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PAPER

Selective removal of mercury ions using thymine-grafted electrospun polymer nanofibers

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Removal of hazardous metal ions from industrial waste water is of paramount importance. Taking advantage of the metal-ligand binding specificity and electrospun nanofibers with a high surface area to volume ratio and a porous structure, we developed thymine (T)-grafted poly(vinyl alcohol) (PVA)/polyethyleneimine (PEI) nanofibers for selective removal of mercury ions (Hg^{2+}) with high efficiency. In this study, thymine-1-acetic acid was first grafted with the primary surface amines of branched PEI *via* an 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide coupling reaction. The formed PEI-T conjugate was mixed with PVA solution for subsequent formation of T-grafted electrospun PVA/PEI (PVA/PEI-T) nanofibers. The formation of PEI-T conjugate and the crosslinked PVA/PEI-T nanofibers were characterized *via* different techniques. We show that the grafting of the T moieties onto the surface of PEI does not appreciably impact the smooth fibrous morphology of PVA/PEI-T nanofibers when compared with the PVA/PEI nanofibers without T grafting, except that the T-grafted fibers have slightly increased fiber diameter. With the grafting of T moieties, the formed PVA/PEI-T nanofibers enabled selective removal of Hg^{2+} in aqueous solution and improved removal efficiency was able to be achieved by increase of the T-grafting density onto the PEI surface. With the good reusability for repetitive Hg^{2+} removal, the newly developed T-functionalized PVA/PEI nanofibers may hold a great promise for high-selectivity and high-efficiency removal of Hg^{2+} in laboratory and industrial wastes.

Introduction

Mercury has been considered to be one of the most toxic heavy metals due to its durability, mobility and biological enrichment. Mercury and mercury compounds can be converted to highly toxic methyl mercury under specific circumstances, which can cause severe damages to human central nervous system, kidneys, and other organs even at a low concentration.[1, 2] Chlor-alkali, paper and pulp, oil refinery, paint, pharmaceutical and battery manufacturing industrial wastewater discharges are the main resources of mercury pollutants introduced to the environment.[3] Much effort has been devoted to develop various absorbents to remove mercury ions (Hg^{2+}) from aqueous media.[4-9] Among the used advanced materials,[10-12] polymer sorbents have attracted considerable attention in the removal of Hg^{2+} owing to their large absorption capacity, easy preparation, and surface functionalization. Based on the finding that Hg^{2+} can selectively bind to DNA to form thymine (T)-Hg(II)-T base pair,[13, 14] Shangguan and his co-workers[15] investigated the selective removal of Hg^{2+} in aqueous solution using T-grafted polymer sorbents. In another study, Liu *et al.*[16] utilized T-rich DNA to functionalize polyacrylamide hydrogel for selective detection and removal of Hg^{2+}. These studies imply that *via* a T-grafting strategy, effective and selective sorbent materials can be developed for Hg^{2+} removal.

Electrospinning is a powerful fiber formation technology,[17, 18] enabling the generation of various electrospun polymer or polymer-based composite nanofibers with a high aspect ratio and high specific surface area.[19-21] Electrospun nanofibers have found a wide range of applications including but not limited to solar cells,[22] filtration,[23] environmental remediation,[24-31] protective clothing,[32] biosensors,[33] drug delivery,[34-38] and tissue engineering scaffolds.[39-46] In our previous reports,[47-49] we fabricated electrospun polyvinyl alcohol (PVA)/polyethyleneimine (PEI) nanofibers that can be used as a super sorbent material for dye removal,[49] and be used as nanoreactors to immobilize Au[48] or Pd[47] nanoparticles for catalysis applications. We show that the formed PVA/PEI-based nanofibers possess the advantages such as easy-handling, good mechanical durability, and easy recyclability. With the abundant amine groups on the molecular chain of PEI, it is expected that T moieties may be grafted onto the surface of PEI, followed by formation of electrospun PVA/PEI-T nanofibers, thereby providing a unique nanofiber-based sorbent material for selective Hg^{2+} removal.

To prove our hypothesis, in this present study, we report the fabrication, characterization, and application of electrospun T-grafted PVA/PEI nanofibrous mats for selective Hg^{2+} removal applications (Scheme 1). T moieties were first grafted on PEI *via* conjugating amine groups of PEI and carboxyl groups of thymine-1-acetic acid. The formed PEI-T was then mixed with PVA to generate electrospun PVA/PEI-T nanofibers. At last, the newly generated PVA/PEI-T nanofibers were crosslinked *via* glutaraldehyde (GA) vapor to render them with water stability. The formed PEI-T conjugate and the crosslinked PVA/PEI-T nanofibers were characterized *via* different techniques. The sorption capability, selectivity, and reusability of the T-grafted fibrous sorbent were investigated by removing Hg^{2+} in aqueous solution. To the best of our knowledge, this is the first report related to the selective removal of Hg^{2+} in aqueous solution using T-functionalized electrospun polymer nanofibers.

