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SYNTHESIS AND CHARACTERIZATION OF POLY[(2-DIMETHYLAMINO)ETHYL METHACRYLATE]-PAN/TIO$_2$ COMPOSITE CRYOGELS AND THEIR USE IN SEPARATION STUDY

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ABSTRACT

The aim of this study was to prepare high surface area nano-sized polyacrylonitrile (PAN) particles and their nanocomposite with TiO_2 (PAN/TiO_2) by using electrospraying method and to use it in super porous composite cryogel preparation using pH responsive monomer, 2-(dimethylamino)ethyl methacrylate. The cryogel composite was synthesized via cryogelation method by including the PAN/TiO_2 nanoparticle within polymeric matrices before cryogelation. The cryogel system was preferred for the polymeric system because of its features such as its super-porous structure, shape retention, reusability, and its fast response to the application. In this way, an increase in performance is expected in separation and purification studies by creating synergy by processing nanoparticles into the macro system.

Keywords: Electrospraying, PAN/TiO_2 Nanocomposite, PDMA cryogel, Separation, Purification

1. INTRODUCTION

Electrospraying or electrodynamic spraying is a simple technology with scalability, reproducibility. This technology formulates a technique based on liquid atomization used for the production of micro- and nanoparticles. Electrospraying conditions generally need to be optimized for each polymer system. Electrospraying by using electro-spinning technic/device is affected by a number of variables such as applied voltage, tip diameter, flow rate, tip-to-collector distance, and environmental influences. In this way, the morphology of the materials obtained by electrodynamic spraying is closely related to the properties of the polymer solution or dispersion used and directly affects the micro-nanoparticle forming performance. The solvent is critical and its volatility is an important factor.

Electrospraying has many advantages compared with the traditional mechanical spraying systems as (1) narrow droplet size distribution with low standard deviation, (2) droplet size can be smaller than 1 μm, (3) droplets are electrically charged, (4) movement of the charged droplets can be easily controlled. The process of electrospraying was reviewed by plenty of researchers because of its many advantages [1-4].

TiO_2 nanoparticle is non-toxic, stable, biocompatible and readily available. It has three main crystal phases; brookite, anatase and rutile. Among them, rutile is thermodynamically stable. Anatase and brookite are semi-stable. These nanoparticles are also an effective photocatalyst and have been the subject of many studies [5]. TiO_2 has found application in many areas such as ceramic industry, paint industry, inorganic membranes, sunscreen, sensors and biological implants [6].

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Cryogels can be defined as a class of hydrogels where controlled polymerization of gel-forming polymers and monomers occurs at sub-zero temperatures and yields macropores surrounded by an elastic network of interconnected ones [7]. Cryogels are naturally interconnected macroporous characteristic structure, allowing water to flow freely in sponge like structure and out of the cryogel, so that the shape of the cryogel can be fixed by squeezing it out of the free water and quickly return to its original shape by absorbing the water. The interesting properties of cryogels such as higher elasticity, flexibility and high mechanical stability, sponge-like porous interconnected microstructures and high porosity make them favorite. Cryogels are widely used as chromatographic materials, tissue engineering scaffolds and high performance materials [8]. In some applications, such as the separation of biomolecules, it can be performed very efficiently due to the large, adjustable and interconnected pore sizes. For effective separation study, cryogel can be modified adding new functional group to the structure. Alternatively, TiO_2, SiO_2, clays, polymeric nano- and microparticles, magnetic particles with different active substances can be embedded to the structure of cryogel. Thus, the interaction between the targeted molecules and the cryogel will increase, thanks to having both very high surface area and the active groups of the embedded substances [9-11].

In the literature, there are several study using polymeric materials such as nano-microgel [12, 13], hydrogel [14-17], cryogel [11, 18-22] and their composite forms [13, 23] in separation and prufication studies for dye removal, biomolecules, ion and so.

Here, we revealed in this study that the species embedded in the cryogel allows controlled study by adjusting the interaction with the target substance in separation and purification [24, 25]. The super-porous cryogel prepared from pH sensitive 2-(dimethylamino)ethyl methacrylate (DMA) monomer and PDMA-PAN/TiO_2 composites formed with PAN/TiO_2 nanoparticles can be used in many applications in the environment and health fields due to their synergistic effects and non-hazardous structures.

