

Preparation of Porous Nanofibers from Electrospun Polyacrylonitrile/ Calcium Carbonate Composite Nanofibers using Porogen Leaching Technique

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ABSTRACT: Production of nanofibrous polyacrylonitrile/calcium carbonate (PAN/CaCO₃) nanocomposite web was carried out through solution electrospinning process. Pore generating nanoparticles were leached from the PAN matrices in hydrochloric acid bath with the purpose of producing an ultimate nanoporous structure. The possible interaction between CaCO₃ nanoparticles and PAN functional groups was investigated. Atomic absorption method was used to measure the amount of extracted CaCO₃ nanoparticles. Morphological observation showed nanofibers of 270–720 nm in diameter containing nanopores of 50–130 nm. Monitoring the governing parameters statistically, it was found that the amount of extraction (ϵ) of CaCO₃ was increased when the web surface area (a) was broadened according to a simple scaling law ($\epsilon = 3.18 a^{0.4}$). The leaching process was maximized in the presence of 5% v/v of acid in the extraction bath and 5 wt % of CaCO₃ in the polymer solution. Collateral effects of the extraction time and temperature showed exponential growth within a favorable extremum at 50°C for 72 h. Concentration of dimethylformamide as the solvent had no significant impact on the extraction level. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Porous structures have recently gained a lot of attraction due to their versatile usability and high functionality.¹ For these types of materials, the typical dimension can be varied from a few nanometers to many micrometers. The elevation of the surface area to volume ratio earns the structure such unique properties that reserve their use for high technological applications. Recently, their presence in filtration industry, solid catalysts, membranes, tissue scaffolds, and drug delivery systems has been dominant.^{1,2} In related literatures, different techniques have been developed to produce porous materials of optimum structures.³ However, no major effort has yet been made to understand and control the pore formation mechanism.

Electrospinning is a versatile method for producing continuous fibers with diameters ranging from a few micrometers to a few nanometers.⁴ In this method, a suspended droplet of polymer solution or melt is charged at a sufficient voltage to overcome surface tension forces. As a result, fine jet of liquid is shot out from the needle tip toward a grounded target.^{5–7} The jet is

stretched and elongated before it reaches the target. The dried, interconnected web of fine fibers is then collected.⁸ The morphology of fibers depends on many material parameters such as polymer properties (molecular weight, molecular-weight distribution, glass transition temperature, and solubility) as well as solution properties (viscosity, viscoelasticity, volatility, surface tension, and electrical conductivity).⁶ Typically, electrospinning produces smooth fibers of circular cross section; nevertheless, it could be advantageous for a variety of applications provided that their surfaces are porous.⁹

Two approaches are possible to generate porous fibers with high overall porosity. Initially, solvents causing high degree of swelling can be used to increase fibers diameter. Following the removal of the swelling agent, porous structure remains. In the second approach, the removal of one of the two phases from a binodal or spinodal mixture is possible using a specific solvent. It has been shown that when a miscible solvent is used with a miscible polymer solution, highly porous fibers were formed due to phase separation.^{3,9} In these approaches, if the separation of polymer-rich and polymer-poor regions occurred following