Experimental section

Materials

PEI (branched, Mw = 25,000) and thymine-1-acetic acid (98%) were purchased from Sigma-Aldrich (St Louis, MO). PVA (88% hydrolyzed, Mw = 88,000) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) were obtained from J&K chemical (Shanghai, China). Mercuric nitrate ($Hg(NO_3)_2 \cdot 0.5H_2O$) was from Guizhou Tongren Chemical Reagent Plant (Tongren, China). HCl (36-38%) was supplied from Pinghu Chemical Reagent Plant (Jiaxing, China). HNO_3 (65-68%), GA (25%), KH_2PO_4, NaOH, and all other chemicals were of reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received. Regenerated cellulose dialysis membranes with molecular weight cutoff (MWCO) of 3 500 were acquired from Fisher. Water used in all experiments was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) with a resistivity higher than 18 MΩ·cm.

Synthesis of PEI-T

The T moieties were conjugated onto the surface of PEI *via* EDC coupling chemistry. Taking the PEI-T conjugate synthesized with N/T of 10:1 as an example, PEI (0.5 g) was first dissolved in 2 mL water under vigorous stirring. In the meantime, EDC-activated thymine-1-acetic acid solution was prepared by dissolving thymine-1-acetic acid (154.12 mg) and EDC (802.17 mg) in 20 mL water under magnetic stirring at 40 °C in a water bath for 3 h. Then the PEI solution was added dropwise into the resulting aqueous solution of EDC-activated thymine-1-acetic acid under vigorous stirring at room temperature for 24 h. Finally, the reaction mixture was dialyzed against water (6 times, 2 L) for 3 days using a dialysis membrane with MWCO of 3 500, followed by lyophilization to obtain a yellowish product PEI-T.

Preparation of water-stable PVA/PEI-T nanofibrous mats

Electrospun PVA/PEI-T nanofibers were prepared according to our previous report with a slight modification[48] using a commercial electrospinning equipment (1006 Electrospinning equipment, Beijing Kang Sente Technology Co., Ltd., Beijing, China). Briefly, PVA (12 wt %) solution and PEI-T were mixed together under magnetic stirring overnight with a PVA/PEI-T mass ratio of 3:1 to achieve a homogeneous polymer solution. The freshly prepared mixed polymer solution was placed in a syringe with a stainless steel needle having an inner diameter of 0.8 mm. The flow rate was controlled by a syringe pump at 0.3 mL/h. The high voltage power supplier was connected to the needle by a high-voltage insulating wire with two clamps. An aluminum (Al) board covered with Al foil positioned vertically was used as the collector and was grounded. The distance between the needle tip and the collector was set at 25 cm and the operating voltage was set at 18.6 kV. The freshly formed nanofibrous mats were vacuum dried for 24 h before further treatment.

The as-prepared PVA/PEI-T nanofibers were then crosslinked by GA vapor to render the fibers with water stability.[50] In brief, a Petri dish containing GA solution (20 mL, 25% aqueous solution) was first placed at the bottom of a vacuum desiccator, and then the electrospun PVA/PEI-T nanofibrous mats on Al foil were covered onto the dish upside down without dipping into the GA solution. Vacuum was applied for 24 h. Then, the mats on Al foil were withdrawn and immersed into water for several minutes to let them detached from the Al foil. The freestanding nanofibrous mats were then washed with water for 3 times to remove excess GA. Then the fibrous mats were dried under vacuum and stored in a desiccator before use. For comparison, water stable PVA/PEI nanofibers without T functionalization were also prepared under similar experimental conditions.

Characterization techniques

^1H NMR spectra were recorded on a Bruker AV400 nuclear magnetic resonance spectrometer. Samples were dissolved in D_2O before NMR measurements. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 5700 spectrometer (Thermo Nicolet Corp., Waltham, MA) in a wavenumber range of 4000-650 cm^{-1} under ambient conditions. The morphology of the electrospun PVA/PEI-T nanofibrous mats was observed using scanning electron microscopy (SEM, JSM-5600LV, JEOL Ltd., Japan) with an operating voltage of 15 kV. Prior to SEM measurements, samples were sputter-coated with 10 nm thick gold films. The diameters of nanofibers were measured using image analysis software ImageJ 1.40G (http://rsb.info.nih.gov/ij/download.html). At least 300 randomly selected nanofibers in different SEM images were analyzed for each sample in order to acquire the diameter distribution histograms.

Hg^{2+} removal experiment

Removal of Hg^{2+} using electrospun PVA/PEI-T nanofibrous mats was evaluated in batch experiment. Briefly, a piece of fibrous sorbent (80 mg, without T grafting or grafted with T at different grafting degrees) was immersed into 20 mg/L Hg^{2+} solution (20 mM KH_2PO_4/NaOH, pH = 7) at room temperature. At each predetermined time interval, 0.5 mL of the aqueous solution was withdrawn and diluted to 2 mL to quantify the Hg^{2+} concentration using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Leeman Prodigy, Hudson, NH). The sorption capability of the fibrous materials was calculated according to the following equation:

$$P\ (\%) = \frac{C_t}{C_0} \times 100\% \qquad (1)$$

Where P is the sorption efficiency (%), C_0 is the initial Hg^{2+} concentration, and C_t is the Hg^{2+} concentration at time *t*.

