Preparation of Mesoporous Materials Modified Nanofiltration Membrane for Measured of Dissolved Organic Nitrogen

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Abstract. The incorporation of nano-materials in commercial nanofiltration composite (NFC) membrane has opened an alternative opportunity to enhance the membrane permeation, retaining macromolecular and dissolved organic nitrogen (DON) measurements properties in many drinking water treatment processes. In this study, mesoporous silica and mesoporous carbon were incorporated into the surface active layer of a NFC membrane via interfacial polymerization (IP) reaction. The structure, composition and pore distribution of the membranes and mesoporous materials were characterized by FT-IR, FE-SEM and BET measurements. The separation performance for DON and the water permeation performance of the mesoporous materials modified NFC membranes were investigated with prepared water in laboratory. The permeate water and the concentrated water samples were analyzed with total dissolved nitrogen (TDN), nitrate nitrogen (NO_2^-), nitrate nitrogen (NO_3^-) and ammonia nitrogen (NH_4^+). Within the range of mesoporous materials loadings assessed in this study, it was found that the NFC membrane incorporated with mesoporous materials offered higher water flux and DON rejection rate, which was ascribed to the favorable change in membrane pore structure, surface morphology and surface charge by the addition of appropriate amount of mesoporous materials, indicating great potential of such membranes in organic nitrogen testing. The dissolved inorganic nitrogen (DIN, including nitrite, nitrate and ammonia) to total dissolved nitrogen (TDN) ratio of finished water is reduced up to 0.88, 0.78, 0.80, 0.70, 0.78, 0.65, 0.81 and 0.69 for NF90, NF270, CPNF90, CPNF270, CFNF90, CFNF270, SNF90 and SNF270 respectively.

Keywords: Mesoporous materials, Dissolved organic nitrogen (DON), Nanofiltration, Drinking water treatment.

1. Introduction

The development of mesoporous materials possessing large specific surface areas is currently an area of extensive research, due to their potential applications in areas such as adsorption [1], catalysis [2], sensor technology and gas storage [3]. Mesoporous materials of e.g. MCM-41 or SBA type are a new class of matrices applied in DDSs. Initially, these materials served as supports in heterogeneous catalysis [4]. Mesoporous materials are characterized by large surface area (>1000 m^2/g), uniform pore size distribution and large pore volume (~ 1.0 cm^3/g). Moreover, high biocompatibility [5], low toxicity [6] and the presence of micropores (in SBA-15) [7] promote their application as carriers in membrane modification.

Nanofiltration composite (NFC) membranes have gained much interest in the applications of drinking water treatment to remove both conventional and emerging contaminants [8]. A typical NFC membrane consists of a commercial nanofiltration composite layer (polyamide as the most commonly used polymer material) on the top of a micro-porous support substrate and is often produced by interfacial polymerization (IP) reaction [9]. In this regard, the research efforts in both academic and industrial sectors have been directed to the searching of appropriate surface modification approach to fine-tune not only the membrane morphology but also its hydrophilicity, thus minimizing the undesired membrane fouling without sacrificing

the water flux [10].In this line of development, the incorporation of nano-sized porous materials either in the top layer polymer matrix or in the polymeric substrate to facilitate higher water flux due to their large pore size and porosity has become a focal point in research.

The presence of DON also contributes to membrane fouling in water treatment processes. It is important to use available analytical methods for DON determination to investigate its fate, properties and reactivity in waters and water treatment processes. The DON concentration in water samples cannot be quantified directly but must be determined by subtracting the sumof DINspecies fromthe total dissolved nitrogen (TDN). Negative DON concentrations were reported in practical measurements in the case of high DIN/TDN ratios. A thorough study on the mesoporous materials modified NFC membrane with real drinking water samples is therefore essential, not only to provide better understanding of the role of mesoporous materials in the membrane performance, but also to demonstrate the feasibility of using such membranes under an industry relevant condition.