2. EXPERIMENTAL

2.1. Material

Materials used in particle synthesis by electrospray technique are polyacrylonitrile (PAN, Carbosynth Mw:150000 g/mol), dimethylformamide (DMF, 99.8%, Sigma-Aldrich), titanium (IV) oxide (TiO_2, mixture of rutile and anatase, < 100 nm particle size, Sigma-Aldrich). Cryogels were prepared using (2-dimethylamino)ethyl methacrylate (DMA, ≥ 99.0%, Sigma-Aldrich) as a monomer, N,N′-methylenebisacrylamide (MBA, 99%, Acros) as a cross-linker, N,N,N′,N′-tetramethylethylenediamine (TEMED, 99%, Across) as accelerator, potassium persulfate (KPS, 99%, Sigma-Aldrich) as redox initiator. Methylene blue (MB, Sigma-Aldrich), 4-nitrophenol (4-NP, 99%, ABCR), congo red (CR, Sigma-Aldrich), eosin yellowish (EY, Merck), gentian violet (GV, Merck) were used application study. Ultrapure water was used throughout the experiment.

2.2. Method

2.2.1. PAN nanoparticle synthesis

The particle was synthesized via electrospraying method using Inovenso NE200 electrospinning device. First, 2% (w/v) polyacrylonitrile solution was prepared in DMF. This solution was sprayed with the Inovenso NE200 electrospinning device with 15.5 kV electrical power, the distance between the collector plate and the tip was 10 cm, using a 30 G needle. The solution flow rate was adjusted to 0.75 ml/h. A total of 5.0 mL of solution was sprayed on the same surface.

2.2.2. PAN/TiO_2 nanocomposite synthesis

TiO_2 nanoparticles were added into a 2% (w/v) polyacrylonitrile solution in DMF and mixed with the aid of a sonication for a long time. The TiO_2 concentration of the mixture was adjusted to 4 mg/mL. The mixture containing titanium oxide was sprayed to the plate in the same way as the PAN nanoparticle at the same flow rate, electrical power and distance.

2.2.3. PDMA cryogel synthesis

For the preparation of PDMA cryogel, 0.50 mL of DMA monomer was dissolved in 7.0 mL of water. Next, 15% of the molar amount of monomer MBA cross-linker was added to this mixture to dissolve for about 2 hours at room temperature and then cooled in an ice bath. Then, 0.05 mL TEMED was added into the mixture. Finally, 1.5% KPS by mole of monomer was added to the medium as an initiator (dissolved in 1.0 mL of water) and vortexed and the mixture was filled into the injectors and the injector tip was closed. The injector was immersed in liquid nitrogen to freeze quickly. The mixture was then placed in the freezer at -20 °C for about 48 hours for cryogelation. After cryogel formation, the cryogel was removed from the injector, cut into cylinders of 3-5 mm in length and cleaned with water for 3-5 hours, and the wash water changed frequently.

2.2.4. PDMA-PAN/TiO_2 composite cryogel synthesis

It was prepared in the same way as PDMA, and PAN/TiO_2 nanocomposite was added to the DMA/MBA/water medium before the addition of accelerator/initiator and dispersed via sonication. Shock freezing is provided with the help of liquid nitrogen to prevent any collapse/clumping. The reaction was continued at -20 °C for 12-48 hours. At the end of the period, the ice was expected to dissolve at ambient temperature, and the species that did not react with plenty of water were washed away.

2.2.5. Application of composite cryogel

The potential use of synthesized PAN/TiO_2 embedded composite cryogels in separation and purification studies was investigated. Cryogel has been used as column filler and used to quickly and effectively separate pesticides, organic pollutants and textile dyes from aqueous solutions with the effect of embedded nanocomposite.

3. RESULTS AND DISCUSSIONS

In this study, electrospraying technique was used for the preparation of all nano- and microparticles. First, PAN particle was synthesized the size smaller than 1 μm diameter. SEM images of the PAN particles is shown in Figure 1. Firstly, it was observed that PAN particles seem to polydisperse size distrubition ranging from 400 nm to 850 nm. Secondly, PAN/TiO_2 nanocomposite was synthesized under the same conditions by adding TiO_2 nanoparticles in PAN-DMF solution. The sizes of used TiO_2 nanoparticles were smaller than 100 nm and it contains two phases as rutile and anatase. Measured specific surface area, pore size and pore volume parameters for TiO_2 is found as 74.29 m^2/g, 16.27 nm and 5.44 cm^3/g, respectively. The particle can be classified as mesoporous material. SEM image of the PAN and PAN/TiO_2 composite was given in Figure 1(a, b).

