in the adsorption process, since the type of surface charges, possessed by the adsorbents and the adsorbent’s ionic character affects adsorption ability to remove heavy metals. To identify the optimum pH for effective adsorption of Pb^{2+} using PA6/CS/GO (0.5%) composite nanofibers, Pb^{2+} solutions were prepared at initial concentrations of 50 mg L\(^{-1}\). Then their pH was adjusted from 1 to 7 with 0.1 M HCl and/or NaOH. The adsorbent dosage of 0.5 g L\(^{-1}\), contact time of 60 min, and room temperature were constant conditions.

As shown in Fig. 8, it can be seen that the adsorption of Pb^{2+} increases with increasing pH. However, at pH 6 a decrease in the adsorption is observed. It can be said that at acidic pH (pH 2, 3), the carbonyl and amine functional groups present on the adsorbent surface appear in positive charge. Consequently, repulsion between Pb^{2+} ions and positive charges of adsorbent might have led to the low adsorption capacity of composite nanofibers, which has been reported in other studies [69, 70]. Further investigation was carried out with help of point of zero charge (PZC) plot, the inset plot in Fig. 8. The pH of PZC for PA6/CS/GO composite nanofibers was determined 4.75 as shown in the plot. According to this plot, the adsorbent surface is positive at pHs less than 4.75 and the adsorption capacity is low due to the electrostatic repulsion mentioned between the lead ion and the adsorbent surface.

In contrast, when the solution pH is greater than 4.75 (pH > pH\(_{PZC}\)), the surface of the adsorbent has negative charge, and it is suitable for the adsorption of positive ions (pb^{2+}). On the other hand, Pb\(^{2+}\) precipitate in the form of lead hydroxide in the solution at pH above 6. The formation of hydroxylated complexes of Pb\(^{2+}\) in the forms of Pb(OH\(_2\)), Pb\(_2\)(OH\(_3\))\(^+\), and Pb\(_3\)(OH\(_4\))\(^+\) for lead ions resulted in decreasing adsorption capacities of Pb\(^{2+}\) using composite nanofibers. This phenomenon causes a problem in the adsorption study at higher pH. Therefore, further experiments and studies was performed with pH 5 [71].

**Effect of Adsorbent Dosage**

Effect of absorvent dosages on the adsorption of Pb\(^{2+}\), was investigated with 0.01 to 0.1 g of PA6/CS/GO (0.5%) at 50 mL of lead ion with initial concentrations of 50 ppm. The other operational parameters were adjusted at pH 5, contact time 60 min, and at temperature of 25 °C. The results are presented in Fig. 9 (inset). It is observed that the adsorption of Pb\(^{2+}\) increased proportionally with PA6/CS/GO (0.5%) dosage, and the highest percentage sorption was recorded by the highest adsorption dosage. The reason behind this is attributed to increased number of adsorption sites on the surface of adsorbent which are available for binding Pb\(^{2+}\) with them [72].

However, the important factor for the selection of optimum dosage is adsorption capacity. As shown in Fig. 9a, the adsorption capacity decreased by increasing the adsorbent
dosage according to the relevant equation. Therefore 0.25 g of PA6/CS/GO was selected for the further experiments.

### Adsorption Kinetics

Effect of contact time on the adsorption of Pb\(^{2+}\) onto PA6/CS16\% and PA6/CS/GO (0.5\%) composite nanofibers are shown in Fig. 10. As depicted in this figure PA6/CS/GO (0.5\%) has higher adsorption capacity in comparison with PA6/CS (16\%) electrospun nanofibers.

According to the results an increase in the adsorption rate is observed up to 20 min, and from 20 to 60 min, adsorption capacity slightly increased, and the interaction reached to equilibrium within 60 min. Due to the small difference in adsorption capacity in this interval, 40 min is selected as the equilibrium time of the adsorption process. Kinetic models including pseudo-first-order (PFO) and pseudo-second-order (PSO) models were used to describe the adsorption kinetics according to the follows equations.

\[
q_t = q_e (1 - \exp(-k_1t))
\]

\[
q_t = \frac{k_2q_e^2t}{1 + k_2q_e t}
\]

where \(q_e\) and \(q_t\) represent the adsorption capacities (mg g\(^{-1}\)) at equilibrium and any time \(t\) (min), respectively. \(k_1\) (min\(^{-1}\)) and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) are the PFO and the PSO rate constant, respectively [73]. The experimental data were fitted by PFO and PSO kinetic models and the results were summarized in Table 4. According to the experimental adsorption capacities \(q_{e,exp}\), the calculated adsorption capacities \(q_{e,cal}\), and the related correlation coefficient \(R^2\) in each of the models, it can be concluded that the adsorption kinetics of lead ions onto the PA6/CS/GO (0.5\%) composite nanofibers follows the PFO kinetic model \((R^2 = 0.996)\).

These results indicate that the adsorption velocity controlled by the diffusion process through the mass transfer layer [74].