In this study, the mesoporous silica and mesoporous carbon modified NFC membranes were prepared via IP process. Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) and Brunauer-Emmett-Teller (BET) tests were utilized to evaluate the composition, structure and surface activity of the membrane. The water permeation performance and concentrated effect of these membranes were systematically studied with prepared water in laboratory. The composition of drinking water as well as the permeate water samples were analyzed by UV to evaluate the concentrated efficiency. The objectives of this study were: (1) to investigate the feasibility of mesoporous materials modified commercial nanofiltration composite membrane pretreatment for DON measurement using different commercial NF membranes; (2) to optimize the mesoporous materials for the modified NF pretreatment system.

2. Materials and methods

2.1 Materials

The triblock copolymer Pluronic F127, Pluronic P123 and formaldehyde solution (36.5-38 wt%) were obtained from Sigma-Aldrich. Phenol, polyethersulfone (PES), dimethylacetamide (DMAC), ammonium chloride, potassium nitrate, humic acid (HA) and tetraethyl orthosilicate (>98% purity) were purchased from Nanjing chemical reagent Co., Ltd. (Nanjing, China), The NF membranes selected in this study were thin-film composite polyamide membranes, including NF90, NF270 (Dow/Filmtec, USA) and HL (GE Osmonics, USA).

2.2 Synthesis of mesoporous materials

Mesoporous silica and mesoporous carbon were synthesized according to our previous report and other literatures [11]. The mesoporous carbon samples were synthesized with the preformed phenolic resin resol solution as a carbon resource, and triblock copolymer F127 and P123 as templates in an ethanol solution.

2.3 Fabrication of mesoporous materials modified polyamide NFC membranes by the interfacial polymerization reaction

PES support nanofiltration membranes were prepared by phase inversion via immersion precipitation technique [12]. The casting solution was prepared by mixing 10.0 g of PES with DMAC (40mL). These components were stirred at 200 rpm and 25 ℃ for 12 h. Then the reaction mixture was added 0.55 g lithium chloride (LiCl) and 5.0 g polyvinylpyrrolidone (PVP). These components were stirred at 200 rpm for 24 h. Then the solutions was prepared by mixing 1.0 wt.% of mesoporous silica or mesoporous carbon and stirring 6 h. After complete mixing and formation of homogeneous casting solutions, they were kept constant for removal of bubbles. The solutions were sprinkled and cast on NFC membranes using a home-made casting knife with 500 μm thickness. The cast films were immersed in a water bath for immersion and membrane formation at room temperature without any evaporation. The prepared membranes were washed and stored in water for at least 1 day to completely leach out the residual solvents and additives. As the final stage, the membranes were dried by placing between two sheets of filter paper for 24 h at room temperature. The total thickness of the membranes was about 1000μm.

2.4 Characterization of the mesoporous materials

The surface area and the porosity of the mesoporous materials were determined using an ASAP2020 surface area analyser by the nitrogen sorption method. SEM (S-3400N) and FT-IR (TENSOR27) were used to image the mesoporous structures in the mesoporous samples.

2.5 Membrane filtration test

The filtration experiments on the in-house fabricated membranes were performed with a ultrafiltration cup, with prepared water in laboratory (NO_3^- 1.0mg/L, NH_4^+ 0.5 mg/L, HA 3.0 mg/L, NO_2^- 0.1 mg/L). The filtration system consists of one closed loop for the feed solution stream. A bypass pipe of the closed loop was connected to a nitrogen gas cylinder and the pressure was controlled by the adjustment of a nitrogen control valve. The tests were conducted at room temperature at the feed pressure of 0.3 MPa and each was repeated three times.

