

Full Length Research Paper

Fabrication and evaluation of multiple template cross-linked molecularly imprinted electro spun nanofibers for selective extraction of nickel and vanadyl tetraphenylporphyrin from organic media

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A nickel vanadyl molecularly imprinted nanofiber (NVMIN) was developed by the electrospinning technique, employing polyethylene terephthalate (PET) and linear polyethylenimine (L-PEI) as the matrix polymers, nickel tetraphenylporphyrin (NTPP) and vanadyl tetraphenylporphyrin (VTPP) as the mixed-template molecules. The fabricated NVMIN was evaluated as a sorbent for the removal of NTPP and VTPP from organic media. The effects of trifluoroacetic acid (TFA), dichloromethane (DCM), dimethyl sulphoxide (DMSO), pentane (PEN) on electro-spinnability of the PET/L-PEI solutions and the morphological appearance of the PET/L-PEI fibers were investigated qualitatively by means of a scanning electron microscope (SEM). Electrospinning of 14 to 30% w/v PET/L-PEI solutions in TFA produced beaded and smooth fibers, depending on the concentration range. The addition of DCM and PEN as modifiers helped improve the electrospinnability, with PEN being the best, while the addition of DMSO made the solutions not spinnable. The results indicated that the NVMIN showed higher affinity (99% higher) for NTPP than the non-imprinted nanofiber (NIN) indicating that the NVMIN contained a lot of specific binding sites. It was determined that the NVMIN exhibited the same selectivity specialism for both NTPP and VTPP. However, the interaction strength was strongly dependant on the type of solvent, where the strongest interaction was achieved in chloroform. In addition, the thermodynamic parameters calculated from the adsorption data suggested that the adsorption of NTPP onto NVMIN was a spontaneous and exothermic process.

Key words: Electrospinning, mixed-templates, adsorption, demetallation, solvents.

INTRODUCTION

The global increase in unconventional crude oil resources in recent years has resulted in increasing quantities of

sour crudes, acidic crudes, or extra heavy crudes being produced (Zhang, 2002). These crude oils contain a large

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variety of metal compounds with vanadium and nickel being the major metals. For example, Cantarell crude oil contains more than 243 µg/g vanadium and nickel, Tahe crude oil has more than 400 µg/g, and Bolivar Coastal crude oil from Lake Maracaibo, Venezuela also has excess of 1200 µg/g of these metals (Xu et al., 2001).

Nickel and vanadium are present in heavy oils, forming porphyrinic structures, and they pose a particular problem for refineries as the metals accumulate as contaminants on catalysts, where they cause permanent deactivation of both desulfurization and cracking catalysts, resulting in serious economic losses (Ware et al., 1985; Welter et al., 2009; Dechainet et al., 2010; Nakamoto et al., 2004). In addition, both nickel and vanadium promote dehydrogenation reactions during cracking sequence, which result in an increase in the amounts of coke and dry gas, thus leading to a decrease in gasoline production (Li, 2001). Therefore, refining such crude oils is a significant challenge for petrochemical processing. Most inorganic metals in crude oil can be removed by electric desalting, but vanadium and nickel organic compounds are oil-soluble and cannot be removed by this method (Xu et al., 2001).

Several techniques have been utilized for the removal of nickel and vanadium from crude oils (Reynolds, 2004). Among these techniques, chemical processes have been commonly used because of their effectiveness; these include hydro-demetalization (Long et al., 2003) and solvent extraction (Mohammed et al., 2006). However, the removal of metal by hydrogenation requires high capital investment and the catalysts for the process are difficult to regenerate, therefore affecting the disposal of waste catalysts. Solvent extraction is suitable only for residues containing the high bitumen content, and its capital and operational costs are high (Shuangchen et al., 2011). Because of these limitations, much better technologies have to be considered.

Molecular imprinting technology (MIT) is a dynamic methodology used to design polymeric receptors against a wide range of target molecules. It was first reported in 1949 by adsorbing different dyes in silica (Mosbach, 2006; Alexander et al., 2006). Originally, it was introduced as a means to create binding sites in synthetic polymers. The technique has now matured and has become established in several disciplines owing to its ability to form stable, robust materials with molecular selectivity for a wide variety of compounds. MIT is based on the formation of a complex between an analyte (template) and a functional monomer. In the presence of a large excess of a cross-linking agent, a three-dimensional polymer network (Ramstrom et al., 1999) is formed. Removal of the template from the formed polymer liberates binding sites with selectivity toward the template molecule. In most of the accounts of MIT, a single template molecule is used to create the specific binding site of the imprinted polymer (MIP). However, the imprinting process does not have to be limited to a single template, and several compounds can be imprinted

simultaneously (Scheme 1). Advantages of multiple-template imprinting are that several different classes of compounds can be extracted, separated, assayed, detected, or otherwise analyzed at one time (Schweitz et al., 2002; Spegel et al., 2003; Sreenivasan et al., 2007; Suedee et al., 2004). A few examples have been reported on different MIP polymers or polymer mixtures that have been imprinted with more than one template. The first example was reported by Sreenivasan and Sivakumar (Sreenivasan et al., 1999), who imprinted both salicylic acid and hydrocortisone in the same MIP formulated with hydroxyethylmethacrylate (HEMA) as the functional monomer and ethylene glycol dimethacrylate (EGDMA) as the crosslinker. Dickert et al. (2001) described the idea of double "molecular imprinting" using two templates that were simultaneously imprinted in a crosslinked polyurethane thin film.

Although MIPs with multiple templates might have been prepared by many researchers, to the best of our knowledge, there is still no published report with respect to the preparation of multiple templates imprinted nanofibers and their application in organic media.

In this study, we sought for a wider selection of solvent systems and utilized the versatile electrospinning technique to fabricate nickel vanadyl molecular imprinted nanofibers (NVMIN), in which functional macromolecules poly(ethyleneterephthalate) (PET) and linear-polyethylenimine (L-PEI) were chosen as matrix polymers, styrene was used as a functional monomer, divinyl benzene as cross-linker, nickel tetraphenylporphyrin (NTPP) and vanadyltetraphenylporphyrin (VTPP) as template molecules (Figure 1). The fabricated NVMIN showed preponderant adsorption capacity and selectivity compared to non-imprinted nanofibers (NIN). The prominent performance of the NVMIN illustrated its potential as a flexible, variable and selective sorbent that is well suited for handling trace metals in organic media.

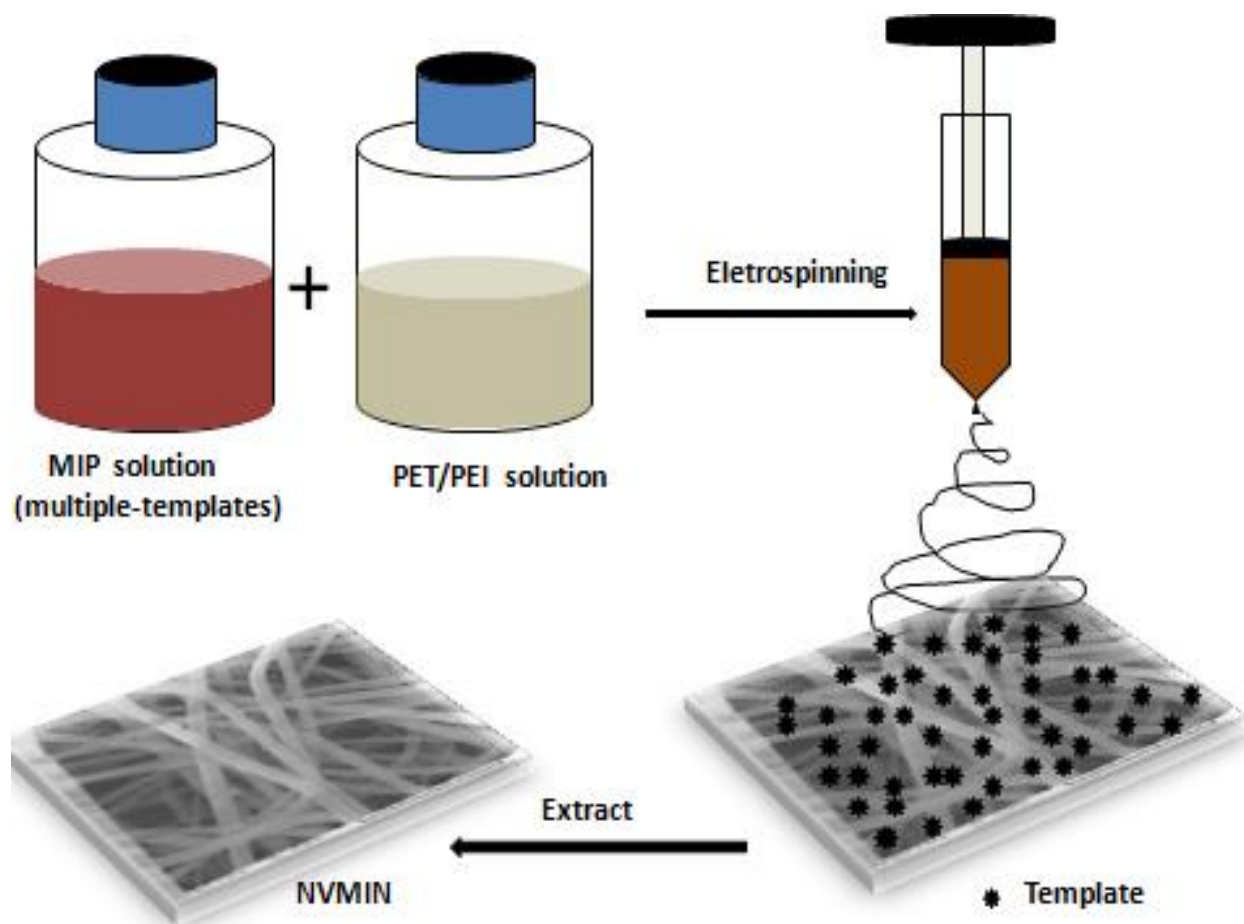
METHODOLOGY

Chemicals

Linear-polyethylenimine with M_w of 250000 g/mol was purchased from PolySciences Inc. (Warrington, PA). Styrene, divinyl benzene (DVB), nickel tetraphenylporphyrin, vanadyltetraphenylporphyrin, 1,1 azobis(cyclohexanecarbonitrile)(ACC), chloroform, methanol (MeOH), poly(ethylene terephthalate), trifluoroacetic acid (TFA), dichloromethane (DCM), dimethyl sulphoxide (DMSO), pentane (PEN) and acetic acid were supplied by Sigma-Aldrich (Johannesburg, South Africa) and used as obtained. All the chemicals used were of analytical grade. The properties of these solvent and the modifying liquids are summarized in Table 1.