Reusability test

After one complete sorption process, electrospun PVA/PEI-T nanofibrous mats were regenerated for the next cycle of sorption according to the method described above. The regeneration of the fibrous mats was carried out according to the literature but with a slight modification.[15] In brief, the fibrous mats were exposed to HCl solution (30 mL, 1 M) once, water (30 mL) trice, and pH 7.0 KH_2PO_4/NaOH buffer (20 mL) once.

Selectivity test

The selectivity test of electrospun PVA/PEI-T nanofibrous mats was carried out by immersing the fibrous mats into an aqueous solution of Hg^{2+} in the presence of a mixture of other metal ions including Cu^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, and Ba^{2+}. After 1 h sorption, the concentration of each type of metal ions in the solution was measured by ICP-OES.

Results and discussion

Synthesis of PEI-T conjugate

Via an EDC coupling chemistry, PEI-T conjugates with two different T grafting degrees were synthesized (Figure 1). In our synthesis, the molar ratio of PEI primary amine/T (N/T) was controlled at 10:1 and 1:1, respectively. FTIR spectroscopy was used to qualitatively confirm the T grafting onto the PEI surface (Figure 2). We can see that before T grafting, the peak at 3280 cm^{-1} is assigned to the N-H stretching vibration, and the peaks at 1605 cm^{-1} and 780 cm^{-1} are associated with the deforming vibration and rocking vibration of PEI amines. After T grafting, the peak at 3280 cm^{-1} decreases at N/T of 10:1, and vanishes at N/T of 1:1 with emergence of a new small peak at 3256 cm^{-1}. Two peaks at 1675 cm^{-1} and 1605 cm^{-1} are enhanced significantly at the N/T of 10:1 and 1:1 due to the amide bond formation. The FTIR data qualitatively confirmed the successful T grafting onto the surface of PEI. The PEI-T conjugates were further characterized *via* ^1H NMR spectroscopy (Figure 3). It can be clearly seen that the peaks observed at 2.35-2.74 ppm are associated with the PEI $-CH_2-$ proton signals, in agreement with our previous reports.[51, 52] After T grafting, especially at the N/T of 1:1, the PEI $-CH_2-$ proton peaks are quite separated to have four individual peaks at 2.58 ppm, 2.67 ppm, 2.79 ppm, and 2.94 ppm, respectively. Likewise, three new peaks appearing at 7.28 ppm, 4.15 ppm, and 1.75 ppm marked with the numbers of 1, 2, and 3 can be attributed to T proton signals marked with a, b, c in Figure 1, respectively. Similar to FTIR results, the T proton signals are enhanced with the increase of the T modification degree. By NMR integration, the actual N/T was estimated to be 9.8: 1 for the case of N/T at 10:1, and 3.1:1 for the case of N/T at 1:1, respectively. Obviously, even at the case of N/T of 1:1, the PEI primary amines cannot be completely modified with T, which is presumably due to the steric hindrance after a significant portion of the PEI amines were reacted with T moieties, further T modification is unlikely possible. The remaining PEI primary amines are essential for the crosslinking with PVA hydroxyl groups in the presence of GA vapor to form water-stable PVA/PEI-T nanofibers (see below).

Formation of water-stable PVA/PEI-T nanofibers

By electrospinning the mixture solution of PVA and PEI-T, electrospun PVA/PEI-T nanofibers were formed (Scheme 1). The morphology of the crosslinked electrospun PVA/PEI-T nanofibrous mats after immersed in water for 7 days were observed *via* SEM (Figure 4). Compared to PVA/PEI nanofibers without T grafting (Figure 4a), the grafting of T moieties with different degrees of modification does not seem to significantly alter the uniform fibrous morphology with a smooth surface and a porous structure (Figures 4b and 4c), except that fiber diameter slight increases from 588 nm to 594 nm for PVA/PEI-T with N/T at 10:1 or to 605 nm for PVA/PEI-T with N/T at 1:1. This might be ascribed to the grafting of T moieties, which exhausts a significant portion of PEI primary amines, resulting in less tightened bonding with the PVA hydroxyl groups during the GA vapor crosslinking process and more swelling of fibers in aqueous environment. Therefore, the diameter of the 3 crosslinked nanofibers follows the order of PVA/PEI < PVA/PEI-T (N/T = 10:1) < PVA/PEI-T (N/T = 1:1).