2.6 Analysis of the concentrated water samples

The UV spectrophotometer was used to measure TDN, NO_2^-, NO_3^- and NH_4^+ of the concentrated water samples with a quartz cuvette. DON (mg/L) was calculated as follows:

$$DON = TDN-DIN = TDN- (NO_2^- + NO_3^- + NH_4^+)$$

3. Results and discussion

3.1 Characterization of the mesoporous materials and the modified NFC membranes

The N_2 adsorption and desorption isotherms of the mesoporous materials studied in this work are plotted in Fig. 1, and the corresponding pore diameter distributions calculated from the desorption isotherm branches are shown in Fig. 2. The BET specific surface areas of the mesoporous materials were determined to be between 405 and 485 m^2/g, which are significantly higher than those of commonly used commercial macroporous resins and spherical activated carbon (396 m^2/g). The pore volumes of the mesoporous materials samples were measured to be between 0.38 and 0.94 cm^3/g, which are also much higher than those of many common adsorbents including spherical activated carbon (0.24 cm^3/g) and other materials.
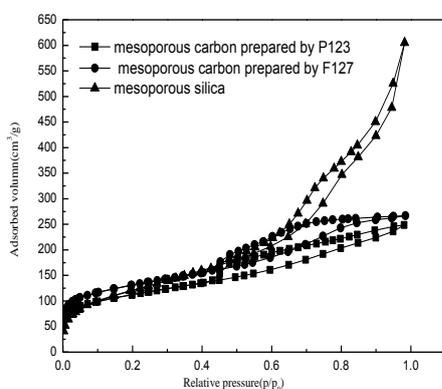

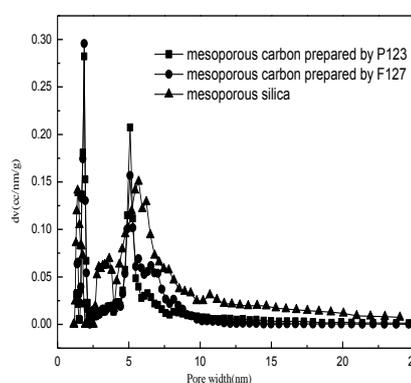Fig. 1: Nitrogen adsorption–desorption isotherms of the mesoporous materials

Fig. 2: Pore diameter distributions of the mesoporous materials

As shown in Fig. 2, two typical pore regions are presented for all the mesoporous materials samples, the most predominant pores are the mesopores with the diameter distributions between 3 and 9 nm and micropores (<2 nm) also exist in these samples, and the average pore diameters were calculated to be between 3.51 and 8.60 nm. The pore textural properties of the mesoporous materials samples studied in this work are consistent with those of mesoporous materials reported in the literature [13].

The main properties of the mesoporous carbon adsorbents including BET specific surface areas, average pore diameters and pore volumes are listed in Table 1.

Three series of NFC membranes with different mesoporous materials loadings in the PA active layer (mesoporous silica, mesoporous carbon prepared by F127 and mesoporous carbon prepared by P123) were

prepared in this work via the interfacial polymerization reaction on the top of the NFC membranes, and these samples were labeled as SNF90/SNF270, CFNF90/CFNF270, and CPNF90/CPNF270, respectively.

Table 1: The main properties of the mesoporous materials.

Sample	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
mesoporous silica	405	0.94	8.60
mesoporous carbon prepared by P123	407	0.38	3.81
mesoporous carbon prepared by F127	485	0.41	3.51

The FTIR of the mesoporous materials studied in this work are plotted in Fig. 3(a) and Fig. 3 (b) presents a comparison of the FTIR spectra of the NFC membranes and mesoporous materials modified NFC membranes (ranging from 4000 cm^{-1} to 600 cm^{-1}). The peak at 1600 cm^{-1} was due to the carbonyl stretching vibration, suggesting that mesoporous carbon was incorporated into the PA layer on the top of the NFC membrane. The strong peak at 1050 cm^{-1} could be ascribed to the stretching vibration of the Si-O bonds. The presence of characteristic peaks suggested that the addition of mesoporous materials successfully load to the membrane surface.
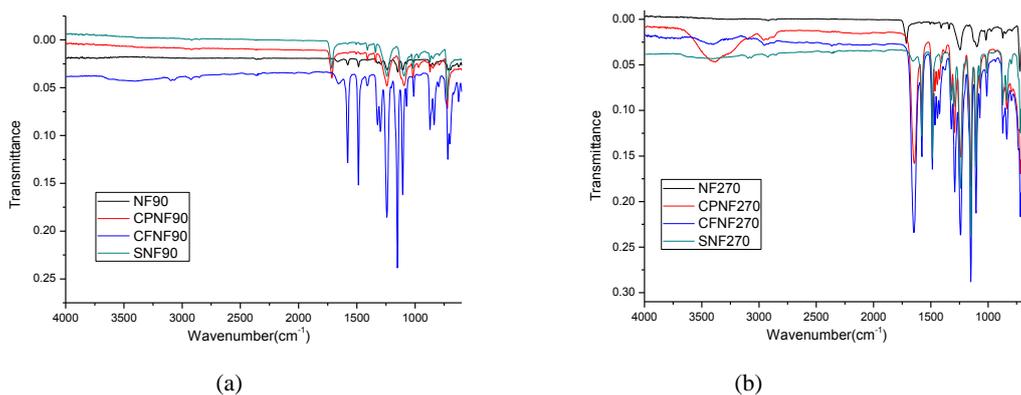

(a)	(b)

Fig. 3: FTIR spectra of pure NFC and mesoporous materials modified NFC membranes.

The scanning SEM images of the surfaces and the cross-sections of the pure NFC membrane and mesoporous materials modified NFC membranes were shown in Fig. 4. Both pure NFC and mesoporous materials modified NFC membranes displayed smooth surface structure, similar to the structure observed on the surfaces of other NFC and thin film nanocomposite (TFN) membranes. Furthermore, the surface of the mesoporous materials modified NFC membranes appeared mesoporous particles than that of the pure NFC membrane. The formation of such a structure was partially due to the reaction between mesoporous materials and membrane during the interfacial polymerization. As such, the formation of the top layer was greatly affected by the incorporation of mesoporous materials, which in turn resulted in a different surface morphology of the mesoporous materials modified NFC membranes. Nevertheless, it must be pointed out that the excessive loading of mesoporous materials might lead to the agglomeration on the surface, compromising the structural integrity of the top surface thus reducing the water permeation flux. Apart from the formation of the mesoporous particles on top layer, it was also found that the addition of mesoporous materials substantially increased the top layer thickness, when comparing the pure NFC membrane with the mesoporous materials modified NFC membranes, as evidenced in Fig. 4(g-l). Such increase in top layer thickness significantly changed the hydrophilia of the membranes and lowered the mass transfer resistance, therefore partially contributed to the enhanced pure water flux, as evidenced in Table 2.

3.2 Analysis of the permeate and retentate water samples
When choosing a suitable NF membrane with low DIN retention but high organic retention for the

pretreatment method, it is essential to evaluate the distribution of DIN species and TDN with different NF membranes. Experiments were performed using NF90, NF270, SNF90, SNF270, CPNF90, CPNF270, CFNF90 and CFNF270 to treat the prepared water in laboratory and the finished water from the WXWTP. A mass balance of each DIN compound and the DIN/DON ratio were calculated using permeate and retentate concentrations to determine whether the compound was lost onto the membrane surface and/or into the membrane pores.

Table 2: Pure water flux of the pure NFC and mesoporous materials modified NFC membranes.

