Functionalized Cellulose: PET Polymer Fibers with Zeolites for Detoxification Against Nerve Agents

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Abstract: Presently activated carbon is used as an adsorptive material for chemical and biological warfare agents. It possess excellent surface properties such as large surface area, fire-resistance and plenty availability, but has disadvantages such as its heavy weight, low breathability (after adsorption of moisture) and disposal. In this paper, we propose to utilize novel electrospun polymeric nanostructures having zeolites as catalyst materials. In this respective, the electrospun polymer nanofibers would serve as the best possible substitutes to activated carbon based protective clothing applications. This is the first in the literature that reports the integration of these types of catalysts with nanofibrous membranes. Electrospinning of cellulose/polyethylene terephthalate (PET) blend nanofibers has been carried out. Zeolite catalysts (Linde Type A and Mordenite) for the detoxification of nerve agent stimulant-paraoxon, were prepared due to their relative simplicity of synthesis. The catalysts were then coated onto nanofiber membranes and their morphology was confirmed using SEM. This is the first report on the coating of nanofibers with zeolites and their successful demonstration against nerve agent stimulant. The UV absorption spectra clearly show the detoxification ability of the functionalized fibers and their potential to be used in textiles for protection and decontamination.

Key words: electrospinning; electrospraying; nano-fibers; cellulose/PET; linde type A (LTA); mordenite

Zeoites are porous aluminosilicates with various applications, having a great impact on domestic life and industrial processes. The porous structure of these materials permits the diffusion of guest molecules into the bulk structure depending on shape and size selectivity. Post-diffusion, chemical transformations of the guests may take place. Examples of such transformations are xylene isomerisation and catalytic cracking. Ion exchange is another property of zeolites, which is exploited in applications such as detergents and water softeners. The unique properties of zeolites arise from their uniform pore size (due to their crystalline nature) and because the pore sizes can be as small as molecules[1-7]. Zeolite Linde Type A (LTA) is a synthetic material whose composition is Na12[Al12Si12O48]•27H2O. Like most zeolite synthesis process at low temperatures, zeolite LTA and Mordenite can be synthesized from a variety of silica and alumina reactants in a highly alkaline medium, the overall starting composition being considerably different from the composition of the resulting crystals. Zeolite LTA is a critical material in the chemical industry as builders and catalysts. It can be used as a container for arranging ferromagnetic potassium clusters[5-13]. Mordenite has parallel elliptical channels and its typical unit cell composition is Na8[(AlO2)8(SiO2)40]•24H2O. Mordenite is used in adsorptive separation[10]. It is widely used in catalysis such as cracking or hydrocracking under severe environments[14]. Although, both these materials are used extensively for various applications, however, to the best of our knowledge, they are not explored so far in the protective clothing and textiles. Protective clothing is widely used by soldiers for the protection against chemical and biological warfare (CBW) agents[15]. Currently activated charcoal impregnated with various metal ions has been widely used as adsorbent in protective clothing[16].

CBW agents are a great threat in the modern age. These hazardous weapons not only harm the current generation, but also affect the future generations. A drastic example of this can be seen at Hiroshima & Nagasaki, where children still suffer from severe physical & mental diseases/illness due to genetic defects. Functionalized nanofibers have shown great potential in recent years to overcome such threats[17]. The nanofibers are lightweight and durable, apart from the effective detoxification properties[18-20].
Another potential that nanofibers offer is the option of preparing Integrated Textiles, which will provide the soldiers—a complete solution. They can fearlessly head to battlefields while their suits are bulletproof and offer complete protection against chemical & biological threats.

The fabrication and functionalization of 1D nanostructured materials has become one of the most active research fields over the past decade. Electrospinning technique is widely applied to prepare polymers nanofibers and it is the most popular technique utilized in production of functional nanofibers due to its simplicity, low cost, and high yield. In the present study, electrospinning of a cellulose/PET blend was successfully carried out. The deposition of zeolites has been carried out on the nanofiber surfaces using electrospaying techniques and demonstrated successfully for the detoxification of nerve agent stimulant, paraoxon.

1 Experimental

1.1 Materials

Microgranular cellulose (C6413) was obtained from Sigma-Aldrich (Germany), PET was obtained from Mitsubishi Chemical (Japan), Sodium Hydroxide was obtained from Merck (Singapore), Aluminium Isopropoxide and Heptane were obtained from Aldrich (Germany), Tetra-ethyl ortho-silicate (TEOS) was obtained from Fluka (Switzerland), methanol was obtained from Sigma (USA) and, 3-trimethoxysilylpropyl methacrylate was obtained from Degussa AG. All chemicals were used as obtained without any further purification/treatment.