The formed PVA/PEI-T nanofibers were further characterized by FTIR spectroscopy (Figure 5). In this case, the PVA/PEI-T (N/T = 1:1) nanofibers were selected for comparison with PVA/PEI nanofibers without T grafting. We can see that the broadened peak at 3332 cm^{-1} may be ascribed to the overlapping of PVA hydroxyl groups and PEI amine groups. The T grafting at N/T=1:1 for the PVA/PEI-T nanofibers display a weakened peak intensity, possibly due to the PEI amine exhaustion after T grafting. Likewise, the peak at 1658 cm^{-1} is largely strengthened when compared to the PVA/PEI nanofibers without T grafting, which is attributed to the amide bond of PEI-T conjugate. Our results indicate that the formation of water-stable PVA/PEI-T nanofibers does not shield the molecular signature of T moieties, which is essential for the selective Hg^{2+} removal applications.

Removal of Hg^{2+} using PVA/PEI-T nanofibers

We next explored the use of water-stable PVA/PEI-T nanofibers for Hg^{2+} removal applications. $Hg(NO_3)_2$ was selected as a model pollutant for Hg^{2+}, and the sorption capability of PVA/PEI-T nanofibrous mats were evaluated. It has been reported that the T-Hg-T binding is largely dependent on the solution pH,[15] and strong binding can be achieved at pH = 7. Therefore, the pH of Hg^{2+} solution was set at 7.

After immersing a PVA/PEI-T fibrous mat (80 mg) into Hg^{2+} aqueous solution, ICP-OES analysis was performed to quantify the Hg^{2+} concentration at different time points. As presented in Figure 6, PVA/PEI nanofibers without T grafting do not have an ability to remove Hg^{2+} within a time frame of 60 min. The slight decrease of the remaining fraction of Hg^{2+} may be caused by the physical adsorption of Hg^{2+} onto the porous PVA/PEI nanofibrous mats with large surface area to volume ratio. In sharp contrast, the T-grafting enabled the PVA/PEI-T nanofibers with remarkably improved Hg^{2+} sorption capability. The PVA/PEI-T (N/T=10:1) mats with a less T-grafting degree have a sorption efficiency of 29.2% within 60 min, while the PVA/PEI-T (N/T=1:1) mats with a higher T-grafting degree are able to achieve a sorption efficiency of 70.9% within 60 min. Our results clearly suggest that the grafted T moieties play a key role for improved Hg^{2+} removal.

For practical heavy metal ion removal applications, the used sorbent material should be recyclable and reusable. To prove the recyclability and reusability of the electrospun PVA/PEI-T (N/T=1:1) nanofibers, the used Hg^{2+}-containing PVA/PEI-T nanofibers were regenerated by desorption of Hg^{2+} in a lower pH environment. The recycled PVA/PEI-T nanofibers were used for 2nd and 3rd cycle of Hg^{2+} sorption (Figure 7a). It is clear that the Hg^{2+} sorption efficiency for the 2nd and 3rd time of experiment can reach 66.8% and 62.7%, respectively, which are quite close to that for the first time adsorption. The gradual deterioration of the Hg^{2+} sorption performance after each cycle could be due to the deterioration of the fiber morphology after repeated sorption and regeneration processes, resulting in swelling of the fiber morphology with a lower specific surface area. We can safely conclude that the developed T-grafted PVA/PEI nanofibers can be regenerated for at least 3 times for Hg^{2+} sorption.

Due to the specific interaction between T and Hg^{2+}, the as-prepared PVA/PEI-T nanofibrous mats also possessed good specificity to eliminate Hg^{2+}. To assess the Hg^{2+} removal specificity, the Hg^{2+} sorption experiment was performed in the presence of mixed types of metal ions including Cu^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, and Ba^{2+} (Figure 7b). It can be seen that the concentration of Hg^{2+} is sharply decreased after the sorption process using PVA/PEI-T (N/T = 1:1) nanofibrous mats in comparison to other metal ions, and the PVA/PEI-T nanofibers display an impressive Hg^{2+} sorption specificity. It should be noted that the concentration of Cu^{2+} is also decreased significantly, which may be caused by the non-specific interaction between Cu^{2+} and the remaining PEI amines of the nanofibrous mat, in agreement with the literature.[53] To overcome this issue, future efforts to completely shield the PEI remaining amines may be explored. We also note that compared to zonal thiol-functionalized silica nanofibers for heavy metal ion removal that lack the specificity in Hg^{2+} removal,[54] the developed T-grafted PVA/PEI nanofibers are much more advantageous due to the T grafting, enabling specific metal ion-ligand interaction. Likewise, the T-grafted polymer microbeads with a diameter of 3 or 7 μm can be used for specific removal of Hg^{2+} in aqueous solution,[15] however, the removal efficiency could be low due to the size of the particles and the recycling of the polymer microbeads could be more complicated than that of the T-grafted nanofibrous mats developed in our work.

Conclusions

In summary, we demonstrate a novel strategy to prepare T-grafted electrospun PVA/PEI nanofibers with a porous structure and a high specific surface area for high-efficiency and high-selectivity Hg^{2+} removal applications. The T-grafting onto the surface of PEI primary amines does not appreciably alter the uniform and smooth morphology of PVA/PEI nanofibers, instead renders the formed electrospun PVA/PEI-T nanofibers with excellent capability to remove Hg^{2+} in aqueous solution with high specificity. Moreover, the freestanding fibrous sorbent materials can be easily regenerated and recycled for repetitive Hg^{2+} sorption. Such T-grafted electrospun nanofibers may be used for different environmental applications related to Hg^{2+} removal and Hg^{2+} sensing.

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Notes and references

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Figure captions

Scheme 1. Schematic illustration of the preparation of water-stable electrospun PVA/PEI-T nanofibrous mat.

Figure 1. Chemical structure of PEI-T conjugate.

Figure 2. FTIR spectra of PEI and PEI-T conjugate with different T grafting degrees.

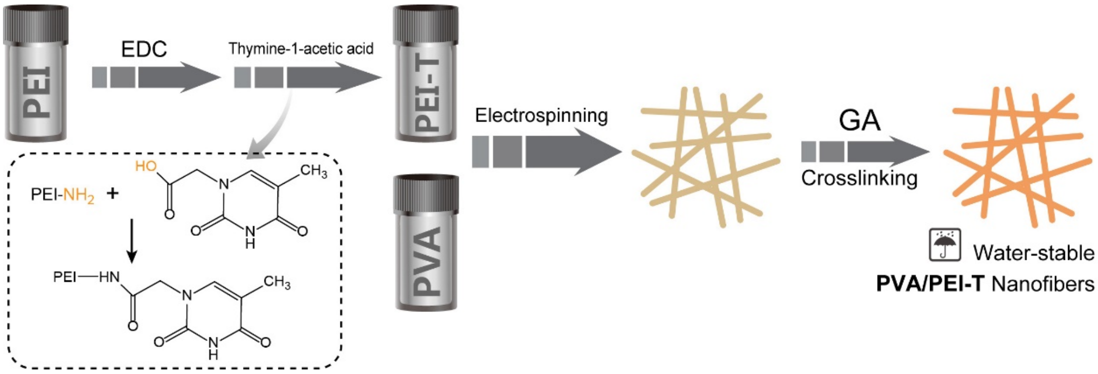
Figure 3. ^{1}H NMR spectrum of PEI (a), PEI-T (N/T=10:1) (b), and PEI-T (N/T=1:1) (c).

Figure 4. SEM images and diameter distribution histograms of water-stable electrospun (a) PVA/PEI, (b) PVA/PEI-T (N/T = 10:1), and (c) PVA/PEI-T (N/T=1:1) nanofibers.

Figure 5. FTIR spectra of water-stable PVA/PEI and PVA/PEI-T (N/T=1:1) nanofibers.

Figure 6. The Hg^{2+}sorption efficiency of water-stable PVA/PEI and PVA/PEI-T nanofibers.

Figure 7. (a) The Hg^{2+} sorption efficiency of PVA/PEI-T (N/T = 1:1) nanofibers for the 1st, 2nd, and 3rd cycle of sorption. (b) Selectivity test of PVA/PEI-T (N/T = 1:1) nanofibers toward the sorption of Hg^{2+} in the presence of different metal ions.



Scheme 1
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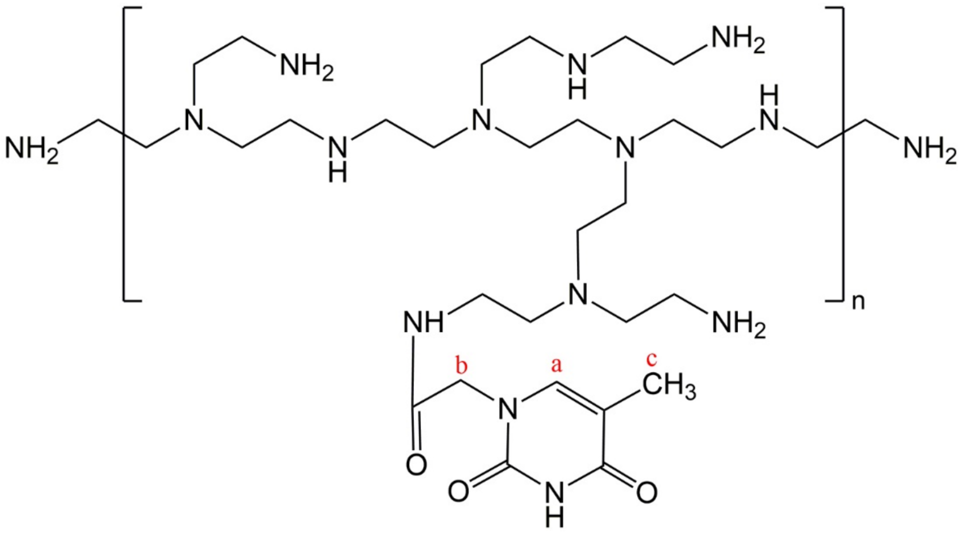