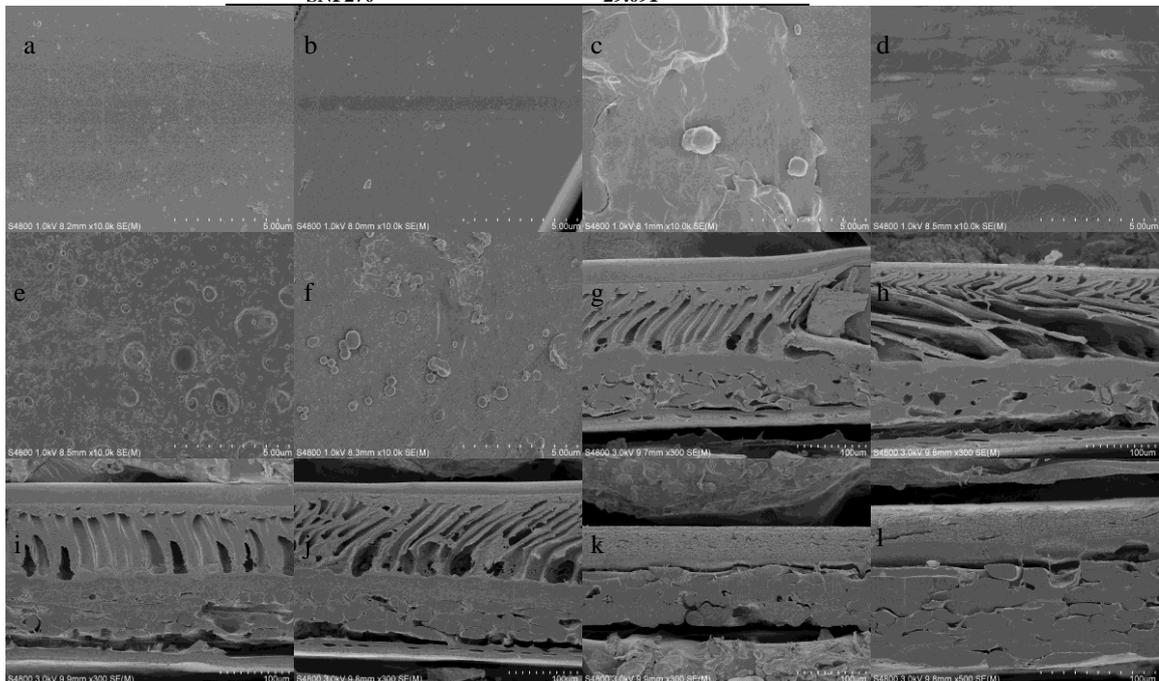| Sample	Pure water flux (L/m^2
NF90	18.815
CPNF90	24.679
CFNF90	37.631
SNF90	30.453
NF270	16.725
CPNF270	23.624
CFNF270	38.718
SNF270	29.091

Fig. 4: SEM images of the top surfaces of: (a) NF90, (b) NF270, (c) CPNF90, (d) CFNF90, (e) CPNF270, (f) CFNF270 and the cross-sections of: (g) CPNF90, (h) CPNF270, (i) CFNF90, (j) CFNF270, (k) SNF90, and (l) SNF270.

With a transmembrane pressure of 0.3 MPa and R of 7.5 cm^3/cm^2, the mass percentages of nitrite, nitrate, ammonia and HA in the retentate and permeate after NF pretreatment are shown in Fig. 5. Low molecular weight ions of nitrite and nitrate were found in a mass percentage of 25-55% in the retentate and 42-74% in the permeate, respectively (Fig. 5). Negligible adsorption loss was found for both nitrite and nitrate for all 8 tested NF membranes. The tighter NF90 had the highest retention rate for nitrate, while the looser NF270 had the lowest retention of 25.0% for nitrate. The results were similar to those of Paugam et al which were obtained with higher nitrate concentrations of feed solution. Approximately 50% of the ammonia was not recovered, which may have been due to the adsorption of ammonia onto/into the membrane surface or due to degassing and high back-pressure depending on the pH of the solution. Only 25% of the ammonia was left in the retention solution, which is beneficial for DON measurements because the decrease of ammonia in the retentate leads to a lower DIN/TDN ratio. HA is a mixture of organic chemicals with a board molecular

weight range and is always seen as a model for natural organic matter. Fig. 5a shows that no HA was detected in the permeate for all membranes. The mass percentage of HA in the retentate for NF90, NF270, CPNF90, CPNF270, CFNF90, CFNF270, SNF90, SNF270 was 62.9%, 83.8%, 68.0%, 85.9%, 88.2%, 91.3%, 85.2% and 88.6%, respectively, which means that there was some mass loss for HA during the NF pretreatment. A possible explanation for the loss of HA is adsorption onto/into the membrane surface. NF270 has a semi-aromatic piperazine based polyamide layer and shows the highest water permeability and lowest organics adsorption loss among the 8 membranes tested, as well as fairly high organic rejection and low retention of DIN species (Fig. 5).