1.2 Synthesis & Functionalization

1.2.1 Synthesis of Zeolite LTA

This zeolite was prepared by the procedure reported by Thompson et al[11]. The source materials for silica and alumina chosen were different from the reported materials. First, sodium hydroxide (0.72 g) was dissolved in 80 mL of distilled water. This solution was divided into two parts. One part of the solution was added aluminium isopropoxide (4.13 g). The other part, 16 mL of TEOS was added. Then the two parts were poured simultaneously into a teflon container, resulting in the formation of a thick gel. This teflon container was sealed in an autoclave (hydrothermal bomb) and heated at (100±5)℃ for 4 h. After cooling, the precipitate was collected by filtration. The obtained white precipitate was washed with water thrice and dried to a constant weight in an oven at 80℃.

Figure 1 shows the SEM images of Mordenite and Zeolite LTA. Typical needle-shaped mordenite could not be obtained from this system and, most crystals formed as plates. Flat and prismatic crystals observed (Fig. 1(a)-(b)), indicate high concentration of silica gel[21]. Sparsely distributed needle-shaped morphology for Zeolite LTA was observed, as shown in Fig. 1(c), a high population of flat/square shaped crystals were observed, which is in accordance to the reported literature[22].

The X-ray diffraction pattern (XRD) of synthesized Zeolite LTA and Mordenite are shown in Fig. 2. The XRD peaks match according to the reported literature. It is to be noted here that the observed XRD peaks for both materials are slightly broader in comparison with the reports, which may be attributed to the choice of different precursors as well as lower crystallization of the materials[21-22].

1.2.2 Synthesis of Mordenite

This zeolite was prepared by the procedure reported by Kim et al[21]. The source materials for silica and alumina chosen were different from the reported materials. First, sodium hydroxide (3.33 g) was dissolved in 4 g distilled water. To this solution, we added aluminium isopropoxide (1.43 g). Further, 64.5 g distilled water was added to the solution followed by TEOS (9.8 g). The solution was transferred into a teflon container. This teflon container was sealed in an autoclave (hydrothermal bomb) and heated at (170±10)℃ for 24 h. The container was consecutively cooled and the precipitate was collected by filtration. The obtained white precipitate was washed with water thrice and dried to a constant weight in an oven at 80℃.

The X-ray diffraction pattern (XRD) of synthesized Zeolite LTA and Mordenite are shown in Fig. 2. The XRD peaks match according to the reported literature. It is to be noted here that the observed XRD peaks for both materials are slightly broader in comparison with the reports, which may be attributed to the choice of different precursors as well as lower crystallization of the materials[21-22].

1.2.3 Fabrication of cellulose:PET fibers

Cellulose:PET:TFA (trifluoro-acetic acid) were taken in 1:3:3 ratios. The solution was stirred at 1000 r/min for 24 h to completely dissolve the polymer and homogenize the solution. The solution was collected in a 10 mL capacity Benton-Dickenson clinical syringe. The electrospinning equipment NANON-01A purchased from MECC (Japan)
was used for preparing the fibers. The applied voltage was 30 kV with a flow rate of polymer solution at 1 mL/h. The distance between the needle and collector was kept constant at 12 cm. A rotating drum at 300 r/min was used to ensure uniform deposition of fibers. The humidity was maintained at 50%−60% at all times.

1.2.4 Functionalization of Cellulose:PET fibers by catalysts

The catalysts (Zeolite LTA/Mordenite) (1.5wt%) were dispersed in methanol. This solution was sonicated in a probe sonicator (Vibra-Cell VCX 130 from Sonics, Switzerland) for 30 min with a Pulse On − 10 s, Pulse Off − 5 s, interval. After sonication, 0.05 g of surfactant (3-trimethoxysilylpropyl methacrylate) was added to prevent agglomeration of the catalyst particles and sonicated for 1 min. This solution was electrosprayed at 12 kV on the cellulose/PET nanofibers.

