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**ADSORPTIVE PERFORMANCE OF HYPER-CROSSLINKED
POLYMERIC RESINS COMPARED TO GRANULAR
ACTIVATED CARBON FOR TOLUENE VAPOURS, UNDER
STATIC CONDITIONS AND IN HUMID ENVIRONMENT**

BY

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Abstract. The purpose of this study is to evaluate the adsorptive performance of two hyper-crosslinked polymeric resins, MN 202 and MN 250 for toluene vapours, under static conditions. All experiments were performed in comparison with toluene vapours adsorption on GAC-AC 20. Since the humidity is one of the crucial parameters that dictate the efficiency of the adsorption process, the influence of relative humidity on the toluene vapour retention efficiency at different concentrations in system was considered. The results included in this study show that the adsorptive performance recorded by MN 202 and MN 250 are very closely to those recorded by AC 20. Moreover, in the humid conditions, the polymeric adsorbents MN 202 and MN 250 behave much better than AC 20. Thus, the adsorption capacity of AC 20 decreased by 80% when the relative humidity in system increased from 0% to 97%, while adsorption capacities of MN 202 and MN 250 decreased with 40% and respectively 50%.

Keywords: adsorption; toluene; VOCs; hyper-crosslinked polymeric resins; relative humidity; humid environment.

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1. Introduction

Volatile organic compounds (VOCs) refer to a group of organic substances characterized by a high vapour pressure under normal conditions which favors their vaporization and subsequently release to the atmosphere. The various definitions of VOCs are conducted by main international organizations. It can be defined as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (Li *et al.*, 2020a; Shafiei *et al.*, 2018; Zhu *et al.*, 2020). The sources of VOCs can be divided into sources of natural processes and human activities. The VOCs released by natural processes are mainly from plants, forest fires, etc. which are uncontrollable emission sources. The main sources of anthropogenic VOCs are petroleum refineries, chemical industries, fuel combustion, pharmaceutical plants, automobile industries, textile manufacturers, solvents processes, cleaning products, printing presses, insulating materials, office supplies, printers etc. Examples of VOCs are halogenated hydrocarbons, aldehydes, aromatic compounds, polycyclic aromatic hydrocarbons, alcohols, alkanes, ketones, olefins, and ethers (Li *et al.*, 2020a; Zang *et al.*, 2019; Zhu *et al.*, 2020).

It is well known that VOCs are one of the major contributors to the formation of photochemical ozone and pollutants and secondary organic aerosols (SOAs) pose serious harms to both the ecological environment and human health. The condensation and nucleation of OVOCS (oxygenated volatile organic compounds), SOAs and SNAs (secondary nitric aerosols) can contribute to PM_{2.5} formation. Most VOCs, in particular aromatic compounds and polycyclic aromatic hydrocarbons, are malodorous, toxic and carcinogenic to human health even at low concentration (above 0.2 mg/m³), leading to respiratory inhalation and skin mucosa and damage of nervous and blood systems (Hu *et al.*, 2009; Zhu *et al.*, 2020). Toluene is one of the VOCs species with the highest ozone formation potential (Li *et al.*, 2020a).

In the last years stringent regulations have been proposed to control VOCs emissions, especially in industrialized countries. VOCs emission can be reduced through process and equipment modifications. Limited by technology and cost, add-on-control techniques are widely used. Add-on-control techniques are divided into recovery methods and destruction methods based on whether or not the VOCs is recovered. Recovery methods include membrane separation, absorption, adsorption, condensation, and the destruction techniques include catalytic oxidation, biodegradation, thermal oxidation and plasma catalysis, etc. (Li *et al.*, 2020a, Shafiei *et al.*, 2018; Zang *et al.*, 2019). The destruction method mainly converts VOCs into CO₂ and H₂O, which consume large amount of energy to generate high temperature for the reaction, and they inevitably produce some toxic byproducts such as NO_x, O₃, OH radicals, secondary organic aerosols, etc. Recovery methods are more economical and

Environmental-friendly duo to the mild reaction conditions and recovery of VOCs (Li *et al.*, 2020a; Zhu *et al.*, 2020).

Adsorption technology is considered an efficient and economical control strategy because of its potential to recover and reuse both adsorption materials and VOCs, the flexibility of the system, low energy consumption and cheap operation cost. Activated carbon is the most widely applied adsorption material that exhibits a high performance on VOCs capture because of its good physical and chemical properties such as large specific surface area, abundant functional groups, chemical stability, high mechanical strength and acid and alkali resistance with a low cost (Gill *et al.*, 2014; Li *et al.*, 2020a; Zhu *et al.*, 2020). The adsorption capacity and kinetics of activated carbon for target VOCs are related to gas phase concentration, temperature, VOCs type and relative humidity. The presence of water is inevitable in the VOCs supported air stream. In this case, water molecule and VOCs compete for adsorption on activated carbons, which degrade the adsorption capacity of VOCs (Li *et al.*, 2020b; Liu *et al.*, 2018; Zhou *et al.*, 2019). However, it has been recognized that activated carbon adsorption always encounters some problems such as fire risk, pore blocking, poor thermal stability, inefficiently desorption of high-boiling solvents and hygroscopicity under wet conditions (Hu *et al.*, 2009; Liu *et al.*, 2018; Shafiei *et al.*, 2018; Valderrama *et al.*, 2007). Hence, novel adsorption materials were desired to be developed to overcome these kind of problems.