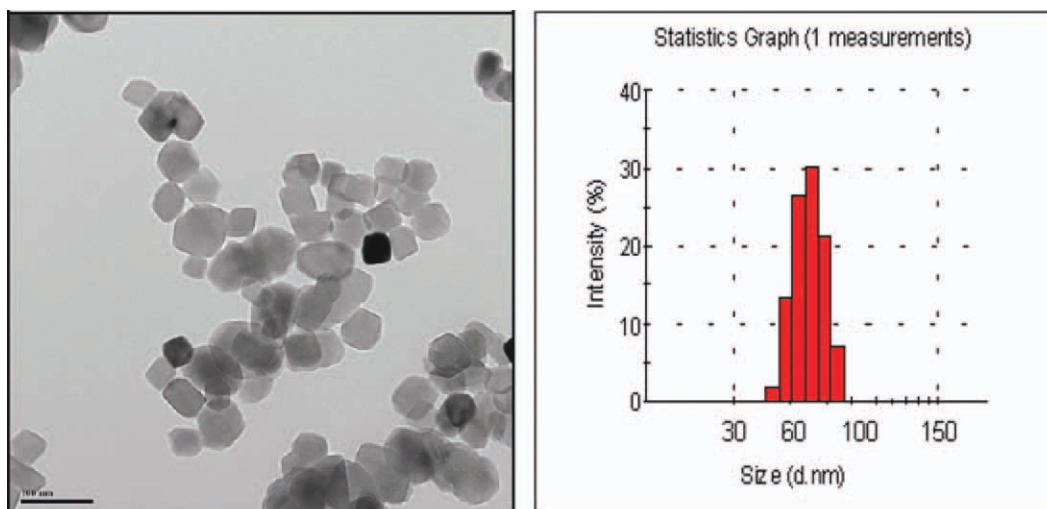


Figure 1. TEM image and statistical size distribution of CaCO_3 nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the evaporation of solvent, there would be a high probability for pores to be formed in the solidified poor region.^{5,9,10} Other researchers sought the same through fabrication of polymeric nanocomposites; a class of materials in which nanoscale particulate such as layered clays or spherical inorganic minerals are dispersed within polymeric matrices.^{11,12} The studies done on polyamide nanocomposite showed that coating agents like fatty acids caused the porogens to disperse uniformly.^{13–15} Porous polymeric membranes have also been produced by phase separation and leaching methods.^{16,17} Nanoporous ultrafine fibers of ultrahigh specific surface were developed for the first time using electrospinning-phase separation-leaching method by Xingsong et al.¹⁸ Alternatively, porous fibers could be produced through condensation processes during electrospinning in a very humid environment.¹⁹

An investigation on nanoporous fibers introduced their production by removing the poly(vinyl alcohol) (PVA) component of chitosan/PVA bicomponent fibers with NaOH.²⁰ Bognitzki et al.²¹ explained the use of volatile solvents such as dichloromethane to generate polymer fibers of regular pore structure. A facile method used to produce nanoporous carbon fiber is one in which a mixture of polyacrylonitrile (PAN), a copolymer of acrylonitril and methyl methacrylate [Poly(AN-co-MMA)] in dimethylformamide (DMF) is electrospun into submicrometer fibers with a microphase-separated structure. During the oxidation process, the copolymer domains are pyrolyzed, resulting in a nanoporous structure preserved after carbonization.²² Shastri and coworkers²³ used of the differences in polymer properties such as molecular weight, hydrophilicity or hydrophobicity, and degradation to induce preferential degradation of one phase in a biphasic polymer system.

In this research, nanoporous PAN nanofibers were produced through a solvent casting/porogen leaching technique. Calcium carbonate (CaCO_3) nanoparticles were extracted from PAN/ CaCO_3 nanocomposite webs. Chemical components of the electrospinning solutions were characterized and PAN/ CaCO_3

nanofibers were produced and leached in various conditions at different levels. Morphological observation of the fibers and pores was also carried out. Material and processing parameters which had presumably an effect on the generation of nanopores were investigated. The amount of extracted CaCO_3 nanoparticles was measured and used as a feedback to study such parameters. Exposed surface area of nanofibrous webs to extraction bath, leaching temperature and time, the percentage of the incorporated CaCO_3 , hydrochloric acid (HCl), and DMF concentrations were all regarded as controlling factors in this experimental design.

EXPERIMENTAL

Materials

DMF and HCl were obtained from Merck, Germany. Fatty acid-coated CaCO_3 nanoparticles were purchased from NanoTech, China. TEM image and statistical size distribution of CaCO_3 nanoparticles are shown in Figure 1. PAN ($M_w = 86,000 \text{ g mol}^{-1}$) powder was supplied by Polyacryl, Iran.

Casting Polymer/Nanoparticles Mixtures

Solutions with different concentrations of PAN in DMF (14 to 17 wt % with unit intervals) were prepared at 50°C and stirred for 6 h. Surface-modified CaCO_3 nanoparticles were placed in an oven at 100°C for 6 h. The dried nanoparticles were then stirred in DMF at 50°C for 12 h, building different concentrations of 1, 5, and 10 wt % dispersions (in three levels). The DMF/ CaCO_3 mixtures were gradually added to the already stirred PAN/DMF solution to have 15 wt % of solid content in the final solution (See Appendix). The resulting mixture was stirred at 50°C for another 18 more hours.

Electrospinning Setup

An adjustable high voltage power supply was used to produce a different electric potential up to 20 kV. Each solution was loaded into a 1 mL insulin syringe, where a positive electrode was clipped onto its 0.7 mm diameter needle to transfer the charge to the polymer solution. The flow rate of the

Table I. Levels of Governing Parameters and Their Units

Parameters	Levels		
	1	2	3
HCl (v/v%)	1	3	5
DMF (v/v%)	10	15	20
Area (cm ²)	81	144	225
Time (h)	48	72	96
CaCO ₃ (wt %)	1	5	10
Temperature (°C)	25	50	75

micropump was adjusted in a way that a pendant drop remained stable at the needle tip during the ejection. The condition of the processing parameters was adjusted as follows: a trajectory distance of 15 cm; 20 mL/h pump flow rate; and 17 kV of applied voltage. Solutions that were electrospun under this conditions had three mixing ratios of PAN/CaCO₃ (wt/wt) 99/1, 95/5, and 90/10.

Porogen Leaching Procedure

The extraction bath containing 1, 3, and 5% v/v of HCl (three levels) was prepared that was accompanied by deionized water with the purpose of extracting the CaCO₃ from the PAN bulk mass. Moreover, various proportions of DMF solvent were added to some solutions as a swelling agent 10, 15, 20% v/v (three levels). The extraction procedure was carried out in a bath equipped with magnetic stirrer at 25, 50, and 75°C for 2, 3, and 5 days according to Table I. The recovered nanofibrous webs were allowed to dry thoroughly.

Table II. Flame Conditions of Atomic Adsorption Test

Flame	Lean-blue
Fuel	Acetylene (~4 L/min)
Support	Air (~28 L/min)
Lamp current	20 mA
Burner height	10 Cm
Wavelength	422.7 nm
Silt width	0.7 nm
Ca lamp	Varian HCl
Delay time between reading	3 S.
Measurement time	2 S.
Replicate	3

Morphological and Analytical Assessment

Flame Atomic Absorption (Perkin Elmer 3030 model) with flame conditions shown in Table II. Fourier Transform Infrared (FTIR, BOMEM-M-B-100, Canada) were applied to evaluate the amount of extracted CaCO₃ nanoparticles. Scanning electron microscope (SEM Philips XL-30, Netherland), transmission electron microscope (TEM; CM200 FEG Philips, Field Emission Gun, Netherland), and electron detection angular X-ray (EDAX; E = 200KV, $\lambda = 0.002507$ nm, L = 300 nm, Camra Constant = 0.7521), which was attached to the TEM, were used for assessing the quality of the pores. Microtome (OMU3 Reichert, Austria) was used for preparing samples for the TEM. Matlab 2008 and SPSS (IBM Company, Chicago, IL) softwares were used for further mathematical quantification and modeling.

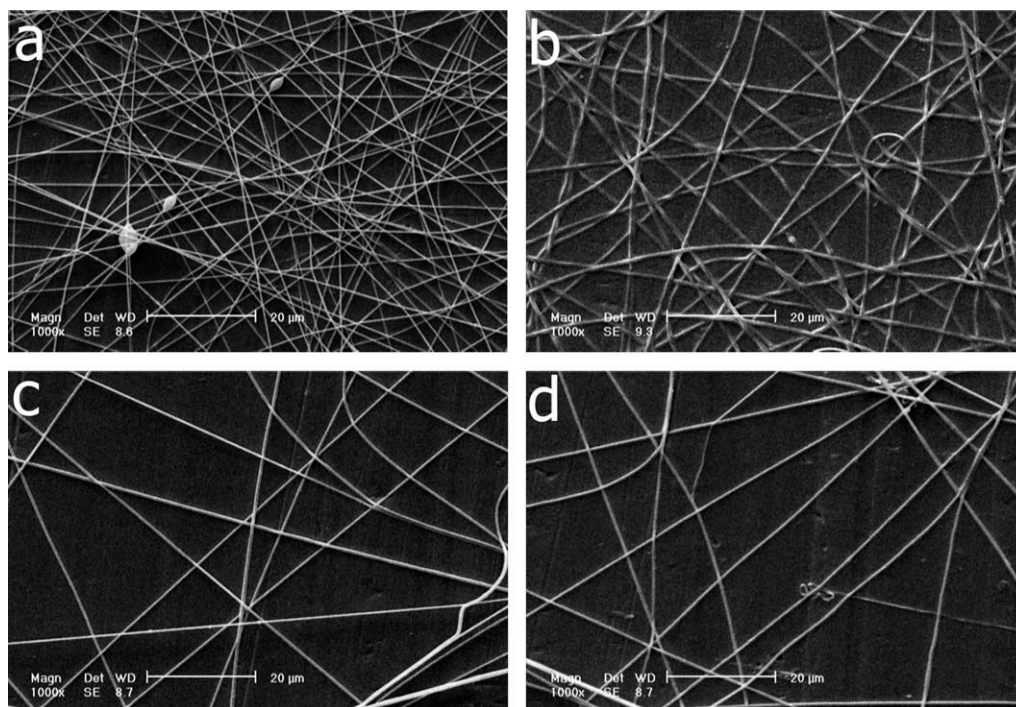


Figure 2. SEM images of PAN nanofibers with polymer concentrations: (a) 14 wt %, (b) 15 wt %, (c) 16 wt %, and (d) 17 wt %.

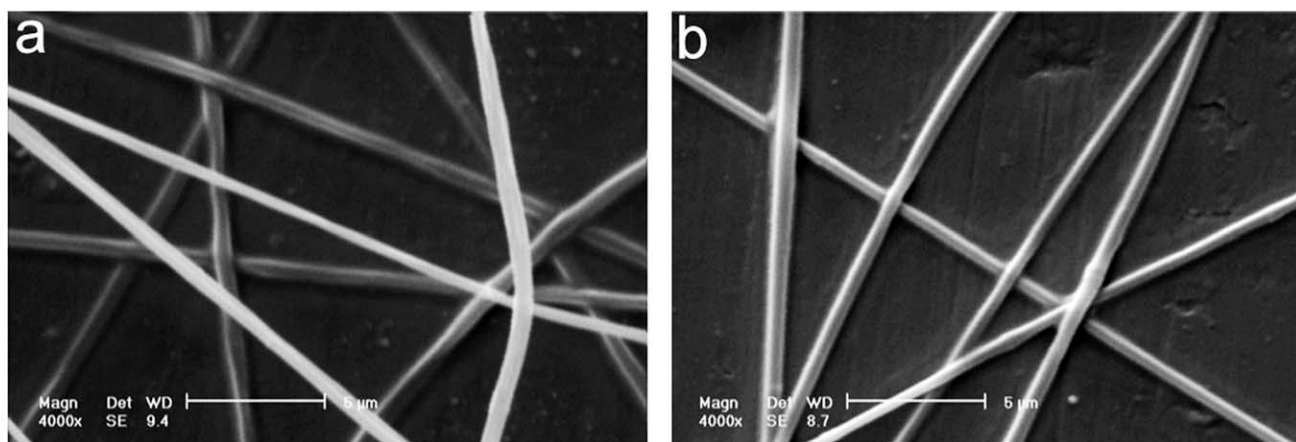


Figure 3. Smooth surface of as-spun nanocomposite nanofibers with 15 wt % contents of PAN and various amounts of CaCO_3 nanoparticles: (a) 5 wt % and (b) 10 wt %.

RESULTS AND DISCUSSION

Nanofibers SEM Evaluation

Figure 2(a–d) shows SEM micrographs of nanofibers obtained from different solution concentrations. This Figure shows that when polymer concentration was increased from 14 [Figure 2(a)] to 17 wt % [Figure 2(d)], the average diameters of the nanofibers were increased from 274 to 720 nm and the beads were progressively vanished. This inference was based on the measurements of more than 100 points on each SEM micrograph. Solutions with higher polymer content became unspinnable. Nanofibers obtained from 15 wt % solution were the finest and had the least beads. These nanofibrous webs were chosen for leaching of CaCO_3 nanoparticles. CaCO_3 nanoparticles were almost dispersed uniformly within the PAN bulk as was expected due to their preceding surface modification through stearic acid.^{24–26} Figure 3(a, b) illustrates the cylindrical smooth topography of as spun nanocomposite fibers with 15 wt % of PAN content and different amount of CaCO_3 contents [Figure 3(a), 5 wt % and Figure 3(b), 10 wt %] as the particles were in nanoscale. However, using additives to modify surface and bulk properties of materials is a well-known strategy to follow.

Spectroscopy Evaluation

FTIR was used for detecting and identifying compounds of PAN and elucidating molecular structure of CaCO_3 nanoparticles by measuring the radiant energy absorbed at the characteristic wavelengths of 400 to 4000 cm^{-1} . Figure 4 shows FTIR spectra absorbance versus wave number for CaCO_3 , PAN/DMF/ CaCO_3 mixture, and PAN/DMF solution. This figure illustrates that pick with wave length 878 cm^{-1} in fingerprint region, related to C=O bond in CaCO_3 , is only present in CaCO_3 and PAN/DMF/ CaCO_3 mixture spectra. Besides, there is no new pick in fingerprint region of PAN/DMF/ CaCO_3 mixture spectra, indicating that CaCO_3 has not reacted with DMF. If such an interaction existed, their bonding energy would need to be overcome for the purpose of extraction. As a result, HCl was properly chosen not only because of its ability to dissolve CaCO_3 nanoparticles but also for its inertness toward PAN macromolecules.

Morphological Observation

Figure 5(a, b) depicts SEM and TEM images of nonporous nanofibers, respectively, after the porogens (CaCO_3) were leached out from the bulk. As some pores are twice bigger than the mean nanoparticles size (70 nm), the possibility of minor agglomeration is acceptable. This phenomenon has been previously reported as a troublesome issue in preparing other nanocomposites as well. Relatively high surface area of such nanosized particles is held responsible for their tendency to agglomerate.¹² TEM cross-sectional image of porous nanofibers in Figure 6 reveals that no leaching has been taken place in cross-sectional area [absence of porosity]. Figure 7(a, b) indicates EDAX analysis of surface of pure PAN as shown in Figure 7(a) and the surface of pores of PAN/ CaCO_3 nanofibers as shown in Figure 7(b). The electron beam of EDAX is focused on the nanofibers surface and their pores.¹² EDAX analysis shows the presence of carbon element which exists in both PAN and CaCO_3 (Figure 7). Meanwhile, the absence of calcium element confirms through the extraction of facial porogens.

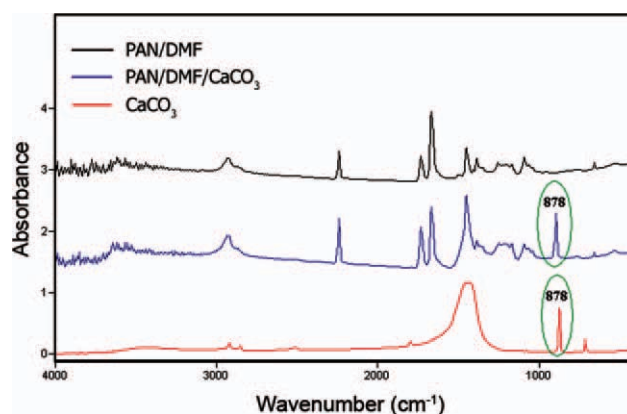


Figure 4. The FTIR spectra of CaCO_3 , PAN/DMF/ CaCO_3 mixture, and PAN/DMF solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

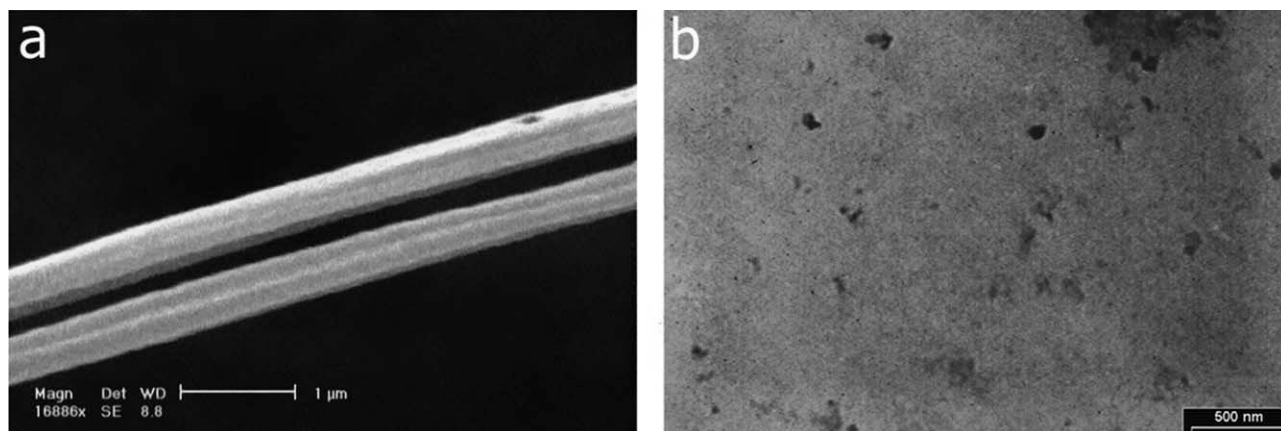


Figure 5. SEM and TEM images of 15 wt % polymer concentration nanofibers; (a) SEM image revealed a detected facial pore; (b) TEM image presented a longitudinal cut of a porous nanofiber with nanopores diameter of 50–110 nm.

Material Parameters

The amount of extraction is measured using gravimetry, titration, and atomic absorption spectrum. Gravimetric method is considered an improper technique to measure small quantities of extracted CaCO_3 particles as sensitive balances are needed. Practically, atomic absorption is judged as the most precise method capable of presenting smaller orders. The following results (See Figures 8–12) were based on averaging three repetitions of atomic absorption measurement of each specimen.

Figure 8 shows the extracted CaCO_3 percentage versus variation of material and processing parameters in three different levels (See also Table I). The bars represent the impact of various controllable parameters on the amount of the extracted CaCO_3 nanoparticles. The extraction bath temperature and the duration in which the leaching procedures are taking place as well as, the concentration of HCl, CaCO_3 , and DMF and surface area of nanofibers web are all assumed to be consistent. Nevertheless, their impact is comparable and of course unique in each case.

The amount of extraction (ϵ) is accelerated when the concentration of acid increased. HCl has no chemical influence on PAN and can rather dissolve CaCO_3 nanoparticles on the surface of the webs but not in depth. The surface area (a), which is exposed to the extraction bath, behaves in accordance with a simple scaling law ($\epsilon = 3.18 a^{0.4}$) which was driven using the curve-fit tool in Matlab 2008. Therefore, by increasing the web surface area, the extraction is increased due to the availability of more CaCO_3 nanoparticles and their stronger reaction with HCl. It is recognized that rising acid concentration from 3 to 5% v/v caused an increase of 73% in the extraction. Higher concentrations have a negligible effect on the extraction that could be due to the optimum strength of HCl and its dissociation constant in solution at 5 %v/v.²⁷

Figure 9 indicates how the extraction was influenced by the amount of CaCO_3 content and the concentration of HCl in the extraction bath. The effect of CaCO_3 on extraction is almost as linear as that of HCl concentration below its medium level. For a specified weight percent of PAN, the presence of more CaCO_3 nanoparticles led to a higher degree of extraction. As a matter

of fact, the probability of immigrated porogens to the surface was increased and their intensive reaction with HCl became inevitable.

The extraction is consistent regardless of DMF concentration in the extraction bath. Chemically, the presence of DMF (solvent) should cause the PAN nanofibers to swell and this would ease the emigration of CaCO_3 nanoparticles.^{28–30} However, the results implied that DMF is not as effective as it should be. Beyond swelling the PAN nanofibers, DMF provided a convenient environment for the CaCO_3 nanoparticles to agglomerate and remain in the bulk. Counteraction of swelling and aggregation phenomena resulted in the consistency observed in the extraction percentage. On the other hand, swelling phenomenon can obstruct the already available path for nonaggregated particles from being extracted. Figure 10(a, b), respectively, shows different conditions that particles experienced during the complex and controversial swelling and leaching phenomena. This picture schematically illustrates that the swelling of the surrounding bulk narrows the departure path and encompasses the particle tightly.

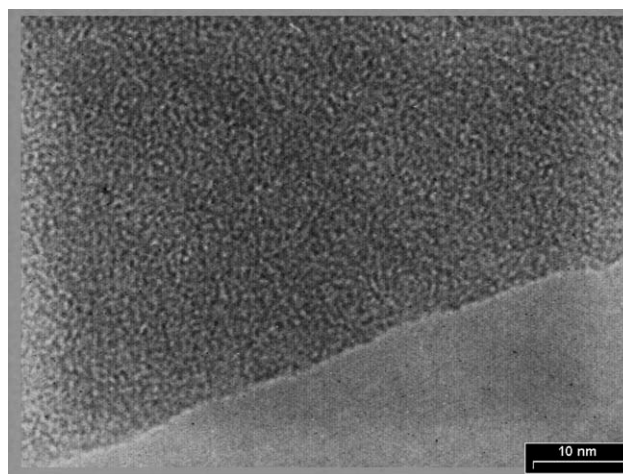


Figure 6. TEM cross-sectional image of porous nanofibers.

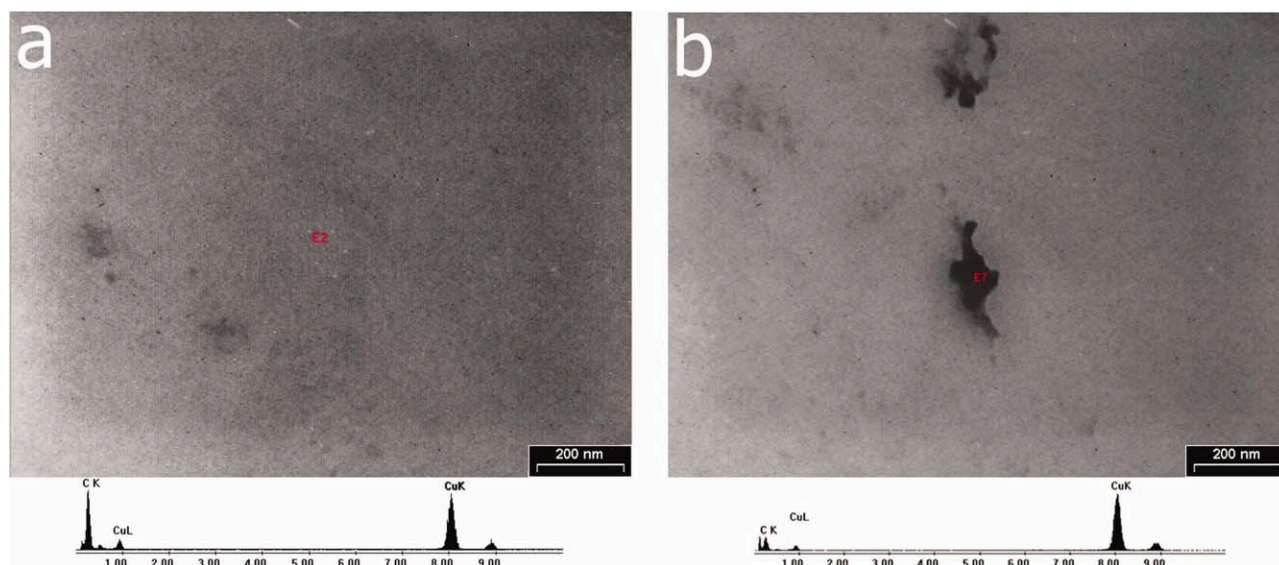


Figure 7. EDAX analysis of (a) the surface of PAN nanofibers; (b) the surface of pores of PAN/CaCO₃ nanofibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In reference to a Bronsted and lowry acid-base equilibrium theory, the dual exchange reaction between the HCl and CaCO₃ nanoparticles can be illustrated as equation shown below.³¹