2 Characterization

Surface features of functionalized fibers were characterized using a Quanta 200 SEM instrument from FEI (Nederlands) operating at 10−15 kV. Gold coating was performed in order to increase the conductivity of the samples using a JEOL FRC 1200 fine coater (Jeol Ltd., Singapore) before taking SEM. The Java image processing software [Image J1.29 (222 commands)] was used to measure the diameter of the fibers. The powder X-ray patterns were obtained on a Shimadzu X-ray diffractometer (Shimadzu XRD 6000, Shimadzu, Singapore) using CuKα (15.1541) radiation. Absorption studies of the hollow fibers against Paraoxon in heptane (solvent) were done using a Unicam UV-Vis 300 series spectrophotometer with a vision data system (Thermo Spectronics). To 10 µL of Paraoxon in a standard measuring flask, 50 mL of heptane was added. To prepare a stock solution, 10 mL of this solution was diluted with 40 mL heptane. To 30 mL of this stock solution, a known amount of membrane (0.2 g) was added, and the decrease in absorbance intensity at λ_{max}=268 nm indicates the hydrolysis of paraoxon.

3 Results and discussion

3.1 Electrospraying and Electrospinning Techniques

In the electrospraying technique, small droplets or particles of submicron or nanometer sizes are formed due to the breakup of electrified jet at the capillary tip by the applied voltage. This technique has been successfully applied to deposit wide range of materials such as inorganic, biological, nanoparticles and nanomaterials on the other targets in literature. Recently, much effort has been directed on the deposition of nanoparticles over nanofibers to get the multifunctional membranes[23-27]. To the best of our knowledge, the combinations of electrospraying techniques (to deposit zeolites) with electrospinning technique have not been explored so far in literature. The attachment of Zeolites with nanofibers will open up a new avenue for the exploration of these materials in various applications.

In the present study, coating of zeolite LTA and mordenite were carried out by electrospraying technique on the cellulose/PET nanofiber surfaces. Cellulose has been widely used for the preparation of semi permeable membranes, which own potential applications in the areas of ultra-filtration, dialysis, and reverse osmosis, catalysis, filtration, NEMS, nanocomposites, nanofibrous structures, tissue scaffolds, drug delivery systems, protective textiles, storage cells for hydrogen fuel cells, etc[28-31]. Cellulose possesses hydroxyl functional groups to attach these materials despite having low mechanical stability. In the case of PET membranes, they have excellent mechanical strength, but do not possess any functional groups. The blending of cellulose/PET might increase adhesion stability (by cellulose) and chemical stability (by PET). Thereby the developed composite materials will have enhanced properties. The SEM images of electrospun nanofibers were recorded.
SEM images of the nanofibers containing Zeolite LTA and Mordenite are shown in Fig. 3(a), 3(b), 3(c), and 3(d), respectively. It has been observed that the morphology of the fibers is more uniform in diameter, smooth and cylindrical in shape. We noticed that some nanofibers were not covered by Zeolite LTA and Mordenite when the coating was carried out for 15 min (Fig. 3). However, when the coating time were increased to 60 min, fully covered nanofibers were obtained (not presented here). This indicates that changing the coating time can control the amount of catalysts coating.

3.2 Detoxification Studies:

Due to toxicity nature of actual nerve agent, we have used paraoxon, a nerve agent stimulant, which is identical in structure to VX. First, the absorbance of the as prepared paraoxon stock solution was noted, which showed an absorbance at 6.8 (not shown in Figure). The decrease in the UV absorbance of paraoxon solution was studied after 15 min and 1 h, when added to the prepared functionalized fibers. The observed decrease in the absorbance (Fig. 4) indicates that the catalyst containing nanofibers are effective in detoxifying the harmful organophosphorous agent.

4 Conclusion

Electrospinning of cellulose/PET nanofibers having hydroxyl functional group was carried out. Successful electrospraying of zeolite catalysts on the nanofiber membranes was achieved. Detoxification studies of these functionalized membranes against nerve agent stimulant paraoxon were successful. It is proposed to attempt the
detoxification studies are proposed with different zeolite materials against different types of harmful/hazardous chemicals and biological agents. It is also intended to use mordenite for decontamination against radioactive elements. This is based on the fact that high-silica zeolites are chemically resistant over a wide pH range and is stable in high radiation fields. While natural zeolites highly selective for caesium are available, only moderate selectivity for strontium is shown by most zeolites. Thus, strontium selective zeolites could be prepared, such minerals might be useful for radioactive-waste treatment and analytical chemistry as well[32]. Functionalized nanofibers offer lightweight, easily disposable and breathable fiber membranes for use in protective clothing applications.

References:


