Environmental Engineering and Management Journal

March 2015, Vol.14, No. 3, 607-613 http://omicron.ch.tuiasi.ro/EEMJ/



"Gheorghe Asachi" Technical University of Iasi, Romania



PNiPAM-FUNCTIONALIZED MESOPOROUS CARBON FOR THE ADSORPTION OF VITAMIN B2

Maria Ignat^{1,2*}, Maria Emiliana Fortuna¹, Liviu Sacarescu¹ Mirela-Fernanda Zaltariov¹, Valeria Harabagiu¹

¹"Petru Poni" Institute of Macromolecular Chemistry, Department of Inorganic Polymers, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania ²"Alexandru Ioan Cuza" University of Iasi, Department of Chemistry, 11 Carol I Bvd., 700506 Iasi, Romania

Abstract

The present research reports the synthesis of poly-N-isopropylacrylamide / mesoporous carbon composites, prepared by radical polymerization of N-isopropylacrylamide inside mesoporous carbon pores functionalized with carboxylic groups. The deposition of poly-N-isopropylacrylamide on mesoporous carbon was confirmed by FT-IR spectroscopy, TEM, N₂-sorption measurements. The mesoporous carbon material was found to adsorb vitamin B2 from aqueous solution at room temperature. The obtained composite, poly-N-isopropylacrylamide / mesoporous carbon, exhibited a higher adsorption capacity for vitamin B2 as compared to un-functionalized mesoporous carbon sample, due to hydrogen bonding between carbonyl groups of poly-N-isopropylacrylamide immobilized on the mesoporous carbon surface and amino groups of vitamin B2 molecules.

Key words: mesoporous carbon (MC), poly-N-isopropylacrylamide, polymer-functionalized MC, vitamin B2

Received: November, 2014; Revised final: March, 2015; Accepted: March, 2015

1. Introduction

Uniform nanoporous polymers have attracted considerable attention for a long time in materials science (David et al., 2008). There are lots of reports on the synthesis of nanoporous polymers, but one of the disadvantages is that such structures are lower in mechanical strength and resistance to chemical treatments.

Recently, the attention have been focused on the synthesis of mesoporous carbon (MC) materials due to their physico-chemical properties, high specific surface area, tunable pore sizes, easiness for functionalization their mesopores (Liang et al., 2008; Nastas et al., 2013), these futures being of great interest in many applications as separation, catalysis, energy storage and conversion (Vinu et al., 2003).

Actually, the randomly porous carbons (active carbon) (Gerçel, 2015) are the product of

conventional synthesis and their performance in the adsorption of giant organic molecule is not optimal because of their disordered pore structure, low specific pore volume, and significant amount of micropores, which only allows the adsorption of relatively small molecules from gas or liquid phases (Bansal et al., 1998; Shen et al., 2003). On the other hand, large biomolecules such as vitamins, amino acids and proteins (Ramos et al., 2004; Vinu et al., 2006; Vinu et al., 2007), should be adsorbed by a mesoporous material, because this allows the adsorption of molecules that are too large to enter micropores. Therefore, a significant effort has been done to develop mesoporous carbon materials with a sufficiently porous matrix to accommodate macromolecules. Actually, its surface chemistry, specific area and pore structure determines its applications (Wenzhong et al., 2008). Over time, many novel ways, as arc discharge, chemical vapor

^{*} Author to whom all correspondence should be addressed: e-mail: ignat.maria@icmpp.ro; Phone: 0746505227

deposition, laser ablation, and template synthesis techniques (Kyotani et al., 2000; Kyotani et al., 2003; Olson et al., 2008; Zhang et al., 2002) to precisely control the pore size and structure of different types of porous carbons have been proposed. The properties of such mesoporous carbons are determined by the nature of the precursor used in the template synthesis method to produce novel forms of carbon with unusual properties (Goncalves et al., 2000; Sakintuna and Yurum, 2005). For example, glycerol (Ignat and Popovici, 2011) when carbonized inside mesoporous silica pores, yielded template carbon. This shows that the confined environment (pore) can control the process of carbonization at molecular level. This method is easy, inexpensive and can be suitable adapted for large-scale production.

In this regard, a simple and reversible delivery system can be envisaged. This system is based on a combination of the MC material with a stimuliresponsive or "smart" polymer. Thus, the access to the pores is controlled by application of a stimulus, such as a change in pH, ionic strength, or temperature. Therefore, poly-N-isopropylacrylamide (PNiPAM) was selected to improve the adsorption capacity of the templated MC material, which will lead to unusually intimate interactions between the polymer and the inorganic phase (Mark et al., 2006; Winey et al., 2006). The PNiPAM/MC composite mesoporous material exhibit the same chemical properties of the used polymer, whereas the specific surface area and the stability of the pores against mechanical compression, thermal and chemical treatments is greatly enhanced. As result, the resultant composite exhibits surface properties of the polymer.

Vitamin B2 (VB2) is a water-soluble Bcomplex, which plays an important role in the oxidation and reduction reactions of fats, proteins and carbohydrates, promoting regular patterns of growth and development. Vitamin B2 assists the energy release from food and is part of the electron transport mechanism involved in this process. When vitamin B2 deficiency in human body occurs, a supplement administration is always requested.

Adsorption of vitamin B2 on solid surfaces has attracted the attention due to its importance for the food industry and medicine. Vadi and Hadipour (2011) have recently reported the adsorption of vitamin B2 on carbon nanotubes. They found that the adsorption of vitamin B2 on carbon nanotubes is of higher efficiency and the adsorption process obeys the Freundlich isotherms.

In this study the polymer-functionalized MC was obtained by a combination of simple surface modification of the MC material and in situ internal polymerization of PNiPAM. The formation of the PNiPAM inside the mesoporous carbon was confirmed by Fourier Transform-Infrared Spectroscopy, Transmission electron microscopy and N_2 adsorption-desorption measurements. Polymer-modified adsorbents and MC have been used for

separation of the VB2 from solutions and the equilibrium adsorption isotherms have been studied.

2. Experimental

2.1. Chemicals materials

All reagents (Analitical Grade) used in the experiment were purchased from Aldrich and Acros Organics: tetraethyl orthosilicate $(Si(OC_2H_5)_4)$ and tri-block copolymer poly (ethylene glycol)-blockpoly (propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, EO₂₀PO₇₀EO₂₀), $(C_{3}H_{5}(OH)_{3}),$ glycerol Nisopropylacrylamide (NiPAM), 2.2'azobisisobutyronitrile (AiBN), N.N'-methylene bisacrylamide, ethanol, chloroform, vitamin B2. All products were used as received. The distilled water requested for experiments was prepared with an ELGA Purelab water system.

2.2. Synthesis of mesoporous carbons

The mesoporous carbon sample was prepared by a hard-template method, reported by Ignat and Popovici (2011), using the ordered mesoporous silica (SBA-15 type) as template (Ryoo et al., 1999) and glycerol as carbon source. The silica template has been synthesized using a tri-block copolymer (Pluronic P123) by a sol-gel method described by Ryoo in 1999.

In a typical synthesis of ordered mesoporous carbon, the SBA-15 silica was loaded with 10% glycerol solution by dry impregnation method. The resulted mixture was then subjected to polymerization and the polymer-silica composite have been pyrolyzed in a nitrogen flow at 800 °C. Afterward, the SBA-15 silica framework was leached with HF solution in order to separate the carbon structure. The obtained powdered sample was labelled as MC.

2.3. Synthesis of PNiPAM-functionalized MC

N-isopropylacrylamide, 0.25g, have been dissolved in 2 ml ethanol. Then, 0.01g of 2,2'- azoisobutyronitrile (AiBN), as free radical initiator, together with 0.02g of N,N' – methylene bisacrylamide (BIS) were added to the prepared solution and stirred at ambient temperature until a clear solution is obtained. Further, 0.1 g of mesoporous carbon material (MC) was impregnated with the above prepared mixture. After 2h of impregnation, the black solid was air-dried at room temperature to remove the alcohol.