The difference between blank and TiO_2-containing PAN particles was very clear. Both particles were spherical, but some sphere composite particles collapsed (inset Figure 1b). TiO_2 nanoparticles also may be the reason for this collapsed view in the PAN spheres after spraying.

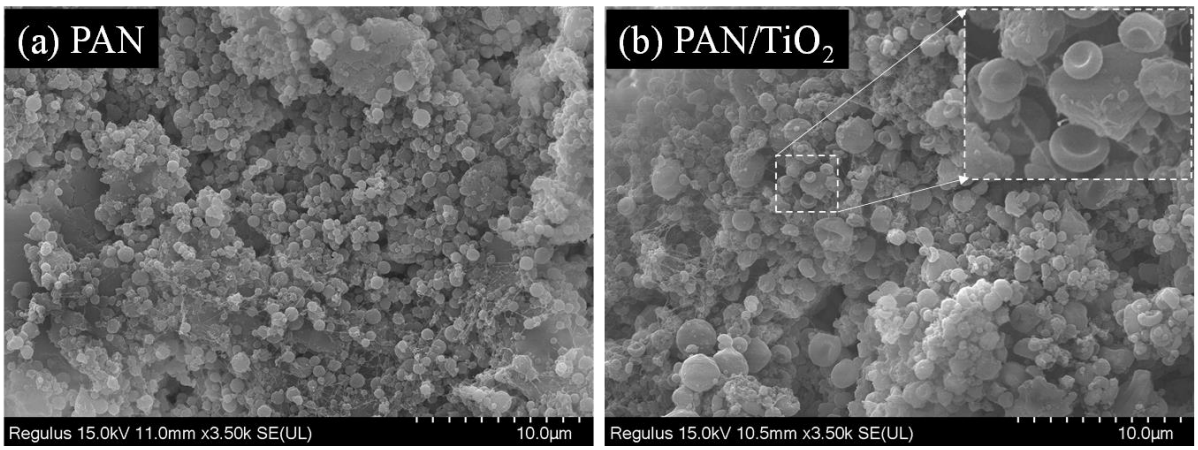


Figure 1. SEM images of PAN nanoparticle (a), and PAN/TiO_2 composite nanoparticles (b) prepared by electrospraying.

PAN and PAN/TiO_2 particles were used for PDMA-PAN/TiO_2 composite cryogel synthesis. Firstly, bare cryogel was prepared by using DMA monomer in cryogenic condition to obtain PDMA cryogel. Both scheme for the pathway of cryogel preparation and digital camera images of PAN/TiO_2 embedded cryogel (PDMA-PAN/TiO_2) were depicted in Figure 2. While PDMA cryogel was transparent, PDMA-PAN/TiO_2 composite cryogel was bright white because of PAN and TiO_2.

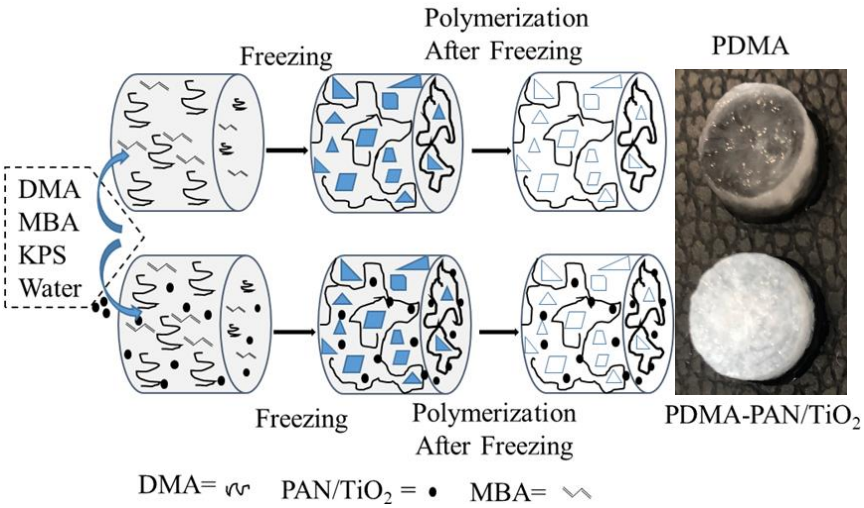


Figure 2. Schematic illustration of the preparation of PDMA cryogel, PDMA-PAN/TiO2 cryogel composite and digital camera images.

It has been observed that gels were soft, compressible, can take their former shape again, and have a structure that absorbs water very quickly. The SEM images of cryogels were illustrated in Figure 3 (a-d) with different magnifications. SEM images indicated macro pores. The pores of the composite cryogel were slightly closed/smaller than the bare one because of fiiling PAN/TiO_2 particles (Figure 3b).

In the Figure 3, as shown at high magnification (inset Figure 1a), PDMA cryogel had a smooth pore surface and super porous structure. Unlike PDMA cryogel, composite cryogel had no flat surfaces on

its surface in high magnification images (Figure 3c, d), and these cryogels were prepared using 15% cross-linker (according to used monomer mole ratio) and 10% PAN/TiO_2 by used monomer weight.

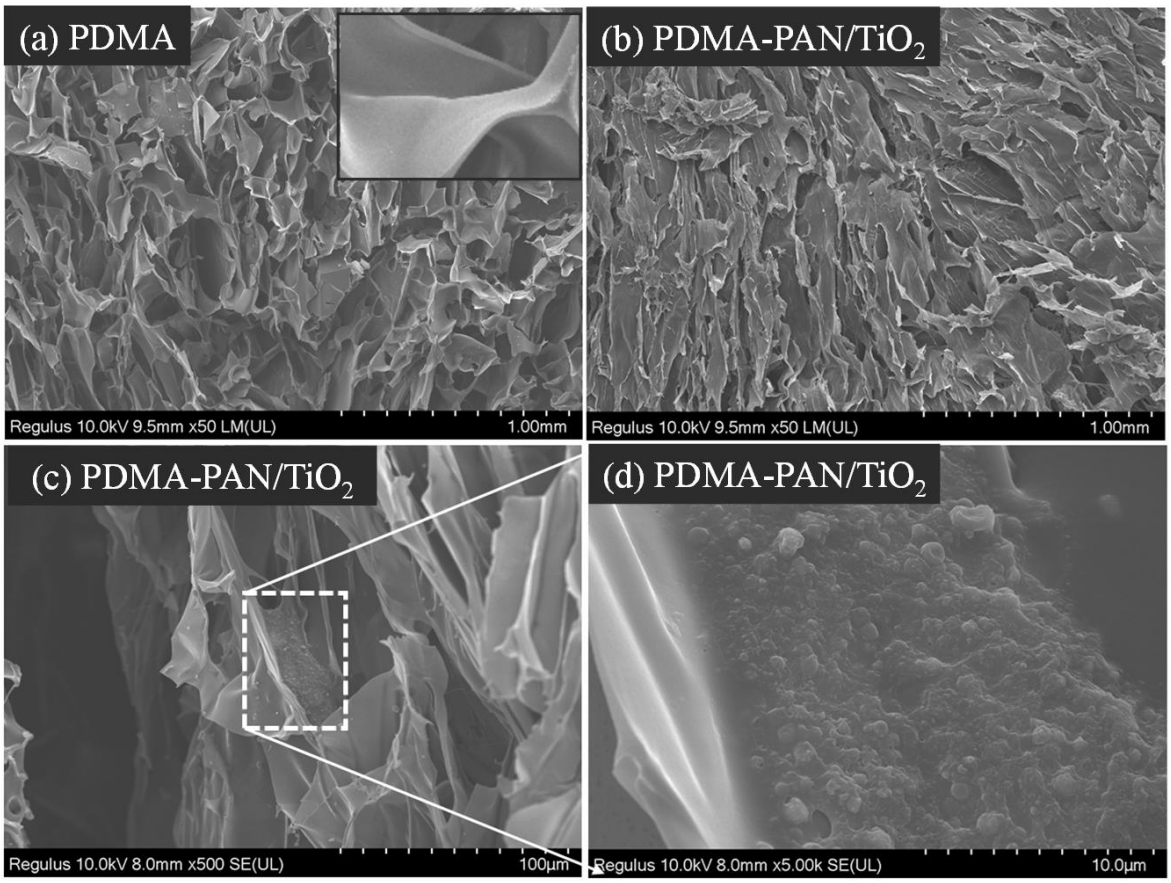


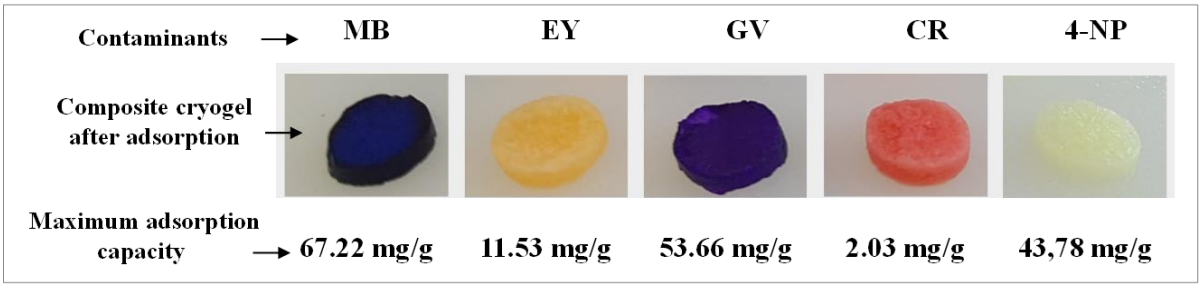
Figure 3. SEM images of PDMA cryogel (a), PDMA-PAN/TiO_2 composite cryogel with different magnifications (b, c, d).

PDMA-PAN/TiO_2 super-porous composites cryogel can be used in different fields to separation and purification applications. In this study, composite cryogels were polymerized in an injector cryogenic condition. After cryogelation, the gels removed from the injectors as a whole were transferred to the larger injector. In this way, the cleaning/washing process was carried out and the gel swelled up to the diameter of the injector and its pores were further opened because of absorbing more water. Therefore, it was aimed to show that PAN/TiO_2 doped PDMA composite cryogels could be used in separation and purification studies.

In parallel with the increasing population and industrialization, water pollution is gradually increasing. It is a common situation that textile dyes/organic pollutants discharged to the clean water sources for various reasons. These pollutants must be removed from the environment in order to increase the quality of life and sustain the life of aquatic organisms. Therefore, textile dyes such as MB, EY, GV, CR and organic pollutant as 4-NP were studied to remove them effectively to obtain sustainable environment. For this purpose, firstly, composite cryogel was used as adsorbent for MB, EY, GV, CR, 4-NP organic contaminants. 100 mg/L initial solution concentration was used in all studies. Approximately 50 mg composite cryogel was filled in the injector/column. Then 5 mL dye solution was passed through column. The interaction of the composite particle doped cryogel with MB, CR, 4-NP solutions was examined separately and visualized. Then their mixture as MB, EY and MB, GV, 4-NP were prepared and passed through PDMA-PAN/TiO_2 containing column. After adsorption study, adsorbed amount of

contaminant was determined by using UV-vis spectrophotometer. Adsorption capacity of the composite cryogel was given in Table 1 as the amount of mg contaminant adsorbed per g composite cryogel. Adsorption capacity was calculated as 67.22 mg/g, 11.53 mg/g, 53,66 mg/g, 2.03 mg/g and 43.78 mg/g for MB, EY, GV, CR and 4-NP, respectively.

Table 1. Maximum adsorption capacity of composite cryogels and their digital camera images after adsorption



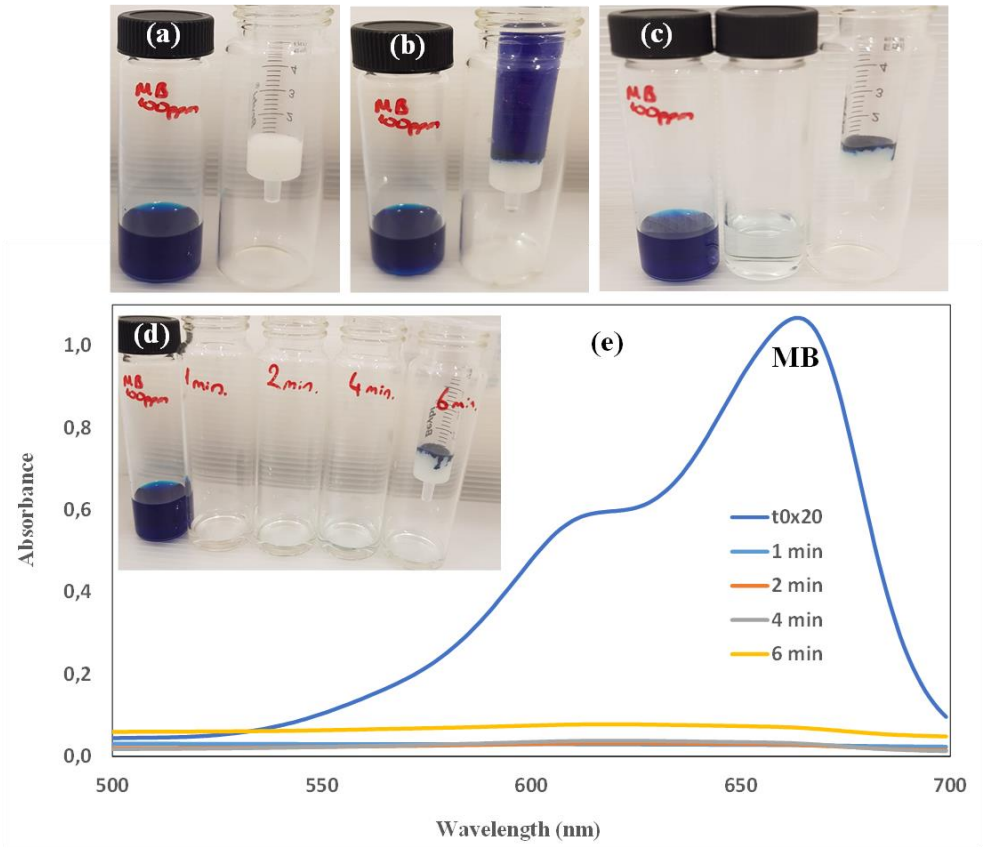


Figure 4. Digital camera images of MB dye and PDMA-PAN/TiO_2 composite filled column (a), dye transferred column (b), MB removal from aqueous solution passing through columns recording to retention time (c, d), UV-Vis spectra of MB solution before (x20 dilution) and after passing through columns (directly) time to time (e) [5 mL 100 ppm MB aqueous solution, 50 mg composite cryogel].

Separation process of MB by using PDMA-PAN/TiO_2 composite cryogel evaluated by UV-Vis spectra of MB eluted solution were illustrated in Figure 4(a-e). As can be clearly seen from Figure 4c composite cryogel adsorb/remove MB dye because of their negatively charged PAN/TiO_2 and opposite to MB dye.

Figure 4d shows the differences of eluents collected 1 min to 6 min. The UV-Vis absorption spectra of eluted MB solution were demonstrated in Figure 4e. Because initial concentration was out of calibration curve, the solution was diluted 20-fold. Then absorbance value were recorded 500-700 nm because of the maximum absorption wavelength at about 664 nm of MB. As seen Figure 4e, initial MB absorbance value at 664 nm was over 1.0, although 20-fold dilution. In same figure, eluent absorbance was recorded directly passing dye solution after 1 min, 2 min, 4 min, and 6 min. The MB concentration of the eluent was a little increased with the increasing retention time. In total, column color was mostly white, only upper site was blue. Considering the separation performance, it can be implied that much more MB solution may be pass through over adsorption capacity.

Figure 5 depicted the separation of CR (a-d) and 4-NP (e-h) apart from by using PDMA-PAN/TiO_2 composite filled column. The retention time of the dye solutions in the column and the concentration of the resulting solution depended on the interaction between the column material and mobile phase (CR, 4-NP). As can be seen from the digital camera images in Figure 5 (c, g), the interaction with the cryogel was not high with CR and 4-NP. The amount of dye adsorbed was determined by measuring the solution after adsorption with UV-vis. The result was different from MB separation because of different charge. For CR, Figure 5c showed before and after passing CR solution through column. 5 mL CR solution passed in 4 min and absorbance recorded by UV-vis spectrophotometer 350-650 nm because of the maximum absorption wavelength at about 498 nm of CR for 1 min, 2 min, and 4 min (eluent diluted 2-fold same as initial sample). When the color of the solution was checked (Figure 5c, after 4min), it was easy to understand change in concentration is little.

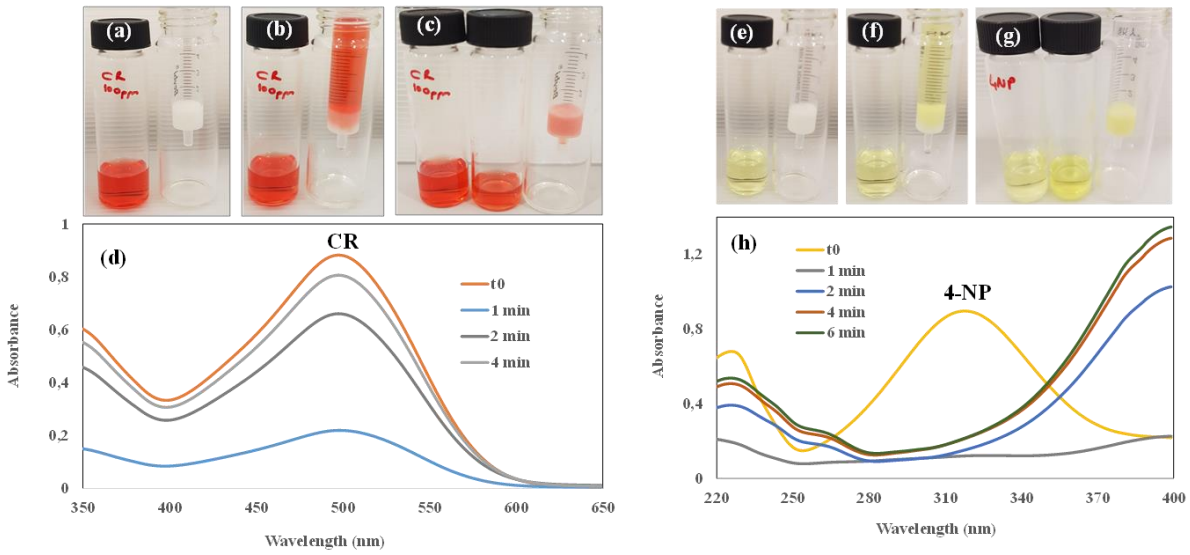


Figure 5. Digital camera images of CR dye and 4-NP organic contaminant PDMA-PAN/TiO_2 composite filled column (a, e), dye transferred column (b, f), CR and 4-NP removal from aqueous solution passing through columns recording to retention time (c, g), UV-Vis spectra of CR (x2 fold dilution) and 4-NP (x6.66 fold dilution) solution before and after passing through columns (d, h) [5 mL 100 mg/mL CR dye and 4-NP aqueous solution, 50 mg composite cryogel].

Separation process of 4-NP by using PDMA-PAN/TiO_2 composite cryogel evaluated by UV-Vis spectra of 4-NP eluted solution were illustrated in Figure 5(e-h). As can be clearly seen from Figure 5g composite cryogel adsorbed/removed 4-NP. Figure 5h showed the differences of eluents collected 1-6 min. The UV-Vis absorption spectra of eluted 4-NP solution were demonstrated in Figure 5h. All the solution was diluted 10-fold including initial one. Then absorbance value were recorded 220-400 nm

because of the maximum absorption wavelength at about 317 nm for 4-NP. As seen Figure 5h, initial 4-NP absorbance max value was 317 nm but after passing through the column the eluent absorbance max was shifted as 400 nm. This means that 4-NP was deprotonated by amino group of DMA, that is, PDMA was protonated.

In this model study, as well as separating dye solutions, dye mixtures were prepared and separation studies were carried out. Figure 6 showed the digital camera images taken from time to time after the transfer of the dye mixtures to the column. From this, it was clearly seen that the dyes interacted differently with the filler in the injector and have different retention time.