In this reaction, the carbonic acid, which is a very weak of its kind, was produced. Hence, the reaction had the least tendency to proceed backward where the much stronger HCl had stood. Kinetically, the elevation of temperature speed up the entire reaction, accelerated the reactants consumption, and led to a higher degree of extraction; extraction at 75°C was twice the amount at 25°C (Figure 8). Raising the temperature turned out

to be a resistant factor due to the reaction exothermic nature that eventually hindered an earlier equilibrium state. Figure 11 represents the simultaneous effect of temperature and time on the extraction percentage. Within the first day of the leaching procedure, the extraction rate was accelerated by raising the temperature up to 50°C. In 72 h, this elevation still seemed effective but diminished. After 96 hours, not only raising the temperature was ineffective but also the extension of the extraction time could not elevate the extraction. It could be seen that raising temperature from 25 to 50°C increased the extraction up to 31.5 wt %. As a result, to optimize the energy consumption and time, the appropriate extraction condition was determined to be at 50°C and up to 3 days.

Statistical analysis presented the most and the least important factors, ranking them based on their significance. The more a

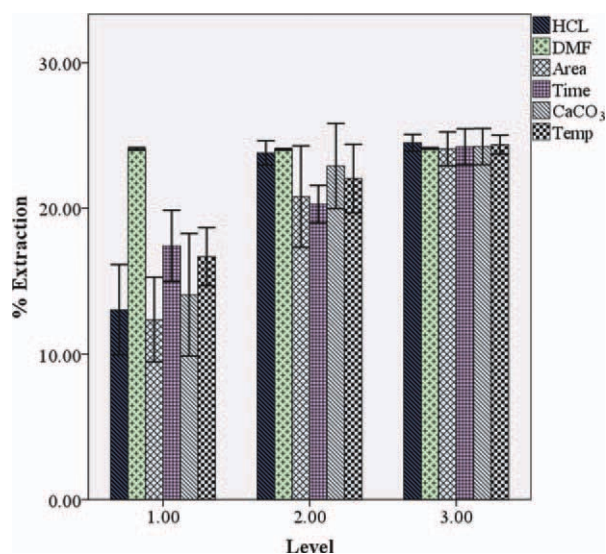


Figure 8. Changes in extracted CaCO₃ percentage by variation of material and processing parameters in three different levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

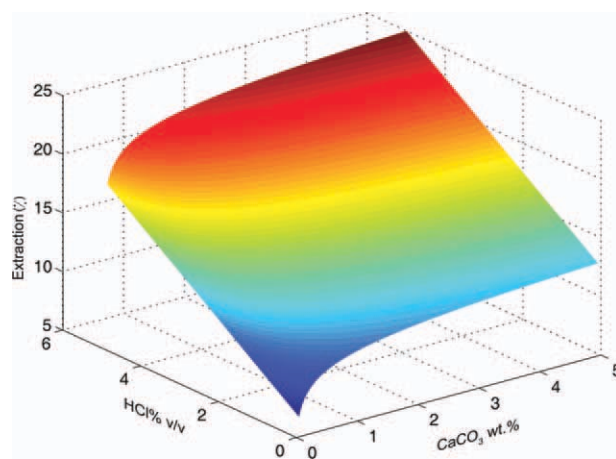


Figure 9. The effect of CaCO₃ content on extraction percentage and the concentration of HCl in the extraction bath by three-dimensional graph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

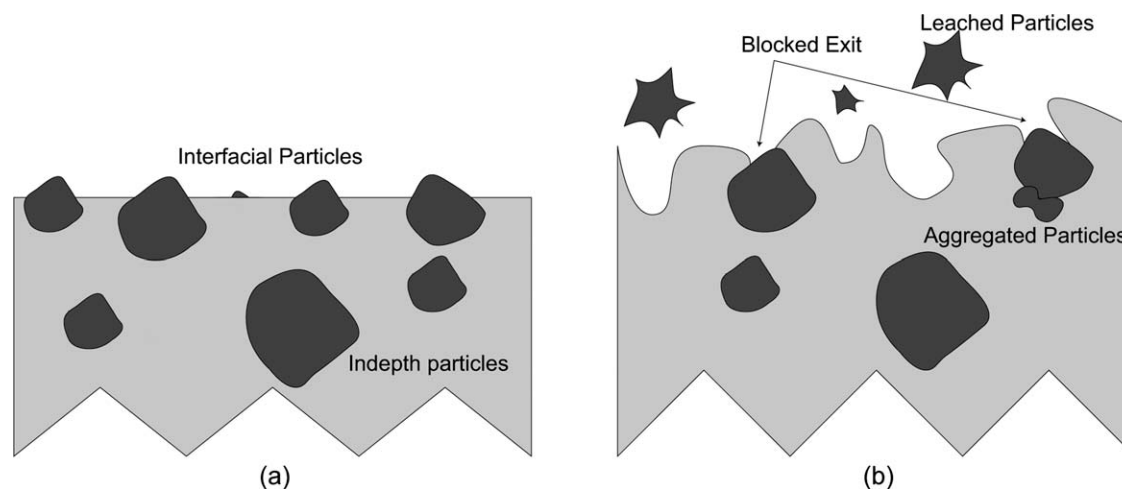


Figure 10. Different conditions that particles were experienced during the complex and controversial swelling and leaching phenomena; (a) before extraction, (b) after extraction.