Afterwards, the polymerization step was performed in a heating oven at 80 °C for 24 h. The resulted powdered sample was washed twice with chloroform and ethanol to remove unreacted chemicals. The obtained product was then dried overnight at 80 °C and the final sample was labeled as PNiPAM/MC composite.

2.4. Adsorption of vitamin B2

For the adsorption tests, a series of standard vitamin B2 solutions with concentrations ranging from 3 to 100 mg/L was prepared first by dissolving it in distilled water. In each adsorption experiment, 0.01 g of different mesoporous carbon based adsorbents was suspended overnight in 10 mL of the vitamin B2 solution. The resulting mixture was continuously magnetically stirred at room temperature until equilibrium was reached (typically 12 h). The amount of vitamin B2 adsorbed was determined by UV-Vis spectroscopy, at 263.5 nm, substracting the amount found in the supernatant solution after adsorption process from the initial found amount of vitamin B2 in that solution. Calibration experiments were done separately before each set of measurements with vitamin B2 solution of different concentrations in distilled water. Filtration prior to the measurements was used to avoid potential interference from suspended scattering particles in the UV-vis analysis.

2.5. Characterization

FT-IR absorption spectra were recorded using a Bruker Vertex 70 FTIR spectrometer in order to investigate the surface chemistry of the synthesized materials. Registrations were performed in transmission mode within 400–4000 cm⁻¹ range with a resolution of 2 cm⁻¹ at room temperature on samples dissolved in KBr pellets.

 N_2 -sorption measurements of the prepared samples were performed on a Quantachrome Nova 2200 Instrument & Pore Size Surface Area Analyzer using nitrogen as adsorbate at -196 °C. Before analysis, all samples have been outgassed under vacuum for 10 hours at room temperature. The specific surface area was calculated using the formula of the BET equation. The total pore volume was taken from the adsorption-desorption isotherm at $P/P_0 = 0.95$. Pore size distributions (PSDs) were determined using Barrett-Joyner-Halenda equation (Barrett et al., 1951).

TEM images were collected on a Hitachi High-Tech HT7700 electron microscope (Hitachi High-Technologies Corporation, Tokyo, Japan) operated at 120 kV, using copper grids (300 mesh) coated with ultrathin carbon film on holey carbon support film (Ted Pella, Redding, CA).

The concentration of the vitamin B2 in solutions was monitored at 263.5 nm wavelength with a Shimadzu UV-1700 PharmaSpec spectrophotometer.

3. Results and discussion

FT-IR spectra of PNiPAM/MC, PNiPAM/MC-VB2, MC-VB2, VB2 and pristine MC solid samples are shown in Figs. 1a and 1b. The FT-IR spectra show the H-bonding between vitamin and PNiPAM/MC composite by the presence of the peak centered at 3400 cm⁻¹. Although, N-H and O-H bonds are also involved in the hydrogen bonding, each individual O-H bond have a slightly different vibrational frequency, causing a broad peak aspect.

It is important to note that the adsorption capacity of PNiPAM/MC composite for vitamin B2 is higher as compared to un-functionalized mesoporous carbon. This happens most probably due to the formation of hydrogen bonds between carbonyl and amino groups (C=O···H-N) from both the PNiPAM-coated mesoporous carbon surface and vitamin B2 molecules. Also, when vitamin B2 is adsorbed on mesoporous materials, a broad peak in the "fingerprint" region (below ~1500 cm⁻¹) of both MC-VB2 and PNiPAM/MC-VB2 spectra could be observed. Vibrations that occur in this region are very complex and are hard to assign to a specific functional group.