### Plausible Adsorption Mechanism

The overall obtained results described the chemical interactions or complexed surface interactions between the surface functional groups of PA6/CS/GO and the Pb\(^{2+}\). A schematic representation possible adsorption mechanism has been shown in Fig. 11. Nevertheless, the adsorption mechanism for Pb\(^{2+}\) ions can be more complicated. Both the electrostatic interaction and surface complexation play a role and their combined effect contributed to the observed phenomenon.

The adsorption performance in the composite may be related to the nature of the adsorbent zeta potential discussed earlier. As mentioned above, pH above pH\(_{PZC}\) (4.75), the net surface charges on the nanocomposite will be negative, in which case the nanocomposite surface will have electrostatic attraction between the nanocomposites and the cations. When the solution pH value increased from 3 to 4 and 5, many of the −COOH groups on nanocomposite dissociate into the -COO\(^-\) groups. This causes the electrostatic
interaction between PA6/CS/GO and lead ions become significantly favorable or attractive and consequently resulted in the observed increase in lead ion uptake [75–77].

Furthermore, the nitrogen atoms of the amino groups in CS and the oxygen atoms of the hydroxyl groups in both CS and GO sheet can interact with lead ions. Both nitrogen and oxygen atoms have a lone pair or lone pairs of electrons that can bind Pb^{2+} through an electron pair sharing to form a complex.

**Adsorption Isotherm Studies**

In this study, the equilibrium data of Pb^{2+} ions sorption onto the PA6/CS/GO (0.5%) composite nanofibers adsorbent were investigated using two models including Langmuir and Freundlich isotherm models. The adsorption isotherms are identified by certain constants that indicate the surface properties and the tendency of the adsorbent. The Langmuir and Freundlich isotherm models assumes the monolayer-surface adsorption and heterogeneous-surface adsorption with uniform energies of active sites, respectively [78, 79]. The isotherm models can be expressed by the following equations:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} k_L} + \frac{1}{q_{\text{max}}} C_e
\]

(10)

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln C_e
\]

(11)

**Table 5** Isotherm parameters for adsorption of Pb^{2+} using PA6/CS/GO (0.5%) composite nanofibers

| Isotherm model          | Freundlich isotherm | Langmuir isotherm |
|-------------------------|---------------------|-------------------|
| Frendlich               | k_f (mg g^{-1})     | n                 | R^2      | k_L (L mg^{-1}) | q_{max} (mg g^{-1}) | R^2    |
|                         | 38.698              | 2.332             | 0.936    | 0.127          | 217.39              | 0.987  |

where \( C_e \), \( q_{\text{max}} \), and \( q_e \), are the equilibrium concentration (mg L^{-1}), the maximum capacity (mg g^{-1}), and the amount of adsorbed species per specified amount of absorbent (mg g^{-1}), respectively. \( k_L \) (L mg^{-1}) is the Langmuir constants associated to the adsorption affinity. \( k_f \) (mg g^{-1}) and \( 1/n \) are the Freundlich isotherm constants related to the adsorption capacity and intensity, respectively. The calculated parameters of isotherm models are given in Table 5. According to these results, it was found that the Langmuir model (R^2 > 0.987) fitted better than that of Freundlich (R^2 = 0.936) model and the maximum adsorption capacity of PA6/CS/GO (0.5%) nanomat was calculated 217.39 mg g^{-1}. This result confirmed the monolayer coating of lead ions onto the adsorbent as well as the homogeneous distribution of active sites on the adsorbent.

The adsorption capacity of PA6/CS/GO (0.5%) nanofibers were compared with the other adsorbent in the removal of lead ions (Table 6). It is clear that PA6/CS/GO (0.5%) has good adsorption capacity in comparison with the other adsorbents.

**Conclusion**

In conclusion, the electrospun PA6/CS/GO composite nanofibers with different weight percents of GO were fabricated successfully via electrospinning technique. The effects of various weight percentage of CS on spinnability and morphology of PA6 were investigated. The SEM results of PA6/CS composite showed that the formation of uniform and bead-free nanofibers accrued in 16 wt% of CS. The SEM results of PA6/CS/GO composite nanofibers revealed that presence of the GO in the polymer matrix causes formation of the spider-web-like structure nanofibers with smaller diameter. The TGA results proved that GO nanosheets can improve the thermal resistance of composite nanofibers. The
Young’s modulus and tensile strength of PA6/CS/GO composite nanofibers were found to increase when the GO content is increased. And showed a maximum Young’s modulus of 9.66 MPa and the tensile strength of 1.27 MPa for PA6/CS/GO (0.5%). Kinetic and equilibrium adsorption studies showed that the PA6/CS/GO (0.5%) nano mat has higher potential adsorption for Pb2+ ions with adsorption capacity of 217.39 mg g⁻¹. This finding confirmed the significant potential of electrospun PA6/CS/GO nanofibers for use in numerous engineering fields particularly in membrane and filtration.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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