parameter can influence the amount of extraction within the confined condition of levels, the more it was known to be dominant among the others; this is illustrated using box-plots diagrams in SPSS. Figure 12 shows the impact of governing parameters and their relative significance on the amount of leaching process. This figure illustrates that how minimum, medium, and maximum level of each parameter has to do with the amount of extraction. In order of relative significant they are the surface area, HCl concentration, temperature, time and CaCO_3 , and DMF concentration in extraction bath.

CONCLUSION

It is favorable to have a complete control over the porogen leaching process to produce a porous structure especially when it comes to nanoporous nanofibrous webs. There are different applications that require materials with maximized surface to volumes ratio. In this research, porous nanofibers of polyacrylonitrile are produced from its nanocomposite with CaCO_3

carbonate nanoparticles using a well-characterized and optimized porogen leaching technique. The produced nanofibers had a diameter of 274–720 nm with an average pore size of about three times larger than that of the nanoparticles. Among various concentrations, nanofibrous webs obtained from 15 wt % PAN solution were the finest ones that had the lowest number of beads. Atomic absorption method, because of its highest precision, was assigned to calculate the amount of extracted porogens. Exposed surface area, HCl concentration, temperature, time, CaCO_3 , and the DMF content were all considered as controllable parameters with respect to their impact on the extraction percentage. TEM analyses show only the presence of carbon element in the pores; an indication of a successful extraction. Finally, 5 wt % of acid concentration, 144 Cm^2 of web surface area, 72 h of extraction in a 50°C bath, and a CaCO_3 concentration of 5 wt % were found to be the most appropriate conditions for the porogen leaching of PAN/ CaCO_3 nanocomposite nanofibrous webs.

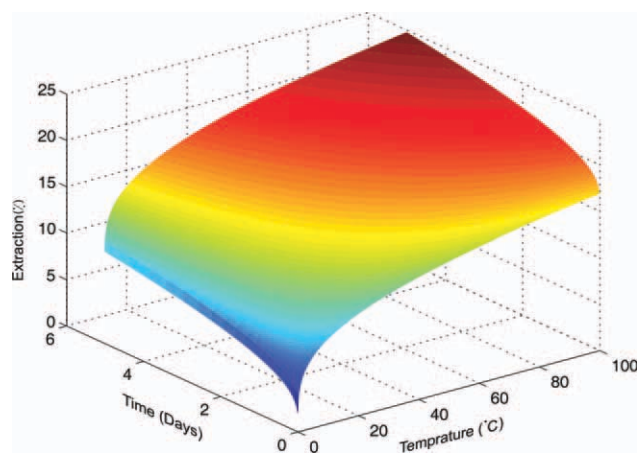


Figure 11. The simultaneous effect of temperature and time on the extraction percentage in a three-dimensional diagram. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

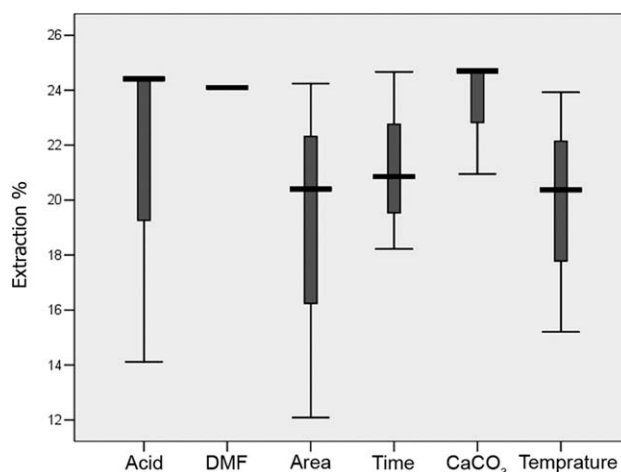


Figure 12. The impact of governing parameters and their relative significance on the amount of leaching process.

APPENDIX

An example of a calculation for producing 2 g of final solution with 15 wt % of solid content in which the mixing ratio of PAN/CaCO₃ (wt/wt) was 95/5:

Solid content's weight: 2 g final solution \times 0.15 = 0.3 g

CaCO₃ weight: 0.3 \times 0.05 = 0.015 g

PAN weight: 0.3–0.015 = 0.285 g

DMF weight: 2–0.3 = 1.7 g

S1: 0.015 g CaCO₃ + 0.485 g DMF = 0.5 g

S2: 0.285 g PAN + 1.215 g DMF = 1.5 g

Final solution (S) = S1 + S2 = 0.5 + 1.5 = 2 g

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