To validate the pretreatment method and evaluate the precision of DON measurement, DON concentrations were analyzed with and without NF pretreatment, as shown in Fig. 6. Because the DON concentration is fairly low in synthetic water, and the DIN/TDN ratio was as high as 1.13, the standard deviation of DON measurements was great, and negative concentration values were measured. The high standard deviation is related to the variances in DIN and TDN measurements. Previous research has indicated that samples with a DIN/TDN ratio greater than 0.7 have high analytical variations, which increases as the DIN/TDN ratio increases. On the other hand, no negative concentrations were measured after any one of the NF pretreatments. As shown in Fig. 6, the highest DON concentration was found for the pretreatment using CFNF270, which is related to satisfactory DOM retention and the lowest DOM lost to membrane adsorption as mentioned above. Because NF90, SNF90, CPNF90, CFNF90 showed the highest DIN rejection and DOM adsorption in Fig. 5, most DIN would remain in the retention solution (DIN/TDN ratio around 0.80) and would affect the DON measurement accordingly. Consequently, the lowest DON concentration and largest standard deviation were observed when using NF90 serious membranes. Because DIN/TDN ratios were lowered using NF270 serious membranes, the standard deviations were fairly low for both of these DON measurements. The results are in accordance with the reports from Vandenbruwane et al. [14] and Lee and Westerhoff [9], which indicated that the standard deviation of DON measurement depends greatly on the DIN/TDN ratio. Because the membrane showed lower HA retention and more adsorption loss than that of NF270 (Fig. 5), the DON concentrations appeared to be lower.
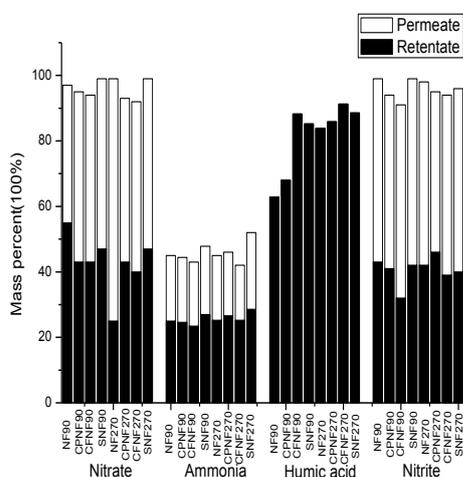

Fig. 5: NF pretreatment for lab synthetic solutions with different NF membranes. Initial concentration of nitrite, nitrate, ammonia, and HA were 0.1, 1.0, 0.5 mg/L and 3 mg/L, respectively. (R refers to retentate, and P refers to permeate in the figure legend).
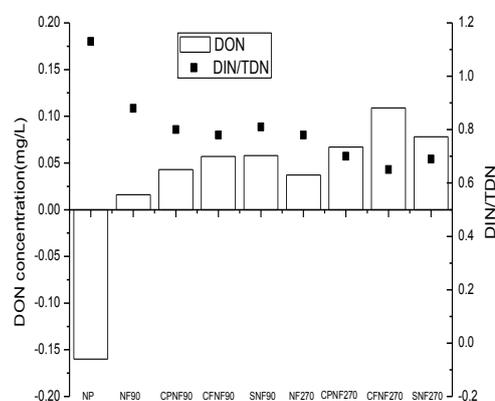

Fig. 6: Comparison of measured DON concentration and DIN/TDN ratio for synthetic water with and without NF pretreatment using NF90, CPNF90, CFNF90, SNF90, NF270, CPNF270, CFNF270 and SNF270, respectively (NP refers to without pretreatment)

The above findings suggest that NF pretreatment is a potential way to increase the precision of DON measurements in water samples with high DIN/TDN ratios. Membranes modified of mesoporous materials can further improve the precision of DON measurements especially the modification of mesoporous carbon. High DOM recovery and low DIN/TDN ratio in the retentate can be achieved after pretreatment by using suitable NF membranes, which is much more practical than the time-consuming and costly dialysis method.