Figure 1
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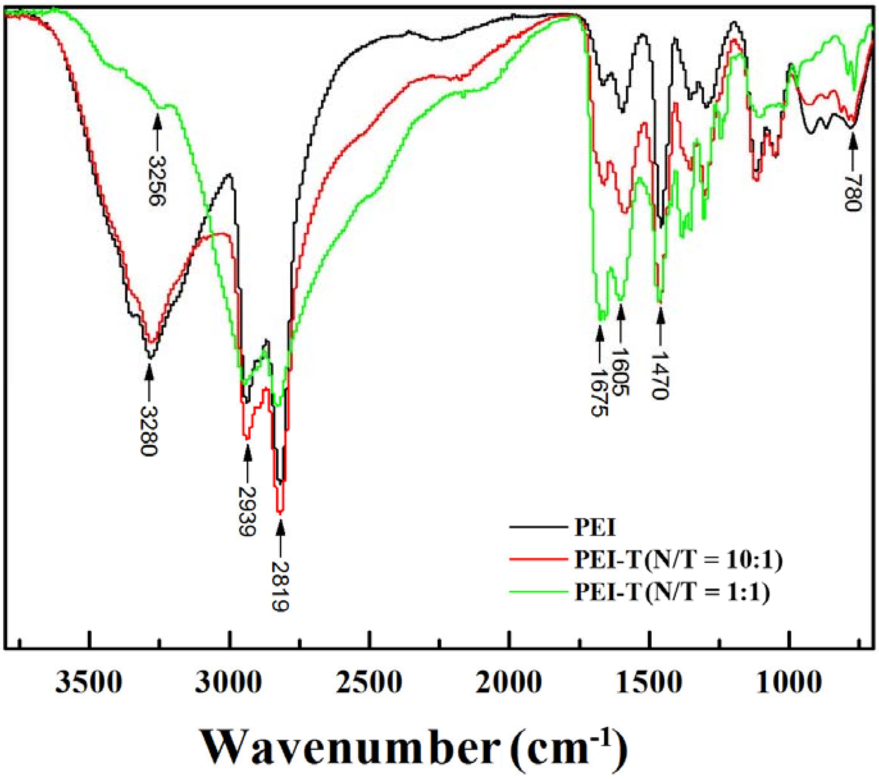

Figure 2
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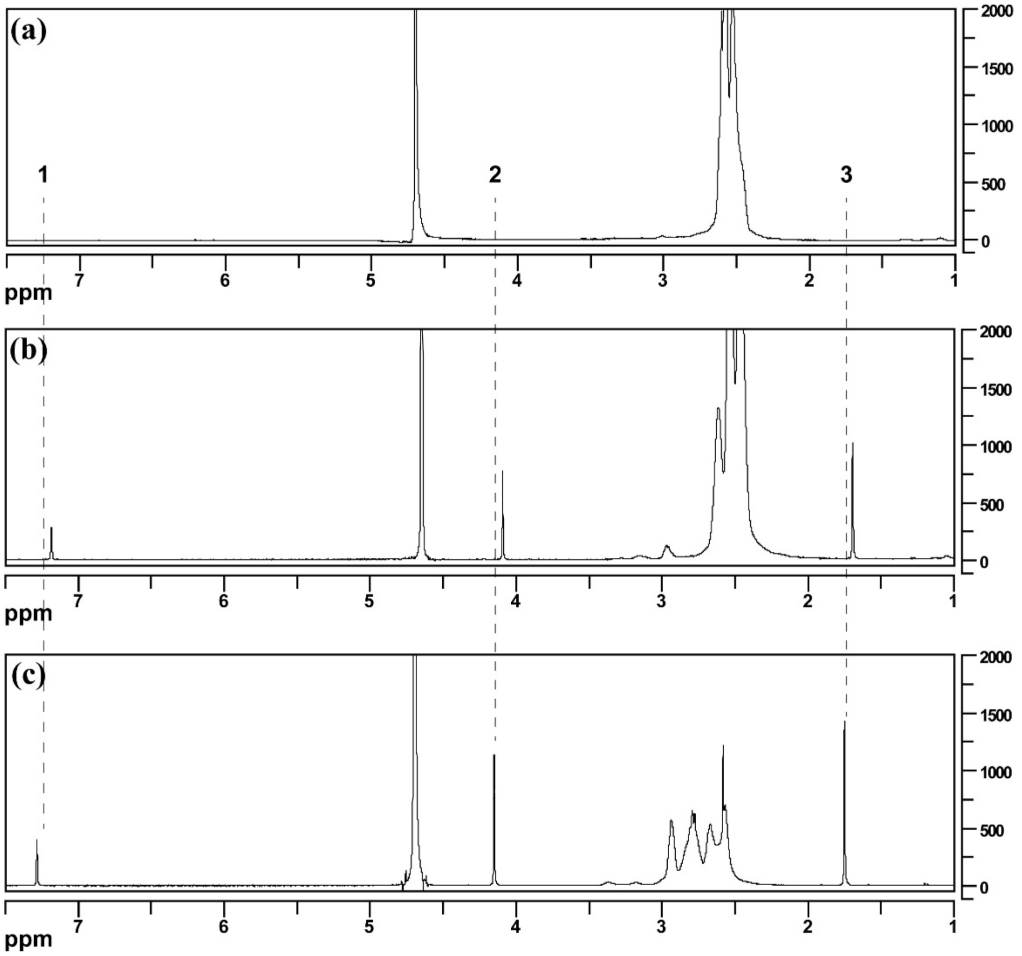