Figs. and show 2 3 the N_2 MC adsorption/desorption isotherms of and PNiPAM/MC samples in comparison to the same adsorbents after adsorption of vitamin B2 from aqueous solutions. The isotherm of MC and PNiPAM/MC samples are of type IV according to the IUPAC classification and exhibits a H1 hysteresis loop, whereas MC-VB2 and PNiPAM/MC-VB2 samples exhibit a type IV isotherm without hysteresis. As is evident from Figs. 2 and 3, the isotherms of MC featured a large capillary condensation step, indicating different sized mesopores, while the isotherm of PNiPAM/MC sample a narrow capillary condensation step, localized at lower relative pressures, indicating narrowed mesopores. The adsorption isotherms of MC-VB2 and PNiPAM/MC-VB2 samples are of type I isotherm, which is characteristic for a microporous material. The textural properties of the mesoporous carbon-based adsorbents before and after adsorption of vitamin B2 are collected in Table 1. As expected, the specific surface area of MC carbon sample (1319 m^2/g) is higher than the specific surface area of PNiPAM/MC (678 m^2/g), due to the pore blocking by polymer particles. As well, the specific pore volume of mesoporous carbon material is 1.26 cm³/g, which is higher as compared to the specific pore volume of PNiPAM/MC system ($0.74 \text{ cm}^3/\text{g}$).

As result, the amount of nitrogen adsorbed decrease with VB2 uptake from solution, leading to a decrease of the BET specific surface area (from 1319 m^2/g to 130 m^2/g for MC system, and from 678 m^2/g to 67 m^2/g for PNiPAM/MC system) and the total pore volume (from 1.26 cc/g to 0.14 cc/g for MC system, and from 0.74 cc/g to 0.08 cc/g for PNiPAM/MC system), because the pores being filled up with vitamin B2 molecules.

An evidenced difference is observed from the adsorption tests that are in line with the different pore diameter of the adsorbents. It is important to note that PNiPAM/MC composite exhibited a high amount of vitamin B2 adsorption (1554 mg/g), which is 1.5 times higher as compared to MC sample (954 mg/g). In fact, the BET specific surface area of the adsorbent

is a crucial factor which determines the adsorption capacities of carbon adsorbents (Noll et al., 1992). Contrariwise, the adsorption capacity of the carbonbased adsorbents increases in the following order, MC < PNiPAM/MC, although MC carbon sample has a higher specific surface area as compared to PNiPAM/MC. The textural properties of the mesoporous carbon-based adsorbents other than BET specific surface area such as pore volume and pore diameter also play an important role in determining the vitamin B2 adsorption capacity. It should also be noted that, although the difference in the pore volume of MC and PNiPAM/MC is very small, there is a large difference in their amount of vitamin B2 adsorption.

Although, PNiPAM/MC system has a decreased BET specific surface area compare to MC sorbent, a reasonable explanation for the higher sorption capacity envisage the PNiPAM polymer particles deposited on the external surface of the

carbon material, confirmed by TEM (Fig. 4). Actually, PNiPAM polymer particles insert on the carbon surface functional groups that are responsible for the hydrogen bonding with vitamin B2 molecules (Fig. 1). So, in this case, the uptake of larger molecules, vitamin B2, is explained in terms of the surface functional groups inserted on the mesoporous carbon surface, not to the BET specific surface area (which normally should lead to a decreased sorption capacity).

In order to describe the absorption process of vitamin B2 on the prepared carbon materials, Langmuir, Freundlich and Temkin isotherms have been drawn (Figs. 5 and 6). All the experimental data and the calculated parameters are listed in Table 2.

Finally, could be observed that the adsorption process of vitamin B2 on MC sample obeys Temkin isotherm, reaching an $R^2 = 0.9997$, while the adsorption on PNiPAM-functionalized MC sample obeys Langmuir isotherm, reaching an $R^2 = 0.7535$.



Fig. 1. FT-IR spectra of MC, PNiPAM and PNiPAM-coated MC (a) and VB2, VB2-adsorbed on simple MC and PNiPAM/MC composite (b)



Fig. 2. Nitrogen adsorption-desorption isotherms with corresponding BJH pore size distributions (inset) of MC, MC-VB2 samples



Fig. 3. Nitrogen adsorption-desorption isotherms with corresponding BJH pore size distributions (inset) of MC, PNiPAM/MC and PNiPAM/MC-VB2 samples

Sample Feature*	МС	MC-VB2	MC/PNiPAM	MC/PNiPAM-VB2
$S_{BET}, m^2/g$	1319	130	678	67
V_{tot} , cc/g	1.26	0.14	0.74	0.08
V _{micro} , cc/g	0	0	0.002	0
$S_{\text{micro}}, m^2/g$	0	0	3.93	0
d _p , nm	3.89	3.26	2.2	2.0

where: S_{BET} is BET specific surface area; V_{tot} - total pore volume calculated as the amount of nitrogen adsorbed at the relative pressure of P/P_0 = 0.95; V_{micro} - micropore volume calculated by the t-plot method; S_{micro} - micropore surface area calculated using t-plot method; d_p - average pore diameter resulted from BJH pore size distribution using adsorption branch





Fig. 4. TEM images of pristine MC (a) and PNiPAM/MC (b) samples



Fig. 5. Langmuir, Freundlich and Temkin isotherms for the adsorption of vitamin B2 on MC adsorbent

Table 2. Langmuir, Freundlich and Temkin parameters for adsorption of VB2 on mesoporous carbon based material

	Post Adsorption VB2 (mg/L)		VB2 Adsorbed (mg)		VB2 Adsorbed per Unit Mass of adsorbent (mg/g)		Langmuir Data				Freundlich Data			
	СМ	CM- PNiPAM	СМ	CM- PNiPAM	СМ	CM- PNiPAM	СМ		CM- PNiPAM		СМ		CM- PNiPAM	
° с	o O				0		$1/q$, $*10^{-1}$	<i>ا/د</i> و	 1/q, *10	1/c •	log c	h Bol	log c	h gol
6	0.15		5.58		557		0.18	2.36			-0.86	1.71		
9	0.25		7.35		735		0.14	0.61			0.49	1.99		
12	0,413		8.37		837		0.12	0.28			1.28	2.12		
15	0.60	3.08	9.10	11.9	909	1191	0.11	0.17	0.84	0.32	1.77	2.20	1.12	7.08
18	0.87	3.63	9.54	14.4	954	1437	0.10	0.12	0.70	0.28	2.13	2.25	1.28	7.27
21		5.91		15.1		1509			0.66	0.17			1.77	7.31
24		8.46		15.5		1554			0.64	0.12			2.13	7.34



Fig. 6. Langmuir, Freundlich and Temkin isotherms for the adsorption of vitamin B2 on PNiPAM/MC material

4. Conclusions

Adsorption process of vitamin B2 over mesoporous carbon-based materials such as MC and PNiPAM/MC has been studied from vitamin B2 solutions with various concentrations, and the obtained results were compared. It has been observed that the vitamin B2 adsorption capacities of the adsorbents depend on the surface chemistry play an important role.

It has been found that the functionalization with PNiPAM polymer is more suitable as compared to un-functionalized mesoporous carbon to achieve high loadings of vitamin B2. The equilibrium adsorption data fitted well to all studied models, giving a better fit to the Langmuir model in the case of PNiPAM-functionalized MC sample, as was evidenced from the higher values of R^2 of 0.9997. Thus, the experimental data allowed determining the extent and degree of favorability of adsorption.

The obtained results showed that the adsorption capacity obtained for PNiPAM-functionalized mesoporous carbon (80%) is greater than the vitamin B2 adsorption on pristine mesoporous carbon (53%).

These results show that the PNiPAMfunctionalized mesoporous carbon compare favorably with un-functionalized mesoporous carbon. Nitrogen adsorption-desorption data after vitamin B2 adsorption reveal that the vitamin B2 molecules entered mesopores of tested mesoporous carbonbased adsorbents.

Acknowledgements

The authors acknowledge the grants of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-PD-2012-3-0357, Contract 30/2013, and project number PN-II-ID-PCE-2011-3-0559, Contract 265/2011 for the financial support.