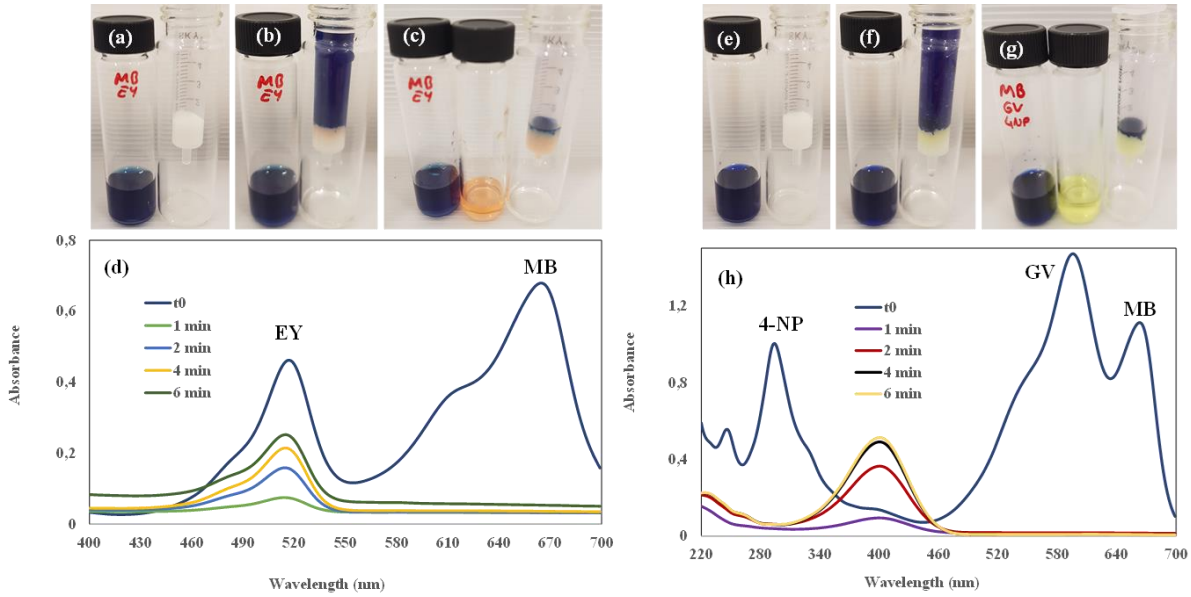


Figure 6. Digital camera images of MB-EY mix and MB-GV-4-NP mix contaminant PDMA-PAN/TiO_2 composite filled column (a,e), dye transferred column (b,f), MB-EY mix and MB-GV-4-NP mix removal from aqueous solution passing through columns recording to retention time (c, g), UV-Vis spectra of MB-EY mix (x10 fold dilution) and MB-GV-4-NP mix (x6 fold dilution) solution before and after passing through columns (d, h) [5 mL 50 mg/mL MB-EY and 33 mg/mL MB-GV-4-NP aqueous solution, 50 mg composite cryogel].

Figure 6 (a-h) showed the mixture of MB, EY and MB, GV, 4-NP separation process. The digital camera images in Figure 6a-c revealed the process step by step, digital camera images of MB-EY mix and PDMA-PAN/TiO_2 composite filled column (a), dye transferred column (b), MB-EY mix removal from aqueous solution passing through column (c). When glancing to the Figure 6c, blue color (MB) was at top of the column and orange color was at the bottom of the column. When checked the eluent absorbance by UV-vis (Figure 6d, x10 dilution), there was no MB in the excite solution checking wavelength at 664 nm. EY passed the column as CR. The cryogel colored with the weak interactions. The mixture of MB, GV, and 4-NP separation process given in the Figure 6(e-h). Figure 6c, the blue color (MB, GV) was at the top of the column and yellow color was at the bottom. Measured absorbance by UV-vis (Figure 6h, x6 dilution), there was no MB and GV in the excite solution checking wavelength at 664 nm for MB and 590 nm for GV. Maximum absorption wavelength at about 317 nm for initial 4-NP solution. After passing column the mixture 4-NP absorbance maximum was shifted as 400 nm because of deprotonation as shown Figure 5(e-h). As a result of the studies, it was predicted that this noncomposite embedded cryogel could be used both as a column filler material and successfully in the separation and purification of different materials.

4. CONCLUSIONS

In this work, PAN particles and TiO_2 dopped PAN composite particles were successfully synthesized by electrospraying technique adjusting the polymer concentration via electrospinning device, used needle tips, applied force/power and distance of between tip and the collector. Besides, super-porous cryogels were synthesized via cryogelation of pH responsive DMA monomer. The cryogel composite including the PAN/TiO_2 nanoparticle within polymeric matrices before cryogelation was prepared. New functional material was prepared by embedding the materials prepared with electrospray in cryogel. By combining the physical-chemical properties/application potential of the synthesized nanoparticles with the property/application potential of the super-porous cryogel, much more functional and positive composite structures have been formed. Both embedded particles in cryogel and cryogel have modifiable nature/structure, therefore both one will be tailored to special application. This prepared composite cryogels might have potential usages in separation and purification studies.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

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