Preparation of NVMIN solution

The method of nanofiber fabrication as described by Awokoya et al. (2013) was employed for the fabrication of NVMIN fibers. Poly(ethylene terephthalate)/Linear-Polyethylenimine solutions were prepared by adding equal quantities of PET and L-PEI in TFA



Scheme 1. NVMIN fabrication in the presence of multiple templates for multi-analyte binding.

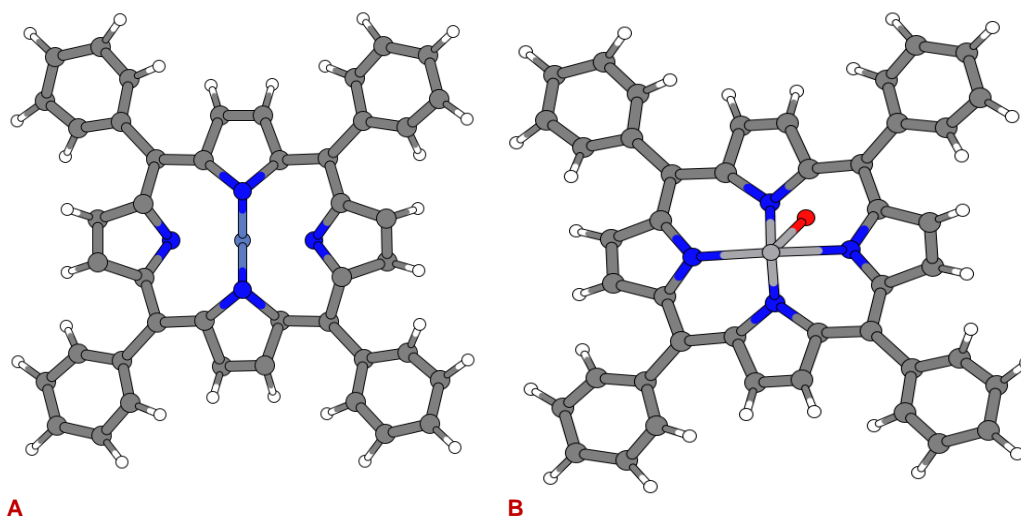
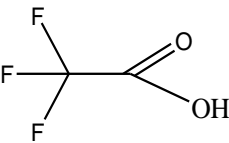
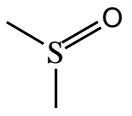
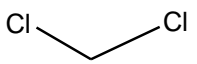



Figure 1. Molecular structures or geometries of (A) NTPP and (B) VTPP.

and some mixed solvent systems of TFA and another solvent or liquid (that is, DMSO, DCM, and PEN) in various compositional ratios. Precisely, the compositional ratios of TFA and DMSO

were 90:10, 80:20, 70:30, 60:40 and 50:50 v/v, while the compositional ratios of TFA and another liquid (that is, DCM and PEN) were 98:2, 95:5, 93:7 and 90:10 v/v, respectively. The

Table 1. Properties of solvents used in this work (25°C)^a

Solvent	Structure and molecular weight	Density (g.cm ⁻³)	Viscosity (10 ⁻³ Pa.s)	Boiling point (°C)	ε- Dielectric constant	Surface tension (10 ⁻³ J/m ²)
Trifluoroacetic acid (TFA)	 114.02	1.49	0.813	72.4	8.55	13.63
Dimethyl sulphoxide (DMSO)	 78.13	1.096	1.996	189.0	46.7	43
Dichloromethane (DCM)	 84.93	1.317	0.423	39.8	8.9	27.2
Pentane (PEN)	 72.15	0.626	0.34	36.1	1.84	15.48

^aSources: <http://www.solvaychemicals.com>; <http://www.trimen.pl/witek/ciecze/liquids.html>.

Table 2. Electrical conductivity, viscosity, surface tension and fiber formation of PET/L-PEI in TFA.

Solution concentration (% w/v)	Electrical conductivity (μS.cm ⁻¹)	Viscosity (cP)	Surface tension (mN.m ⁻¹)	Fiber formation
14	180.6	385	74.90	Beads
16	191.2	513	74.38	Fused beads
18	230.4	621	73.85	Beads
20	241.3	1207	69.63	Fiber and beads
22	245.2	1475	68.58	Fiber and beads
24	304.2	1699	66.47	Fiber and beads
26	315.4	2800	64.36	Fused smooth fiber
28	332.2	3300	62.94	Fused smooth fiber
30	594.0	4000	61.19	Smooth fiber

solutions of PET/L-PEI in TFA were prepared in various concentrations ranging from 14 to 30% w/v, whereas those of PET/PEI in mixed solvent system were fixed at the concentration of 22% w/v, with continuous agitation in a closed vial for 5 h at room temperature. The solution of molecularly imprinted polymer containing cross-linker, monomer and the templates in chloroform was blended into PET/PEI solutions and stirred overnight (Scheme 1). Prior to electrospinning, all of the as-prepared solutions were measured for their surface tension, shear viscosity, and electrical conductivity (Table 2) by a KRÜSS School Tensiometer K6, a Brookfield Digital viscometer Model DV-1+(at 5.0 RPM), and a Mettler Toledo FE 30/EL 30 conductivity meter, respectively.

Electrospinning process

The resultant homogeneous solution was placed in a 20 ml disposable plastic syringe driven by a piston syringe pump, NE-1000, Farmingdale, (NY, USA). The positive electrode of a high voltage supply was applied to the metal spinneret (0.5 mm) tip of the syringe. The applied voltage used for the electrospinning was 15 kV, and the tip to collector distance was 13 cm. The entrapped template molecules (NTPP and VTPP) were removed from the resultant nanofiber by MeOH and acetic acid (90:10) until no NTPP and VTPP were observed to leach from the fiber using ICP-OES. Figure 2 shows the removal of NTPP and VTPP from the nanofiber

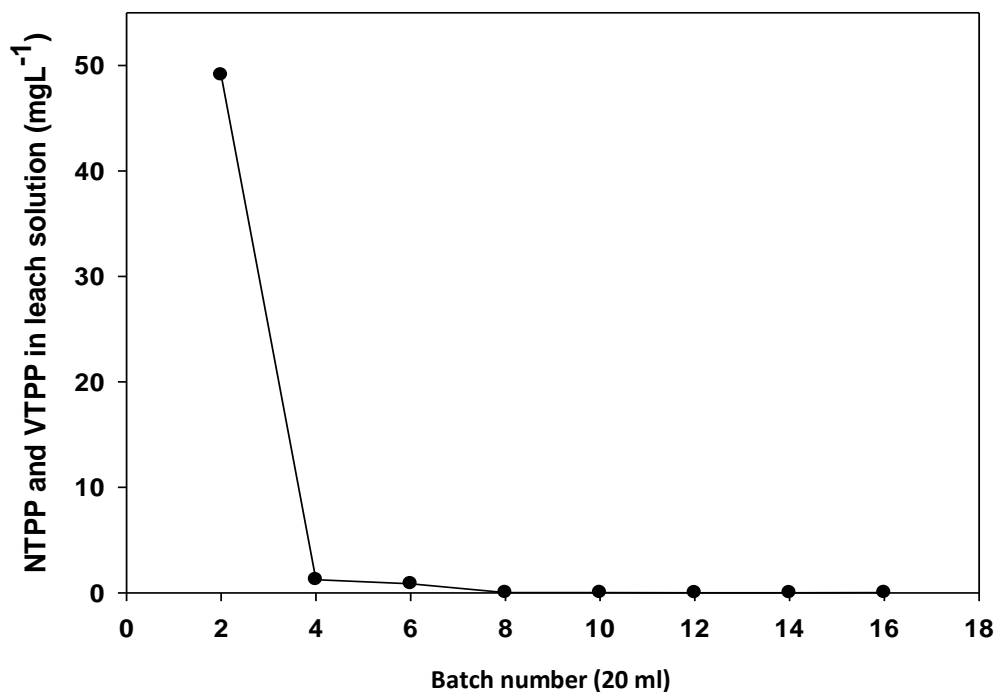


Figure 2. Removal of NTPP and VTPP in successive batches.

in successive batches. The electrospun fiber mat was dried under vacuum at room temperature to remove the trace solvents and kept in a desiccator until analysis. As a control, non-imprinted nanofibers (denoted as NINs) were prepared following the same procedure without NTPP and VTPP as templates.

Scanning electron microscopy (SEM)

To determine the surface morphology of the NVMIN and NIN, the nanofiber mats were taken and dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using VEGA TESCAN SEM instrument. Energy dispersive X-ray spectroscopy (EDX) (INCAPentaFETx3Oxford ISIS EDS) was used to observe the chemical composition of products.

FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of non-imprinted and molecularly imprinted nanofibers were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an AutoIMAGE System.

Adsorption experiment

The adsorption experiment was carried out on a mechanical shaker at room temperature by adding an optimal quantity of the washed NVMIN (30 mg) into 20 ml volume of NTPP solution which was prepared in chloroform varied in the concentration of 10 to 50 mg L⁻¹ at 15, 25, and 35°C to study the thermodynamics of adsorption. After shaking for 6 h, NVMINs were centrifuged at 12,000 rpm for 5 min, from which a 15 ml supernatant was collected for the determination of free analyte by ICP-OES. Three replicate

extractions and measurements were performed for each solution. The extraction percentage of NTPP was calculated from equation 1:

$$\text{Extraction (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Where C_i is the initial NTPP concentration (mg L⁻¹), C_f is the NTPP concentration at adsorption equilibrium (mg L⁻¹).

Selectivity of the NVMIN

The selectivity of the NVMIN was conducted by immersing the NVMIN into chloroform solutions containing NTPP and VTPP at room temperature, respectively. The recognition coefficient (α) was used to evaluate the selectivity (Yang et al., 2005) and could be calculated using equation 2:

$$\alpha = \frac{[S]_{(\text{imprinted})}}{[S]_{(\text{non-imprinted})}} \quad (2)$$

Where $[S]_{\text{imprinted}}$ is the DBT binding amount to the MIP (mg g⁻¹), and $[S]_{\text{non-imprinted}}$ is the binding amount to the NIP (mg g⁻¹).

RESULTS AND DISCUSSION

Effects of a single solvent system on the general spinnability characteristics of NVMIN

PET/L-PEI dissolved easily in TFA and formed a clear homogenous solution at room temperature without any precipitates and air bubbles, while in solvents such as

DMSO, DCM and PEN PET/L-PEI did not dissolved. The nickel vanadyl PET/L-PEI solutions in pure TFA were prepared at various concentrations ranging from 14% (w/v) to 30% (w/v) to investigate the effect of the solution concentration on morphology of the fibers. As is known, electrospinning is a technique that utilizes the electric force to drive polymer fluid and to produce polymer nanofibers. The shear viscosity, electrical conductivity, and surface tension of the polymer solution are the most important properties affecting the formation of nanofibers (Bhuvanesh et al., 2007).

The increase in solution concentration could adversely affect the cohesiveness of the liquid/air interface, thus leading to the reduction in the surface tension of the solution. On the other hand, both the viscosity and electrical conductivity of the solutions were found to increase. The increase in the solution viscosity could be explained by the fact that the increased polymer mass fraction in the solution led to the increase of the entangled actions of polymer molecule chains, which facilitated the formation of the electrospun nanofibers. The increase in the solution electrical conductivity with increasing solution concentration could be due to hopping of charged species between conducting polymer chains resulting from the dissolution of PET/L-PEI in the acidic condition of the solutions (Schmidt et al., 2012).

The SEM images of electrospun nanofibers with pure TFA are shown in Figure 3. For solution concentration less than 18 %, droplet spray occurred and a continuous jet of polymer, that is spinning was not formed. The jet from low viscosity solutions breaks up into droplets due to the lower amount of polymer and lower entanglement density than that needed to form a stable jet. With solution concentration between 20 and 24% w/v, the presence of beads was observed. However, the beads completely disappeared and the formation of finer and more uniform electrospun fibers were observed as the concentration of the solution was increased to 26, 28 and 30% w/v. It is believed that the combination of the relatively high viscosity of the solution and dielectric constant of the solvent (that is, 8.55, Table 1) improved the morphology of the fiber.

Mixed-solvent systems

The second solvent was mixed with TFA, so as to qualitatively observe the effects of solvents on electrospinnability of the as-prepared PET/L-PEI solutions and the morphological appearance of the obtained PET/L-PEI fibers. Based on the results obtained on the single solvent system, 22% w/v of the PET/L-PEI solution was chosen to further investigate the effect of the mixed-solvent systems because the viscosity of the solution at the particular concentration in TFA was high enough to allow the formation of fibers with less beads. Another important reason for choosing 22% w/v was to observe whether the addition of the second solvent was

able to totally suppress the formation of beads.

Trifluoroacetic acid and dimethyl sulphoxide

The morphology of the as-prepared fibers from the PET/L-PEI solutions in mixed solvents of TFA and DMSO are shown in Figure 4. The DMSO was mixed with TFA to produce the mixed solvent at the compositional ratios of 95:5, 93:7, 90:10, and 80:20 v/v (TFA/DMSO), respectively. Judging from the high dielectric constant value (Table 1) of the DMSO solvent, the PET/L-PEI solutions in TFA/DMSO should have been readily spinnable. However, it was not the case, as the solutions were not spinnable in every ratio prepared. It was observed that, upon spinning, the solutions jetted out rather easily, but the ejected streams of the solutions did not form into fibers. The most likely explanation might be as a result of the extremely high boiling point of DMSO (that is, 189°C) that caused the ejected streams to stay in the liquid form even after being collected on a collective target.

Trifluoroacetic acid and dichloromethane

The morphology of the as-prepared fibers from the PET/L-PEI solutions in mixed solvents of TFA and DCM are shown in Figure 5. The DCM was mixed with TFA to produce the mixed solvent at the compositional ratios of 95:5, 93:7, 90:10, and 80:20 v/v (TFA/DCM), respectively. At 95:5 ratio, a large amount of beaded fiber was obtained. Interestingly, the increase in the quantity of DCM in the solvent mixture increased the thinning of the jet and the fiber formed appeared to be smaller than those from the solution in pure TFA.

Trifluoroacetic acid and pentane

The morphology of the as-prepared fibers from the PET/L-PEI solutions in mixed solvents of TFA and PEN are shown in Figure 6. The PEN was mixed with TFA to produce the mixed solvent at the compositional ratios of 95:5, 93:7, 90:10, and 80:20 v/v (TFA/PEN), respectively. In comparison with PET/L-PEI solutions in TFA, TFA/DMSO, and TFA/DCM, the electrospun PET/L-PEI nanofibers using TFA/PEN as mixed solvent were continuous and smooth without any beads or droplets on the surface, indicating excellent electrospinnability of the PET/L-PEI solutions in TFA/PEN mixed solvent. It might be caused by the low boiling point and low surface tension of PEN solvent (Table 1).

Characterization of NVMIN

In order to get more structural information and understand the adsorption mechanism of the NVMIN, an energy dispersive X-ray spectrometer (EDS) was used to

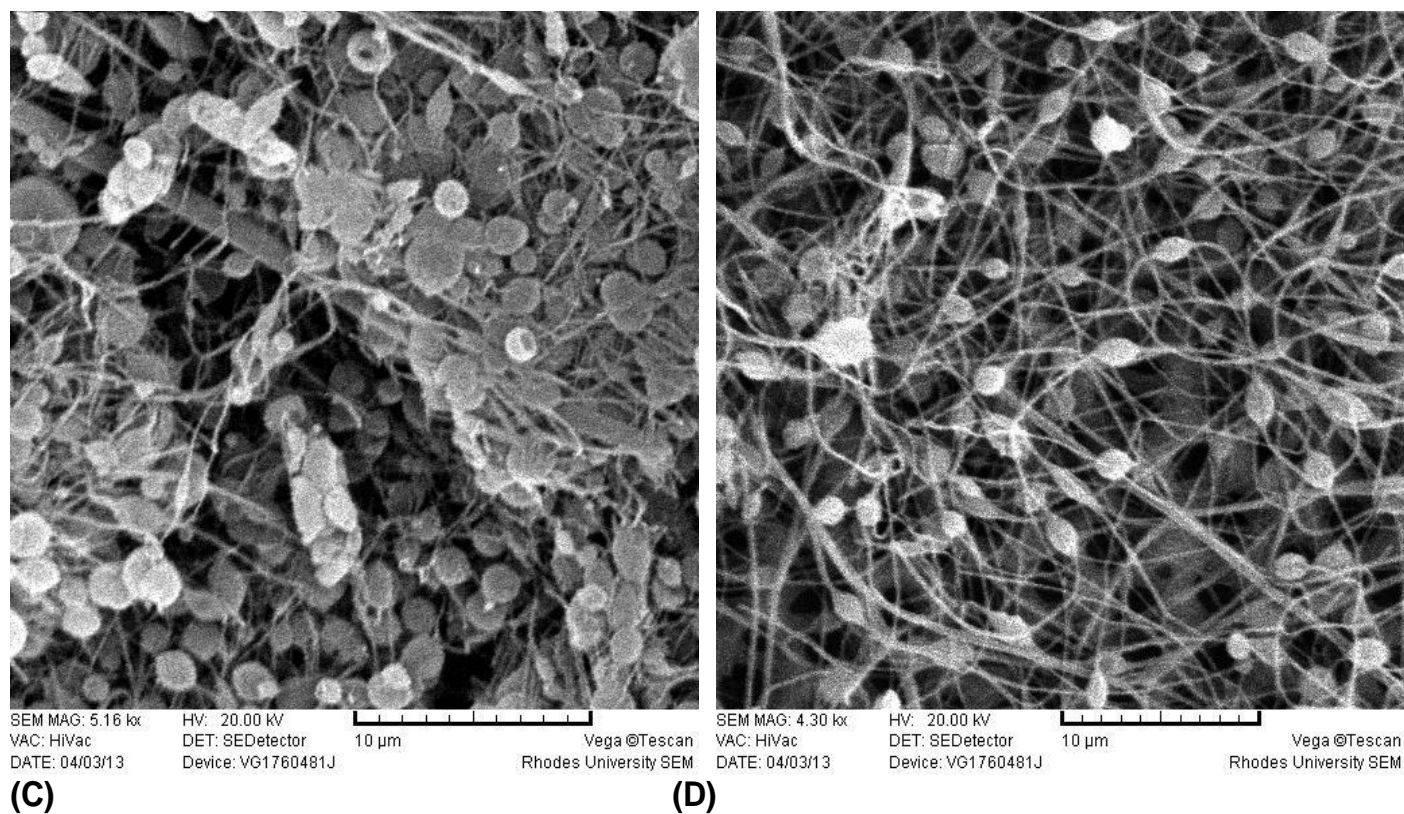
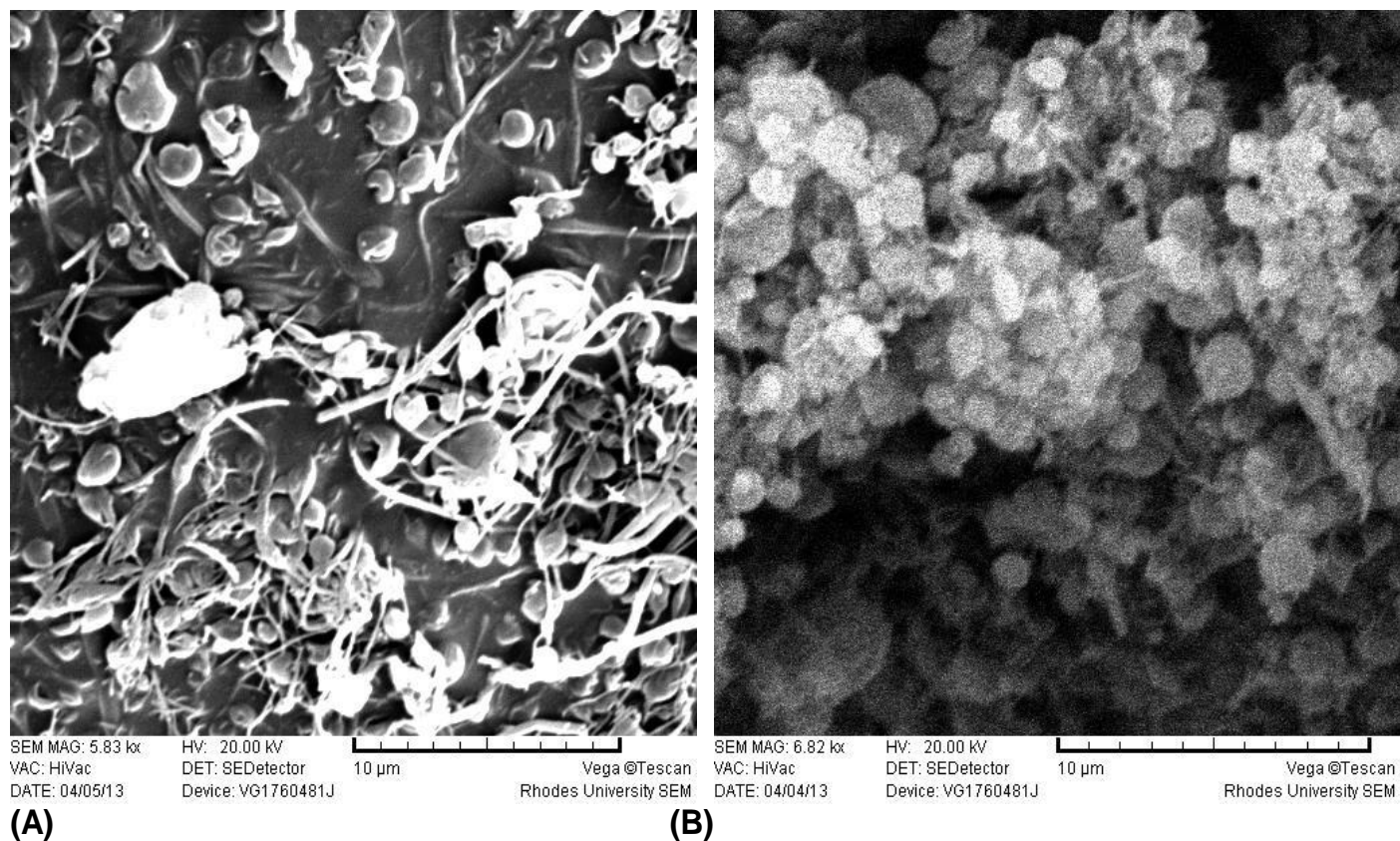
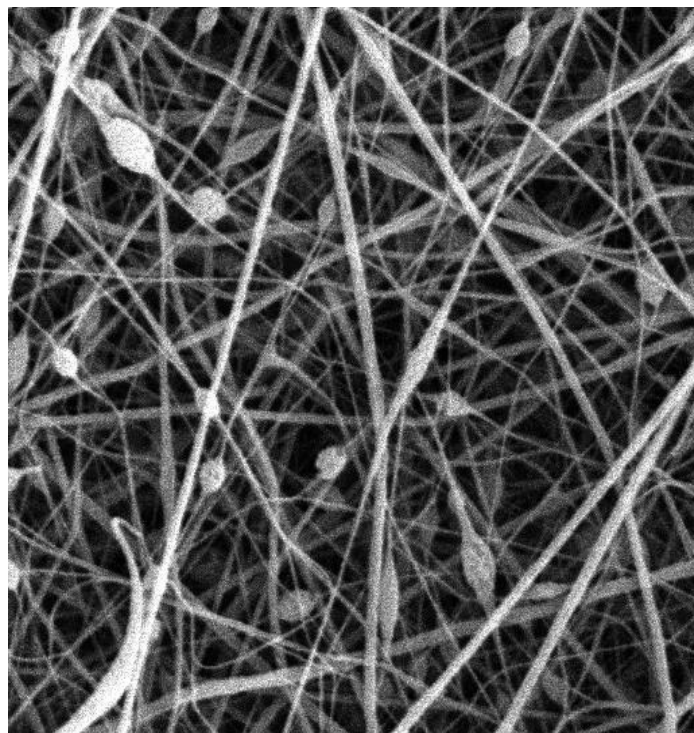
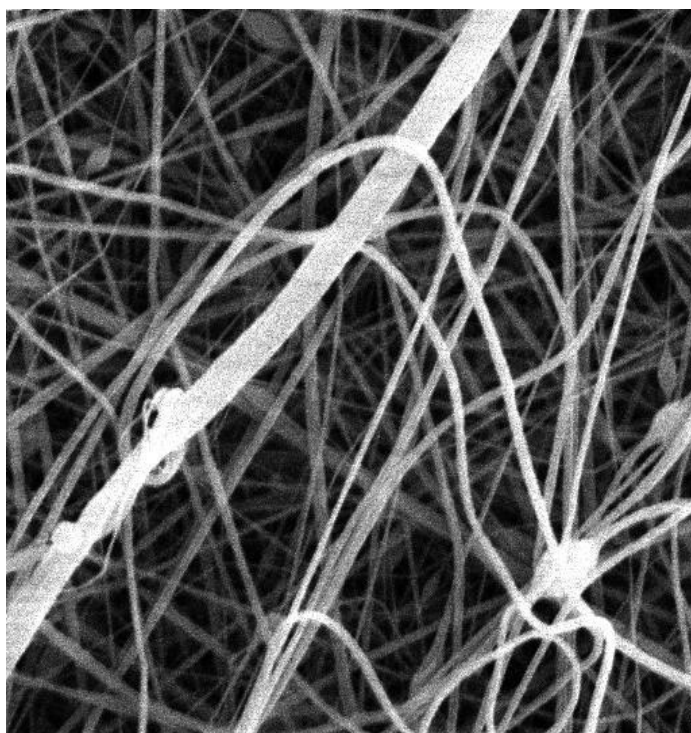


Figure 3a. SEM images (scale bar = 10 µm) showing the morphology of fibers electrospun from PET/L-PEI solutions in TFA, at concentration of (A) 14, (B) 16, (C) 18, (D) 20% w/v (voltage of 15 Kv and at a constant spinning distance of 13 cm).



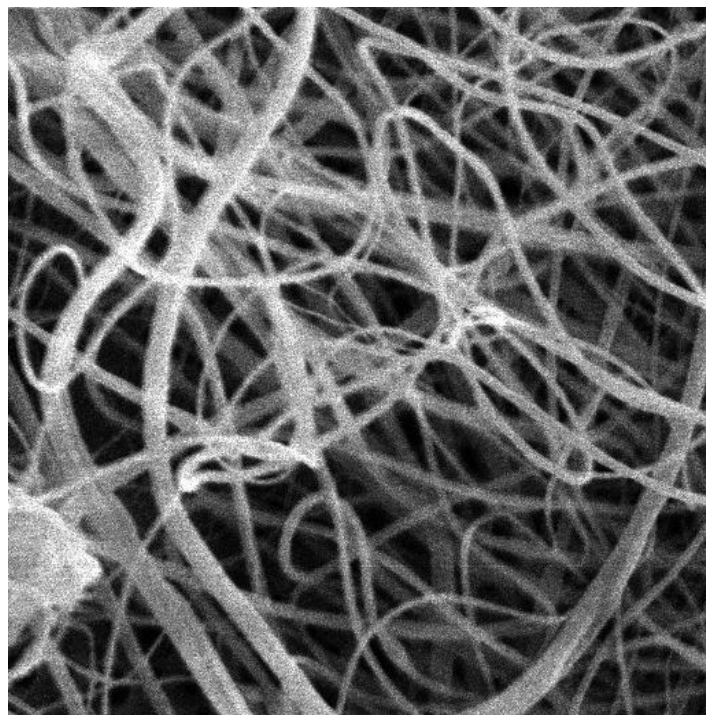
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 VAC: HiVac DET: SEDetector
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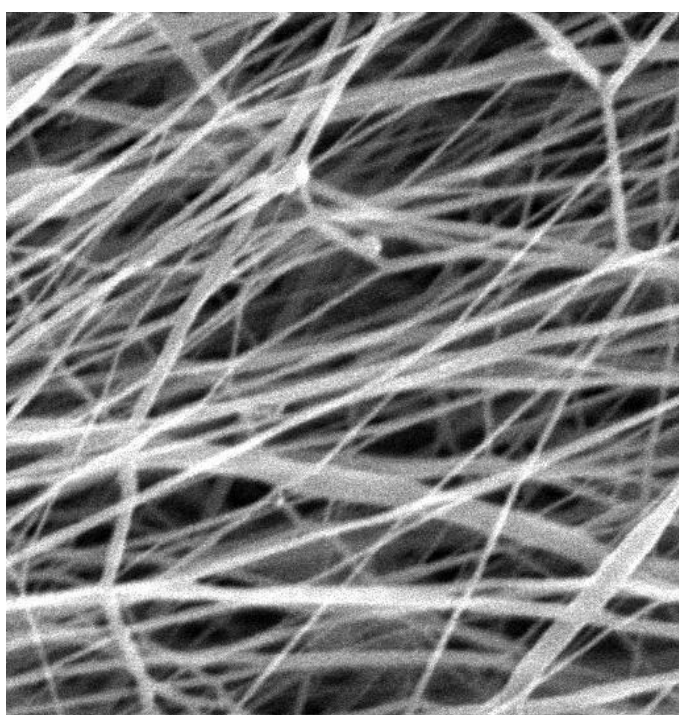
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 Vega@Tescan
 Rhodes University SEM

(F)



SEM MAG: 4.59 kx HV: 20.00 kV
 VAC: HiVac DET: SEDetector
 DATE: 04/03/13 Device: VG1760481J
 Vega@Tescan
 Rhodes University SEM

(G)



SEM MAG: 7.50 kx HV: 20.00 kV
 VAC: HiVac DET: SEDetector
 DATE: 04/04/13 Device: VG1760481J
 Vega@Tescan
 Rhodes University SEM

(H)

Figure 3b. SEM images (scale bar = 10 μ m) showing the morphology of fiber selectro spun from PET/L-PEI solutions in TFA, at concentration of **(E)** 22, **(F)** 24, **(G)** 26, **(H)** 28% w/v (voltage of 15 Kv and at a constant spinning distance of 13 cm).

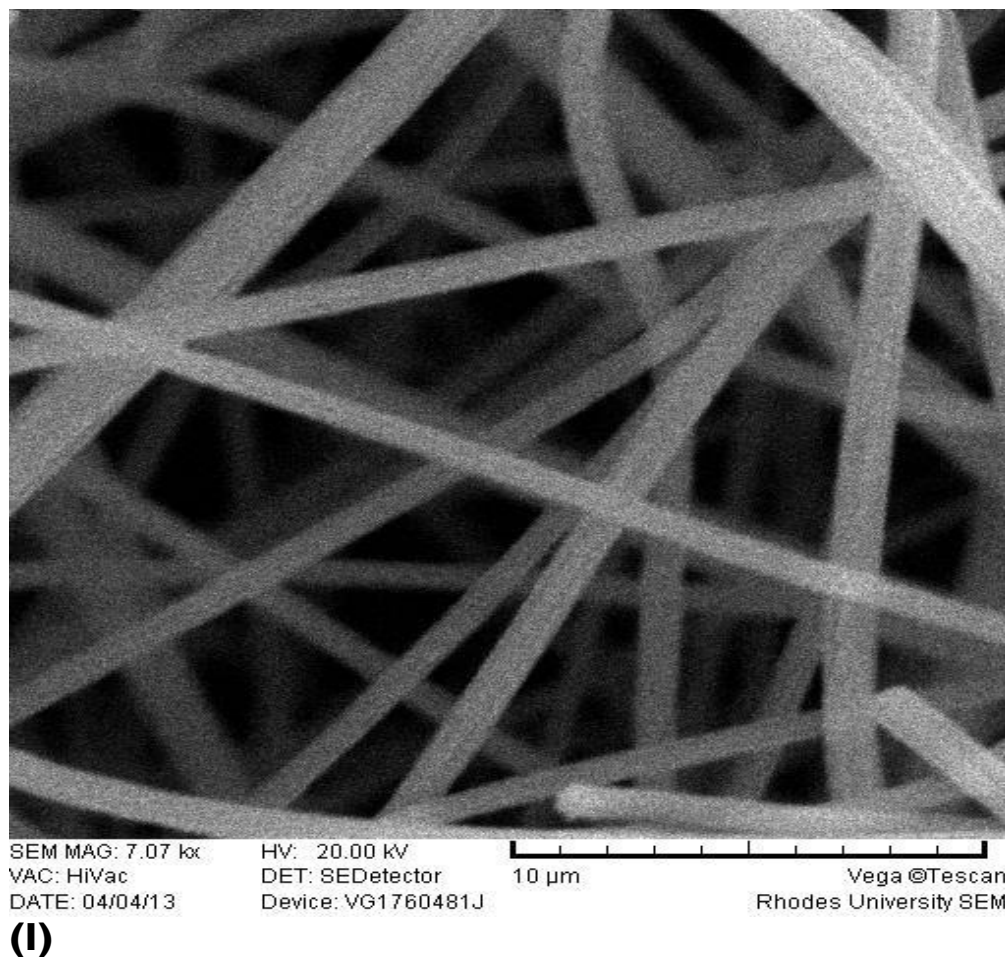


Figure 3c. SEM image (scale bar = 10 μm) showing the morphology of fibers electrospun from PET/L-PEI solutions in TFA, at concentration of **(I)** 30 % w/v (voltage of 15 Kv and at a constant spinning distance of 13 cm).

investigate the elemental composition of the imprinted fibers as shown in Figure 7. The EDS detects X-rays from the sample excited by the highly focused, high-energy primary electron beam penetrating into the sample. Comparing EDS images of NVMIN and nickel vanadyl removed-MIN confirmed that signals caused by the presence of VTPP and NTPP were clearly observed for NVMIN-containing fiber but not for nickel vanadyl removed-MIN which implies complete removal of the templates from the imprinted fiber and this is in corroboration with FT-IR study.

FTIR spectra of both NVMIN and NV removed-MIN are shown in Figure 8. FTIR can be used to qualitatively identify functional groups that are present in fiber structures. Both NTPP and VTPP were composed of central metal atoms surrounded by nitrogen atoms. The NVMIN imprinted fiber spectrum showed absorption bands at 559, 1013, 1200, 1600 and 1671 cm^{-1} that were attributed to Ni-N, V=O, C-N, conjugated C=N, and C=C systems, respectively, and indicated the success of the

imprinting process. The spectrum for the NV removed-MIN showed a distinct characteristic peak at 701 cm^{-1} which could be attributed to C-H vibration and the peaks of the NTPP and VTPP molecules at 559, 1013 and 1200 cm^{-1} vanished after excessive washing. The observation spectral absorptions implied that all template molecules had been completely removed.

Solvent effect

There are several variables, such as the type of monomer or the nature of the cross-linker and the choice of solvent that affect the adsorption efficacy in terms of capacity, affinity and selectivity for the target analytes. Acetonitrile, ethyl acetate, dichloromethane and chloroform were selected as solvents to optimize extraction solvent by using 50 mg L^{-1} NTPP standard solution. As shown in Figure 9, the effect of the solvent nature on the adsorption is obvious. NTPP adsorbs

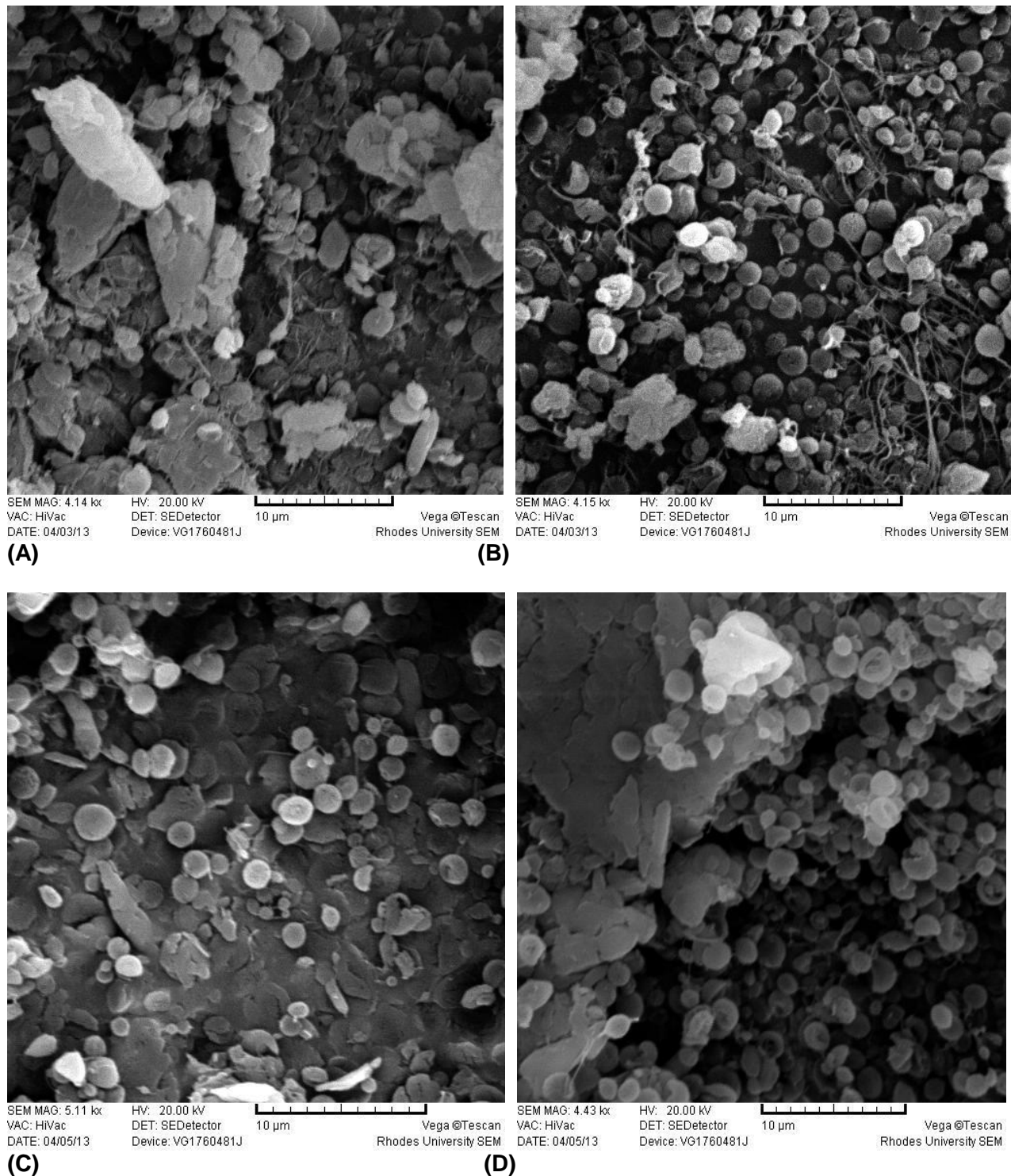


Figure 4. SEM images (scale bar = 10 µm) showing the morphology of fibers electrospun from 22 % PET/L-PEI solutions in a solvent mixture between TFA and DMSO (A) 95:5, (B) 93:7, (C) 90:10, and (D) 80:20 (voltage of 15 kV and at a constant spinning distance of 13 cm).

strongly in chloroform and dichloromethane because both solvents contained more oxidizing species with chloroform being the best. However, in ethyl acetate the

strength decreased and in acetonitrile the adsorption strength is the weakest among the solvents. In addition, the highest extraction percentage achieved in chloroform

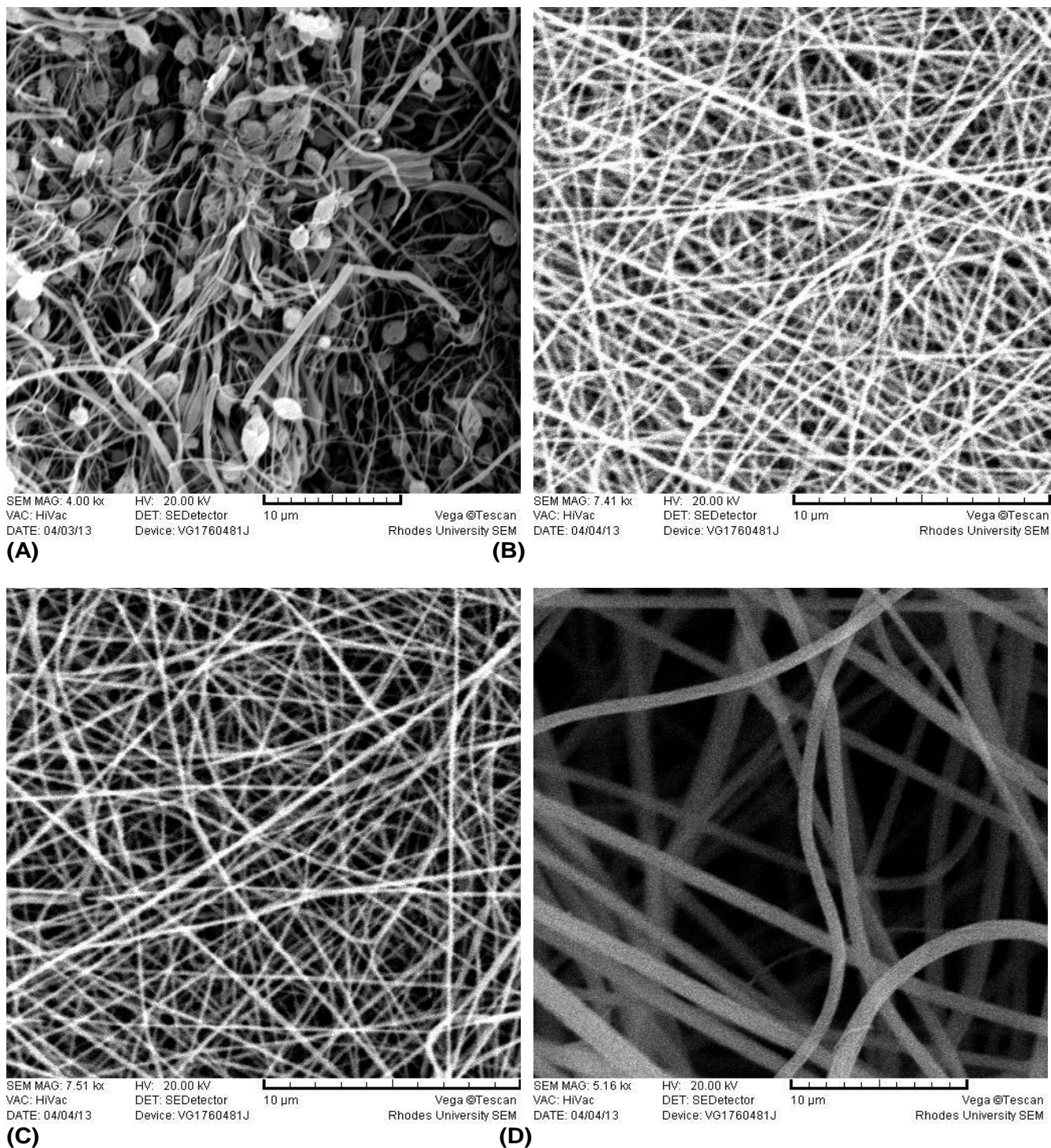


Figure 5. SEM images (scale bar = 10 μm) showing the morphology of fiberselectrospun from 22 % PET/L-PEI solutions in a solvent mixture between TFA and DCM **(A)** 95:5, **(B)** 93:7, **(C)** 90:10, and **(D)** 80:20 (voltage of 15 kV and at a constant spinning distance of 13 cm).

could be attributed to its low dipole moment ($\mu = 1.04$), compared to other solvents which have higher dipole moments (dichloromethane $\mu = 1.60$, ethyl acetate $\mu = 1.78$, and acetonitrile $\mu = 3.92$).

Adsorption of NTPP onto NVMIN

The successful application of imprinted fibers necessitates the availability of materials with appropriate

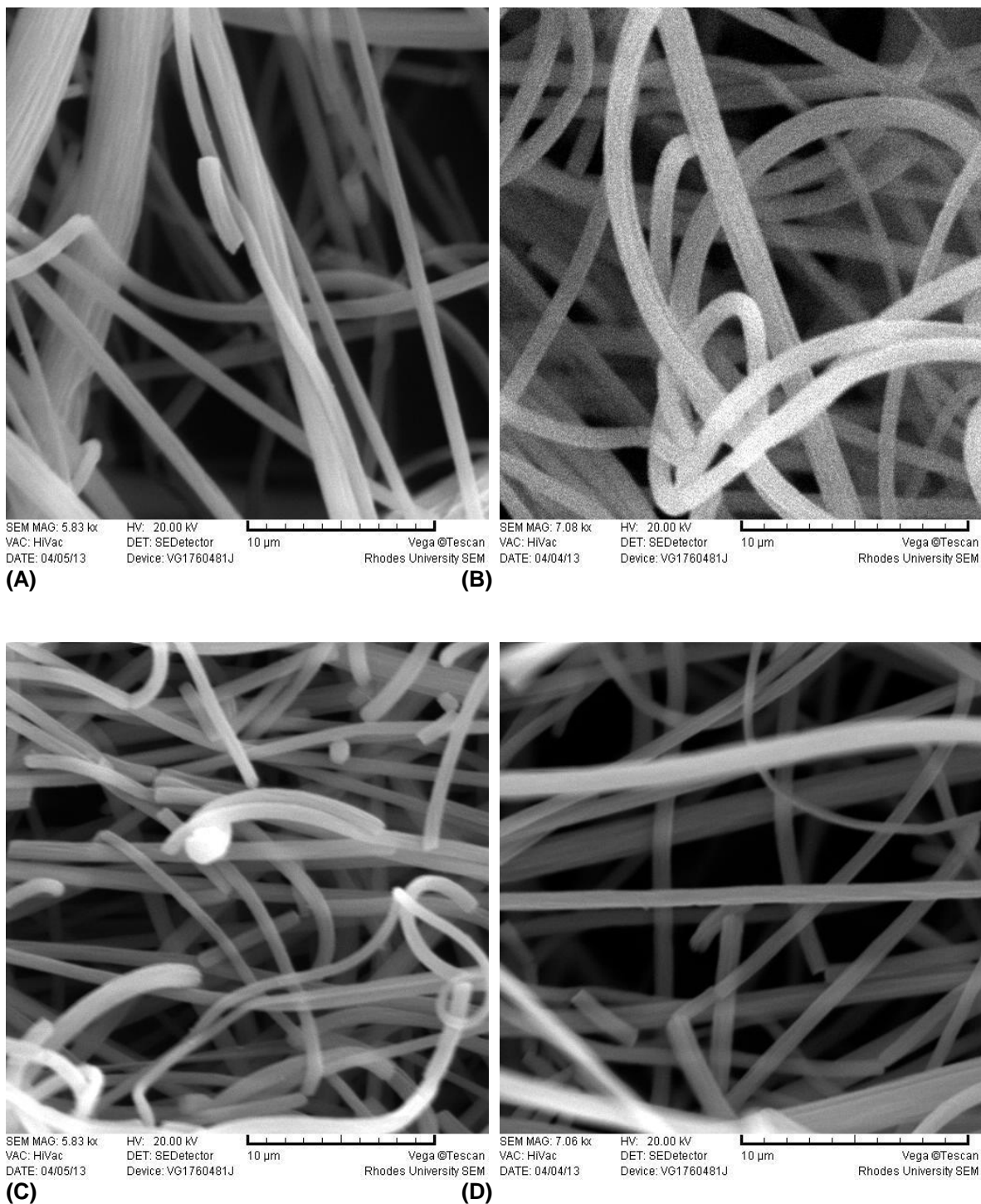


Figure 6. SEM images (scale bar = 10 µm) showing the morphology of fiberselectrospun from 22 % PET/L-PEI solutions in a solvent mixture between TFA and PEN(A) 95:5, (B) 93:7, (C) 90:10, and (D) 80:20 (voltage of 15 kV and at a constant spinning distance of 13 cm).

physical properties and selectivity. NTPP binding was studied in an organic environment at a low concentration level. Figure 10 shows that the rebinding capacity was varied from 99.3 to 99.9% at a concentration range from

10 to 50 mg L⁻¹. The result illustrated that the NVMIN showed higher affinity (99% higher) for NTPP than NIN, indicating that the NVMIN contains a lot of specific binding sites.

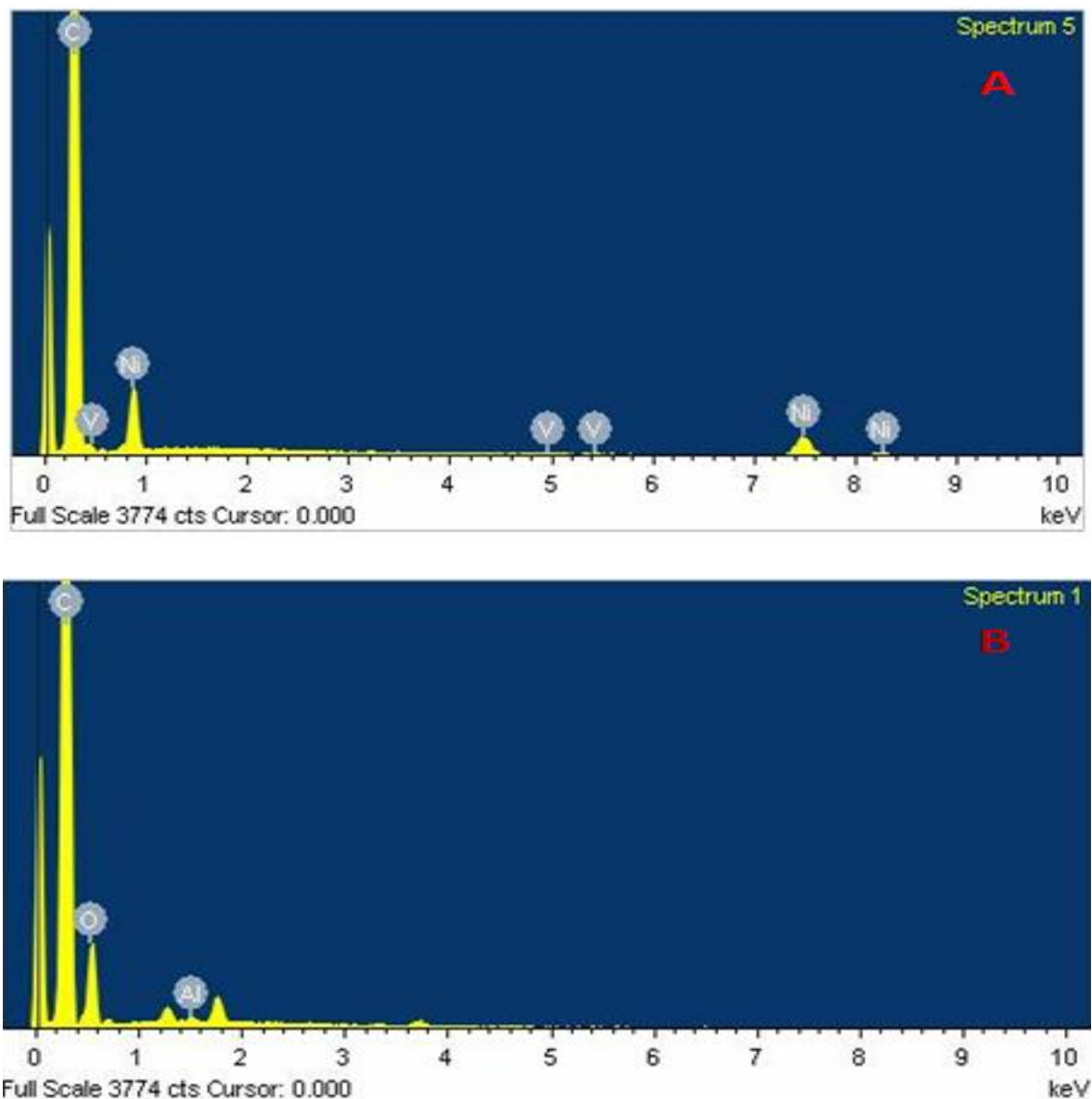


Figure 7. SEM-EDX spectra of imprinted fiber (A) NVMIN (B) NV removed-MIN.

Adsorption selectivity

Competitive adsorption experiments on NVMIN and NIN were conducted in chloroform solution containing NTPP and VTPP, respectively. All the concentrations were 50 mg L^{-1} . As shown in Figure 11, the adsorption capacities of NTPP and VTPP to the NVMIN were about 33.3 and 33.3 mg g^{-1} , respectively; whereas those to the NIN were about 0.8 and 0.8 mg g^{-1} , respectively. Obviously, the adsorption capacities of NTPP and VTPP on the NVMIN were higher than those on the NIN. The recognition coefficients (α) of NTPP and VTPP were 41.6 and 41.6 , respectively, according to Equation (2). It can be demonstrated that NVMIN synthesized for both NTPP

and VTPP had the same selectivity specialism for these molecules.

Adsorption thermodynamics

The thermodynamics parameters were calculated using the following equations (Li et al., 2009).

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

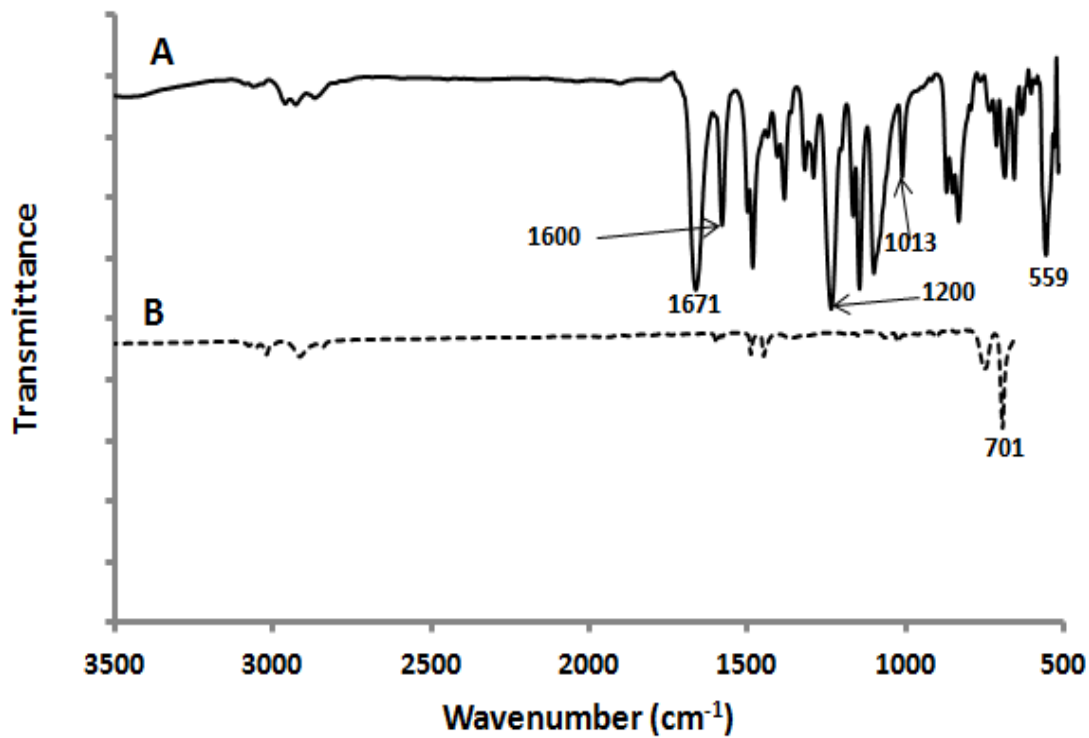


Figure 8. FT-IR spectra of imprinted fiber(A) NVMIN (B) NV removed-MIN.

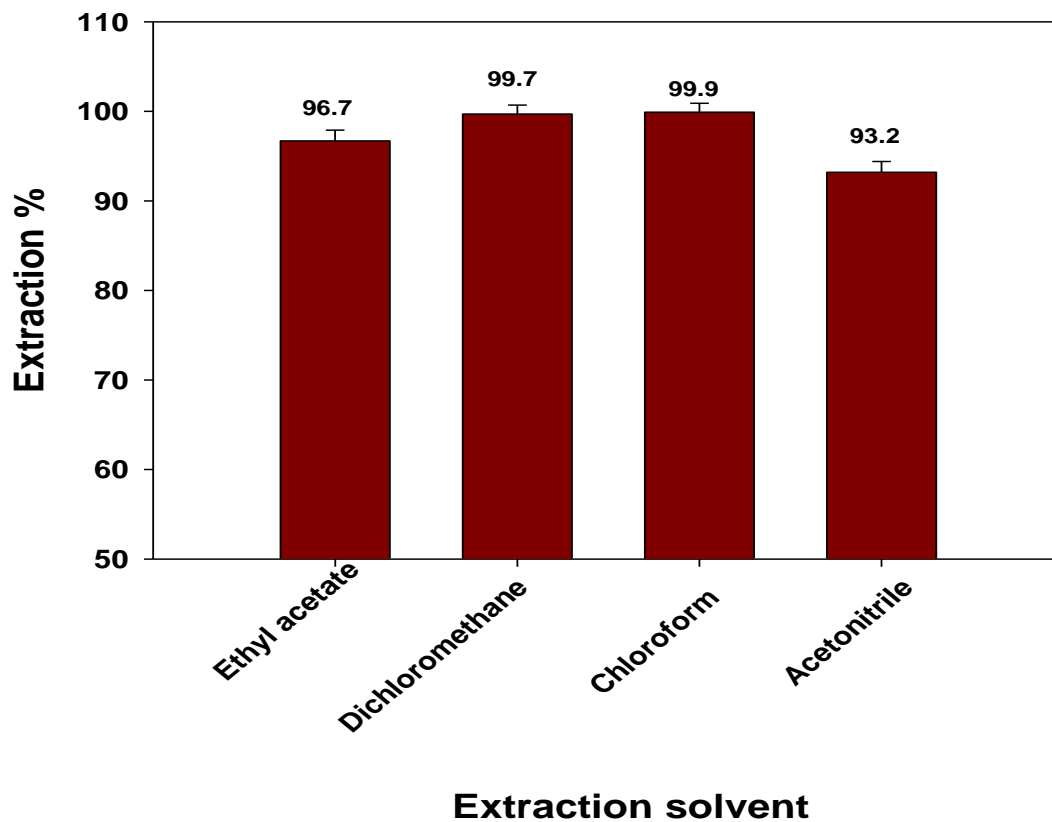


Figure 9. Percentage of NTPP adsorption from extraction solvents.

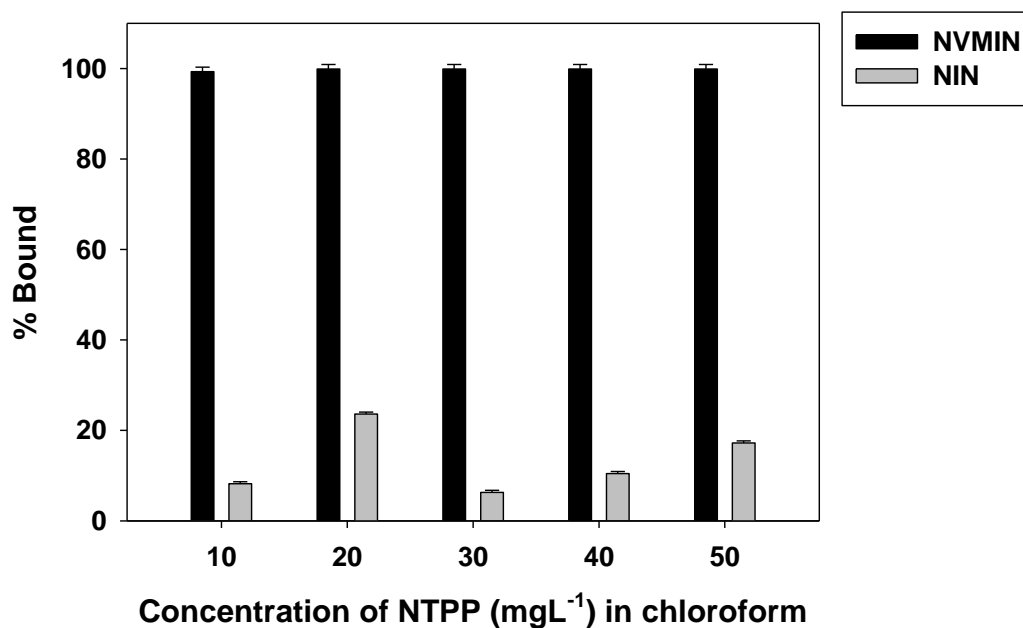


Figure 10. Percentage of rebinding capacity of NVMIN and NIN at different NTPP concentrations.

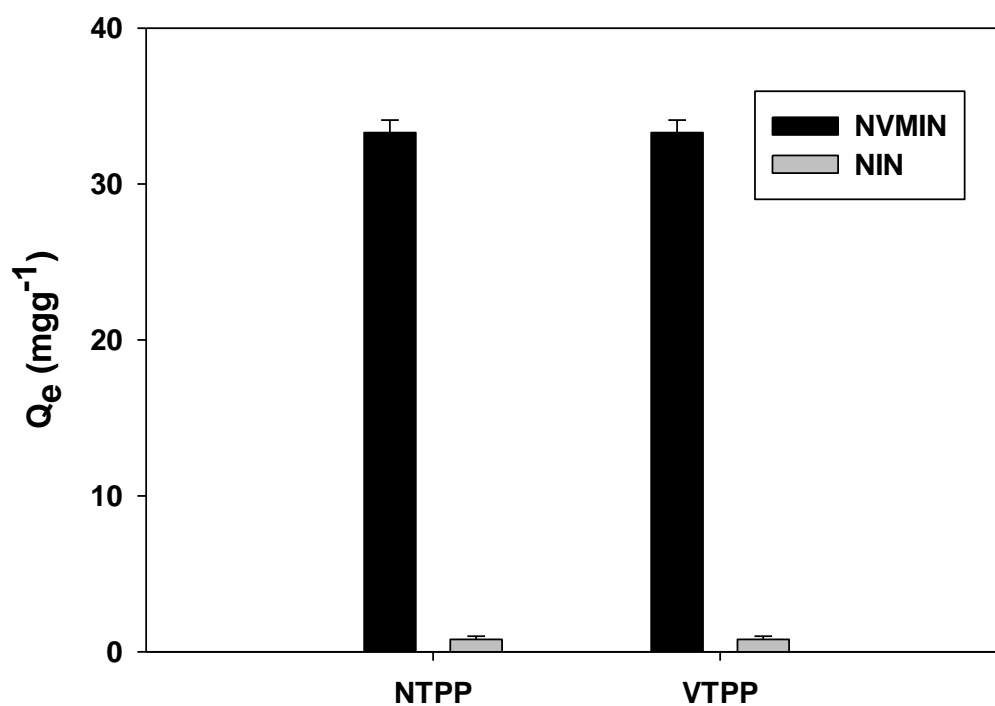


Figure 11. Competitive adsorption of NTPP and VTPP onto NVMIN and NIN.

Where R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T (K) is the absolute temperature and K_D is the equilibrium constant ($K_D = Q_e/C_e$), where Q_e (mgg^{-1}) corresponds to the amount of NTPP adsorbed by NVMIN at adsorption equilibrium and C_e (mg L^{-1}) is the

equilibrium concentration of NTPP in the solution. Thus, ΔH° and ΔS° were obtained from the slope and intercept of the line plotted by K_D versus $1000/T$, respectively. The obtained thermodynamic parameters are listed in Table 3. The negative values of ΔG° indicate the spontaneous

Table 3. Thermodynamic parameters for the adsorption of NTPP onto NVMIN.

Polymer	C _i (mg L ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS° (J/mol k)	ΔG° (kJ mol ⁻¹)		
				15°C	25°C	35°C
NVMIN	10.0	-23.63	9.98	-173.28	-273.13	-372.93
	20.0	-38.83	9.97	-188.48	-288.08	-387.78
	30.0	-166.20	13.00	-361.12	-491.20	-621.21
	40.0	-152.42	14.97	-376.97	-526.67	-676.37
	50.0	-138.60	16.63	-388.11	-554.35	-720.65

nature of adsorption process. When the initial concentration increased from 10.0 to 50.0 mg L⁻¹, the free energy change shifts to high negative value, and suggested that the adsorption was more spontaneous and favourable at higher concentration and temperature, respectively. Moreover, the negative values of enthalpy change ΔH° indicated that the binding of NTPP was exothermic in nature. By adsorption of abundant NTPP onto NVMIN surface, the number of the organic molecules surrounding NTPP molecules decreased and the degree of the freedom of the organic molecules increased. Therefore, the positive values of ΔS° suggested an increase in randomness at the solid-solution interface during the adsorption process.

Conclusions

The present study has demonstrated the feasibility of preparing novel NVMINs using NTPP and VTPP as the mixed-templates for the recognition and selective removal of a group of metalloporphyrins from organic media. The results indicated that mixed-templates NVMINs exhibited outstanding selectivity and adsorption ability for metalloporphyrin group and the recognition coefficients of NTPP and VTPP were 41.6 and 41.6, respectively. Thus, demonstrated that synthesized NVMIN had the same selectivity specialism for these molecules. The effects of solvents and their properties on electrospinnability of the PET/L-PEI solutions and the morphological appearance of the PET/L-PEI fibers were investigated qualitatively by means of a scanning electron microscope (SEM). The complex effect of some solvent properties such as dielectric constant, surface tension and evaporation rate on the electrospinning process and final properties of the electrospun nanofiber mats was demonstrated. The spinnable concentration of PET/L-PEI in the single solvent system was around 20% and solution concentrations higher than 24% favours the formation of nanofibers without beads. Among the three modifying liquids, DCM and PEN helped improve the electrospinnability of the PET/L-PEI solution with PEN being the best modifying liquid, specifically, at all the solvent mixture ratios the nanofibers were continuous and smooth without any beads or droplets in the surface

of the electrospun nanofiber.

It was found that adsorption is not only dependent on the cavities but also strongly on the extraction solvent. Thermodynamic parameters indicated that the adsorption process was spontaneous, exothermic with good affinity nature. It can be concluded from the results that imprinting mixtures of templates simultaneously is the best method for producing multi-analyte molecular recognition in complicated samples. It is our strong belief that the knowledge and success of this reactive electrospinning technology to produce cross-linked nanofibers provides a new and versatile opportunity for the processing and application of functional macromolecules.

Conflict of Interests

The authors have not declared any conflict of interests.

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REFERENCES

- Alexander C, Anderson HS, Anderson LI, Ansell RJ, Kirsch N, Nicholls IA, O'Mahony J, Whitecombe MJ (2006). Molecular imprinting science and technology: A survey of the literature for the years up to and 2003. *J. Mol. Recognit.* 19:106-180.
- Awokoya KN, Moronkola BA, Chigome S, Ondigo DA, Tshentu Z, Torto N (2013). Molecularly imprinted electrospun nanofibers for adsorption of nickel-5,10,15,20-tetraphenylporphyrin (NTPP) in organic media. *J. Polym. Res.* 20:148.
- Bhuvanesh G, Nilesh R, Jons H (2007). Poly (lactic acid) fiber: An overview. *Progr. Polym. Sci.* 32:455-482.
- Dechain GP, Gray MR (2010). Chemistry and association of vanadium compounds in heavy oil and bitumen, and implications for their selective removal. *Energy Fuels* 24:2795-808.

- Dickert F, Achatz P, Halikias K. (2001). Double molecular imprinting– A new sensor concept for improving selectivity in the detection of polycyclic aromatic hydrocarbons (PAHs) in water. *Fresen. J. Anal. Chem.* 371:11-15.
- Li CN (2001). Residue processing. Beijing: China Petrochemical Press. pp. 404-405.
- Li KQ, Wang XH (2009). Adsorptive removal of Pb(II) by activated carbon prepared from *Spartina alterniflora*: Equilibrium, kinetics and thermodynamics. *Bioresour. Technol.* 100:2810-2815.
- Long FX, Gevert BS (2003). Kinetic parameter estimation and statistical analysis of vanadyl etioporphyrin hydrodemetallization. *Comput. Chem. Eng.* 27:697-700.
- Mohammed FA, Saeed A (2006). A review of methods for the demetallization of residual fuel oils. *Fuel Process Technol.* 87:573-84.
- Mosbach K (2006). The promise of molecular imprinting. *Sci. Am.* 295:86-91.
- Nakamoto Y, Ishimaru T, Endo N, Matsusaki K (2004). Determination of vanadium in heavy oils by atomic absorption spectrometry using a graphite furnace coated with tungsten. *Anal. Sci.* 20:739-741.
- Ramstrom O, Mosbach K (1999). Synthesis and catalysis by molecularly imprinted materials. *Curr. Opin. Chem. Biol.* 3:759-764.
- Reynolds JG (2004). Removal of nickel and vanadium from heavy crude oils by exchange reactions. *Prepr. Symp– Am. Chem. Soc. Div. Fuel Chem.* 49:79-80.
- Schmidt J, Prignitz R, Peschka D, Münch A, Wagner B, Bänsch E, Peukert W (2012). Conductivity in nonpolar media: Experimental and numerical studies on sodium AOT-hexadecane, lecithin-hexadecane and Al(dips)3-hexadecane systems. *J. Coll. Interf. Sci.* 386:240-251.
- Schweitz L, Anderson LI, Nilsson S (2002). Molecularly imprinted CEC sorbents: Investigation into polymer preparation and electrolyte composition. *Analyst* 127:22-28.
- Shuangcheng W, Jingyi Y, Xinru X (2011). Effect of the cationic starch on removal of Ni and V from crude oils under microwave irradiation. *Fuel* 90:987-991.
- Spegel P, Schweitz L, Nilsson S (2003). Selectivity toward multiple predetermined targets in nanoparticles capillary electrochromatography. *Anal. Chem.* 75:6608-6613.
- Sreenivasan K (2007). Synthesis and evaluation of multiply template molecularly imprinted polyaniline. *J. Mater. Sci.* 42:7575-7578.
- Sreenivasan K, Sivakumar R (1999). Impacting recognition sites in poly (HEMA) for two compounds through molecular imprinting. *J. Appl. Polym. Sci.* 71:1823-1826.
- Suedee R, Srichana T, Chuchome T, Kongmark U (2004). Use of molecularly imprinted polymers from a mixture of tetracycline and its degradation products to produce affinity membranes for the removal of tetracyclin from water. *J. Chromatogr.* 811:191-200.
- Ware RA, Wei J (1985). Catalytic hydrodemetallation of nickel porphyrin I. Porphyrin structure and reactivity. *J. Catal.* 93:100-121.
- Welter K, Salazar E, Balladores Y, Marquez OP, Marquez J, Martinez Y (2009). Electrochemical removal of metals from crude oil samples. *Fuel Process Technol.* 90:212-221.
- Xu H, Yu DY, Wang ZX (2001). Progress of research on the chemistry of porphyrins compounds in petroleum. *Chem. Res. Appl.* 13:347-352.
- Yang KG, Liu ZB, Mao M, Zhang XH, Zhao CS (2005). Molecularly imprinted polyether sulfone microspheres for the binding and recognition of bisphenol. *Anal. Chim. Acta* 546:30-36.
- Zhang D (2002). Expedite the development of the hydrogenation craft and technology of our country. *Pet. Ref. Eng.* 32:1-6.