References

- Bansal C.R., Donnet J.B., Stoeckli F., (1998), *Active Carbon*, Marcel Dekker, New York.
- Gerçel O., (2015), Adsorption properties of activated carbon from wild plant prepared by chemical activation, *Environmental Engineering and Management Journal*, **14**, 129-137
- Goncalves A.B., Mangrich A.S., Zarbin A.J.G., (2000), Polymerization of pyrrole between the layers of alphatin (IV) bis(hydrogen phosphate), *Synthetic Metals*, 114, 119–24.
- Ignat M., Popovici E., (2011), Synthesis of mesoporous carbon materials via nanocasting route – comparative study of glycerol and sucrose as carbon sources, *Romanian Journal of Chemistry*, **56**, 947-952.
- Kyotani T., Tsai I.F., Tomita A., (2000), Formation of ultrafine carbon tubes by using an anodic aluminium oxide film as a template, *Journal of Materials Chemistry*, 7, 1427-1428.
- Kyotani T., (2000), Control of pore structure in carbon, *Carbon*, **38**, 269–86.
- Kyotani T., Ma Z., Tomita A., (2003), Template synthesis of novel porous carbons using various types of zeolites, *Carbon*, **41**, 1451–1459.
- Liang C., Li Z., Dai S., (2008), Mesoporous carbon materials: synthesis and modification, *Angewandte Chemie International Edition*, **47**, 3696–3717.
- Mark J.E., (2006), Some novel polymeric nanocomposites, Accounts of Chemical Research, **12**, 881-888.
- Nastas R., Rusu V., Lupascu T., (2013), Copper impregnated activated carbon for the treatment of sulpfurous waters, *Environmental Engineering and Management Journal*, **12**, 937-942.
- Noll K.E., Gournaris V., Hou W.S., (1992), Adsorption technology for air and water pollution control, Lewis Publishers: Chelsea, MI.
- Olson D.A., Chen L., Hillmyer M.A., (2008), Templating nanoporous polymers with ordered block copolymers, *Chemistry of Materials*, **20**, 869-890.

- Ramos A., Otero M., Rodrigues A.E., (2004), Recovery of vitamin B12 and cephalosporin C from aqueous solutions by adsorption on nonionic polymeric adsorbents, *Separation and Purification Technology*, 38, 85–98.
- Ryoo R., Joo S.H., Jun S., (1999), Synthesis of highly ordered carbon molecular sieves via templatemediated structural transformation, *Journal of Physical Chemistry B*, **103**, 7743-7746.
- Sakintuna B., Yurum Y., (2005), Templated porous carbons: A review article, *Industrial & Engineering Chemistry Research*, 44, 2893.
- Shen W.Z., Zheng J.T., Zhang Y.L., (2003), The effect of pore structure of activated carbon on the adsorption of Congo red and vitamin B12, *Studies in Surface Science and Catalysis*, **146**, 779–82.
- Vadi M., Hadipour I., (2011), Adsorption isotherm study of Vitamin B2 on carbon nanotube, *Oriental Journal of Chemistry*, 27, 1037-1040.
- Vinu A., Streb C., Murugesan V., Hartmann M., (2003), Adsorption of Cytochrome C on New Mesoporous Carbon Molecular Sieves, *Journal of Physical Chemistry B*, **107**, 8297–8299.
- Vinu A., Hossain K.Z., Kumar G.S., Ariga K., (2006), Adsorption of 1-Histidine over mesoporous carbon molecular sieves, *Carbon*, 44, 530-536.
- Vinu A., Hossian K.Z., Srinivasu P., Miyahara M., Anandan S., Gokulakrishnan N., Mori T., Ariga K., Balasubramanian V.V., (2007), Carboxy-mesoporous carbon and its excellent adsorption capability for proteins, *Journal of Materials Chemistry*, **17**, 1807-1819.
- Wenzhong S., Zhijie L., Yihong L., (2008), Surface chemical functional groups modification of porous carbon, *Recent Patents on Chemical Engineering*, 1, 27.
- Winey K.I., Moniruzzaman M., (2006), Polymer nanocomposites containing carbon nanotubes, *Macromolecules*, 39, 5194-5205.
- Zhang W.H., Liang C., Sun H., Shen Z., Guan Y., Ying P. Li C., (2002), Synthesis of ordered mesoporous carbons composed of nanotubes via catalytic chemical vapor deposition, *Advanced Materials*, 14, 1776–1778.