Figure 3
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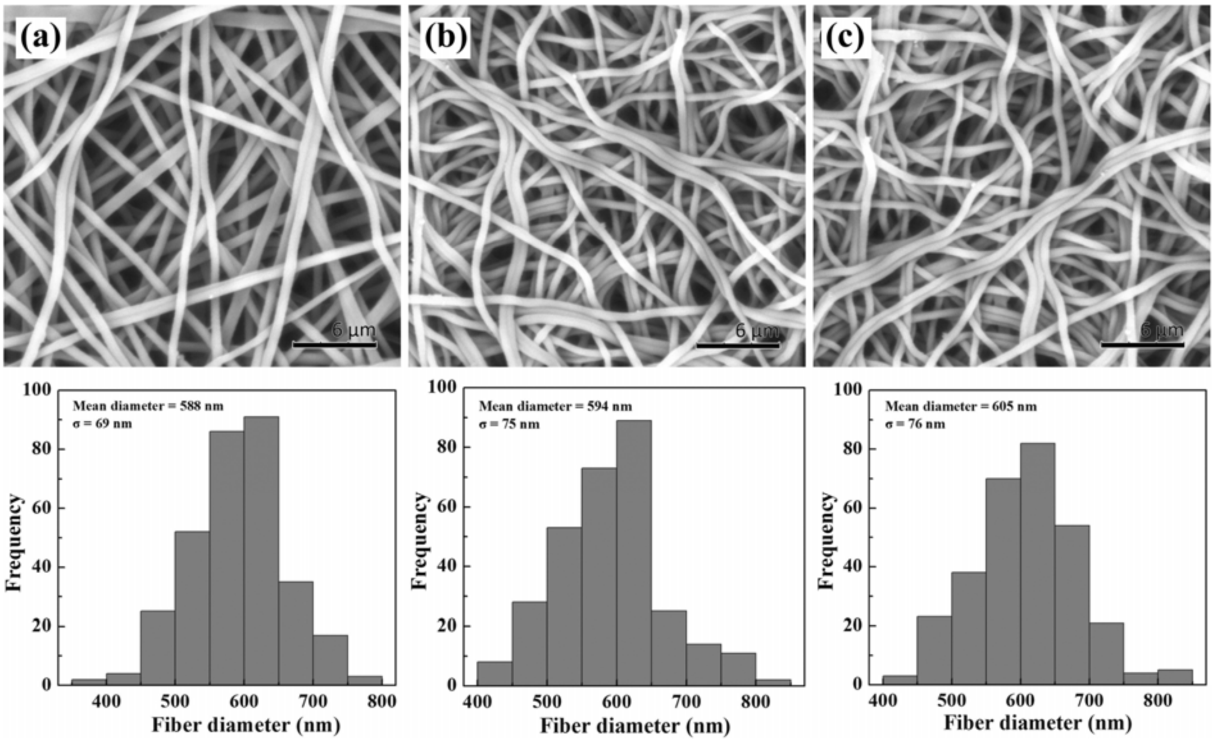

Figure 4
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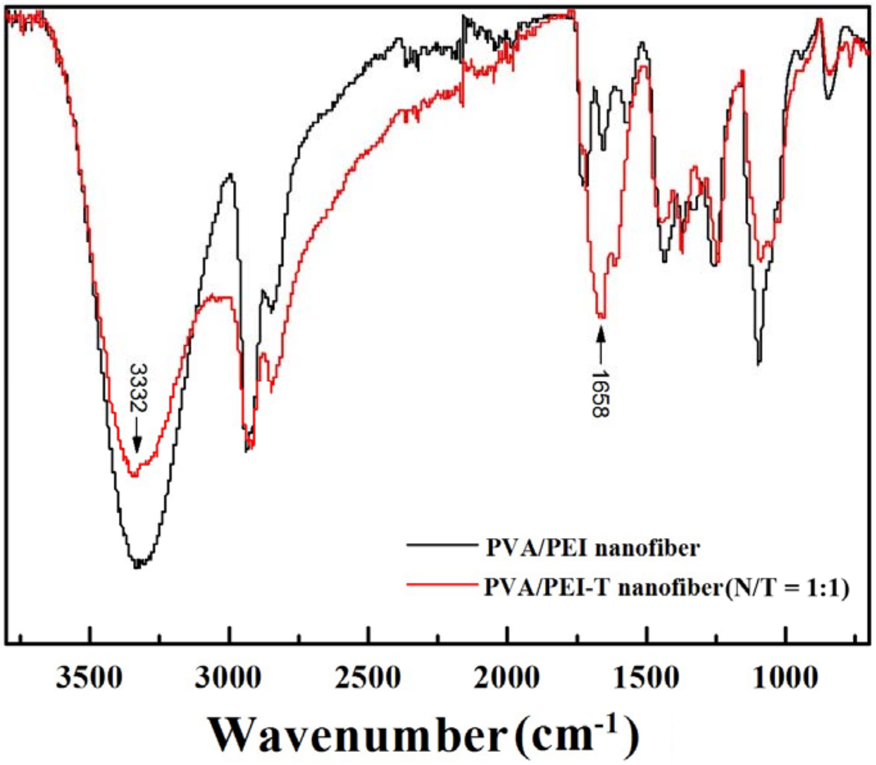