4. Conclusions

In this study, the mesoporous materials modified NFC membranes were prepared via IP reaction on the top of commercial NFC membranes. A variety of techniques were applied to characterize the in-house modified membranes, FTIR results revealed the presence of hydroxyl groups on the membrane surface, suggesting the increased carbonyl and Si-O bonds owing to the addition of mesoporous materials. The SEM images of the surfaces and the cross-sections of the membranes indicated that the active layer became denser and thicker due to the incorporation of mesoporous materials, which might contribute to the higher pure water flux observed in the water permeation tests compared to that of the pure NFC membranes. Nanofiltration is a feasible pretreatment for DON measurement with selective NF membranes. CFNF270 showed the highest DIN permeability and DON retention (~60%) among the selected membranes, and was able to lower the DIN/TDN ratio from around 1 to less than 0.65. The nanofiltration mechanism of the mesoporous materials modified NFC membranes will be investigated more in details in our future studies.

5. Acknowledgements

6. References

[1] P.J. Branton, P.G. Hall, K.S. Sing, Physisorption of alcohols and water vapour by MCM-41, a model mesoporous adsorbent, Adsorption, 1(1995) 77-82.

[2] Y. Sun, H. Sai, K.A. Spoth, K.W. Tan, U. Werner-Zwanziger, J. Zwanziger, S.M. Gruner, L.F. Kourkoutis, U. Wiesner, Stimuli-Responsive Shapeshifting Mesoporous Silica Nanoparticles, Nano Lett, (2016).

[3] H. Koller, M. Weiß, Solid state NMR of porous materials,Springer, 2011, pp.189-227.

[4] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C. Su, Applications of metal–organic frameworks in heterogeneous supramolecular catalysis, Chem Soc Rev, 43(2014) 6011-61.

[5] T. López, E.I. Basaldella, M.L. Ojeda, J. Manjarrez, R. Alexander-Katz, Encapsulation of valproic acid and sodic phenytoin in ordered mesoporous SiO 2 solids for the treatment of temporal lobe epilepsy, Opt Mater, 29(2006) 75-81.

[6] S.P. Hudson, R.F. Padera, R. Langer, D.S. Kohane, The biocompatibility of mesoporous silicates, Biomaterials, 29(2008) 4045-55.

[7] C.G. Sonwane, P.J. Ludovice, A note on micro-and mesopores in the walls of SBA-15 and hysteresis of adsorption isotherms, Journal of Molecular Catalysis A: Chemical, 238(2005) 135-37.

[8] A. Rahimpour, M. Jahanshahi, N. Mortazavian, S.S. Madaeni, Y. Mansourpanah, Preparation and characterization of asymmetric polyethersulfone and thin-film composite polyamide nanofiltration membranes for water softening, Appl Surf Sci, 256(2010) 1657-63.

[9] N. Widjojo, T. Chung, M. Weber, C. Maletzko, V. Warzelhan, The role of sulphonated polymer and macrovoid-free structure in the support layer for thin-film composite (TFC) forward osmosis (FO) membranes, J Membrane Sci, 383(2011) 214-23.

[10] D. Rana, T. Matsuura, Surface modifications for antifouling membranes, Chem Rev, 110(2010) 2448-71.

[11] Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, A family of highly ordered mesoporous polymer resin and carbon structures from organic-organic self-assembly, Chem Mater, 18(2006) 4447-64.

[12] A. Rahimpour, S.S. Madaeni, S. Mehdipour-Ataei, Synthesis of a novel poly (amide-imide)(PAI) and preparation and characterization of PAI blended polyethersulfone (PES) membranes, J Membrane Sci, 311(2008) 349-59.

[13] M. Dai, B.D. Vogt, High capacity magnetic mesoporous carbon–cobalt composite adsorbents for removal of methylene green from aqueous solutions, J Colloid Interf Sci, 387(2012) 127-34.

[14] J. Vandenbruwane, S. De Neve, R.G. Qualls, J. Salomez, G. Hofman, Optimization of dissolved organic nitrogen (DON) measurements in aqueous samples with high inorganic nitrogen concentrations, Sci Total Environ, 386(2007) 103-13.