Figure 5
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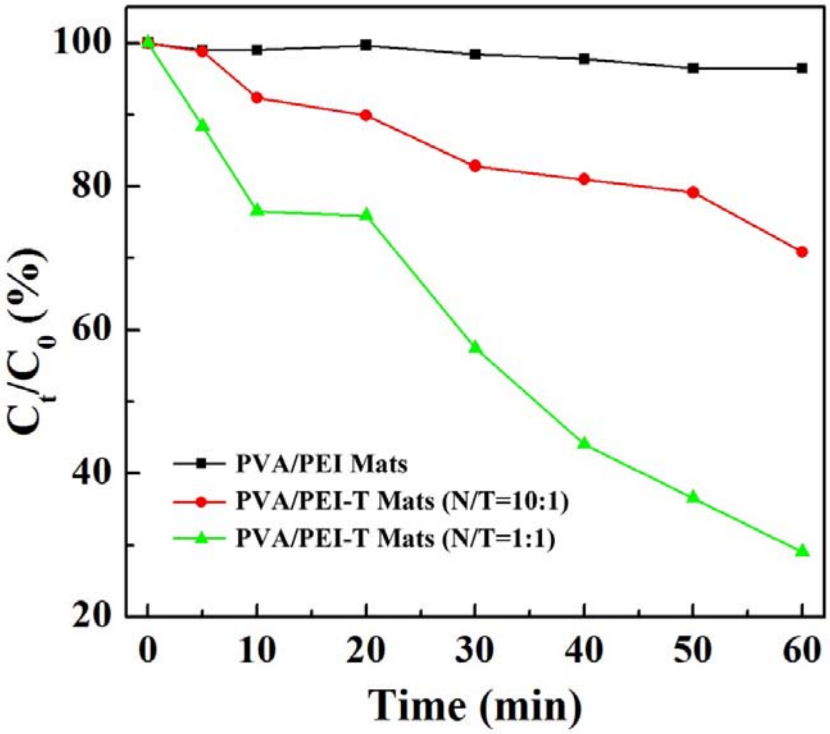

Figure 6
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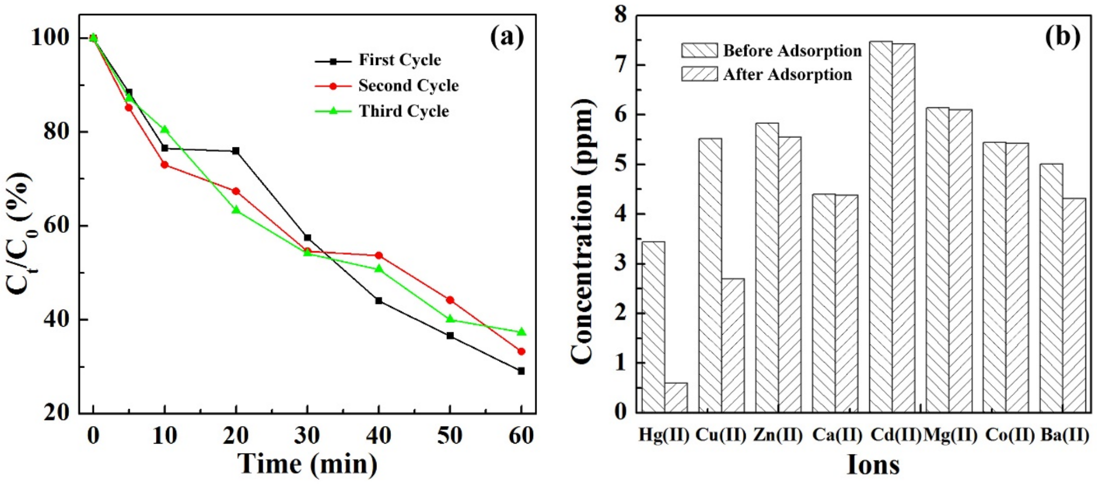

Figure 7
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