In general, gaseous streams are likely to have a relative humidity, sometimes even very high. However, in many sources of VOCs, a large amount of water vapours comes from air and reactors. The relative humidity (RH) of exhaust gas is normally more than 60% and even supersaturated because of a large amount of condensed water existing in adsorption containers. Thus, quantifying the effect of relative humidity on the properties of adsorbents is absolutely necessary. The competitive adsorption of organic molecules and water molecules also affects the overall performance of adsorption. The higher the adsorption capacity of an adsorbent for water vapour, the more water will be co-desorbed with VOCs in the regeneration step. This will lead to the generation of liquid effluents that need to be further treated. Also, if the capacity of the adsorbent for VOCs retention will be diminished in the presence of water vapour, then a larger volume of adsorbent will be needed to be able to purify a given volume of VOC-contaminated air (Li *et al.*, 2020b; Rodríguez-Mirasol *et al.*, 2005; Zhou *et al.*, 2019).

In this context, this work is focused to evaluate the performance of toluene vapours adsorption from atmosphere by two types of non-functionalized hyper-crosslinked polymers Hypersol Macronet, MN 202 and MN 250 compared to adsorption on granular activated carbon, at different concentrations of toluene vapours under static conditions. Also, this study is aimed to explore the influence of abound water vapour from atmosphere on polymeric resins and granular activated carbon and the effect of the humid environment over toluene vapour adsorption by these adsorbents.

2. Materials and Methods

2.1. Materials

MN 202 and MN 250, two commercial non-functionalized hyper-crosslinked polymeric resins and a bituminous granular activated carbon AC 20 were used for evaluate the adsorption potential for toluene vapours. Both polymers present a hyper-reticulated structure, macroporous polystyrene crosslinked with divinyl-benzene, which provide macroporosity and microporosity to the solid at the same time. This means a control on the size of pores and relatively high surface areas. The physical characteristics of MN 202, MN 250 and AC 20 are listed in Table 1 (Purolite Technical Bulletin, 1999). All adsorbents were supplied from Purolite International Ltd., Country offices of Purolite Corporation in Bucharest, Romania.

Table 1
The Physical Characteristics of MN 202, MN 250 and AC 20 Adsorbents

Characteristics	MN 202	MN 250	AC 20
Structure	Macroporous Polystyrene Crosslinked with Divinyl-benzene		Bituminous granular carbon
Physical Appearance	Opaque Spherical beads		Black Spherical beads
Functional group	None		-
Whole Bead Content	> 90%		-
Shipping weight, g/L	700	670-700	-
Screen size range	16-50 mesh		-
Bead size range	< 5% greater than 1.2 mm, < 1% smaller than 0.3 mm		0.4-1.4 mm
Volatile moisture	cca. 55%		-
Specific Gravity, g/mL	1.04		1.4
pH range	0-14		-
Surface area (m ² /g) (BET)	931 m ² /g	985 m ² /g	900-1000 m ² /g
Pore volume (mL/g)	1-1.1	0.6-0.8	-
d ₅₀ , A° meso and macropores	600-900	300-400	-
d ₅₀ , A° micropores	15	14	-
Moisture, %	50-60	50-58	max. 2

The type of VOCs studied is toluene, a typical nonpolar and inert aromatic hydrocarbon, which is widely used like industrial solvents. Toluene (C₆H₅-CH₃), with an analytical grade of 99.9% was purchased from Chemical Company and used in this study without further purification.

2.2. Static Adsorption Experiment

All the experiments were analyzed in static conditions and it were performed in headspace vials of 20 mL volume with septum, in which an amount of 0.01 g from each adsorbents (MN 202, MN 250 and AC 20) were introduced. Also, the different concentration of toluene were created in the vials (0-56550 ppm), by injection of liquid toluene through the septum using a 0.1 μ L syringe (Hamilton). For achieve the adsorption equilibrium, the vials were kept in the dark, at a temperature of 298 K, for 24 hours.

For study the effect of relative humidity on the toluene vapour adsorption efficiency, the vials with 0.01 g of each adsorbent were kept in a controlled humidity atmosphere, in a perfectly tight vessel, until the equilibrium of water vapours has been reached. The studies were conducted at different relative humidity's ($RH = 33\%$, 75% , 84% and 97%), which were obtained by means of supersaturated solutions of salts that dictate these humidity. After that, the vials were sealed and different concentrations of toluene vapours was created inside them by injecting different volume of toluene. Then the vials were kept in the dark, at a temperature of 298 K until the adsorption equilibrium of toluene vapours was reached.

In order to determine the concentration of toluene vapours in each vials after adsorption equilibrium, using a Gastight syringe, a volume of 3 mL from headspace of each vials were taken and were introduced in a Gas Chromatograph with FID detector. Each test was performed three times in order to obtain an accuracy of the experimental results.

Prior to each test, the adsorbents were pretreated in an oven at 120°C for 24 h to remove the moisture and other contaminants that were physically adsorbed during storage. Then, the adsorbents were cooled to room temperature and stored until their use in a desiccator.

The adsorption efficiency of AC 20, MN 202 and MN 250 was evaluated by the toluene vapours removal, R , [%], (Eq. (1)):

$$R (\%) = \frac{C_0 - C}{C_0} \cdot 100 \quad (1)$$

and by adsorption capacity (q – amount of toluene vapours adsorbed per 1 gram adsorbent), [mg/g] (Eq. (2)):

$$q (\text{mg/g}) = \frac{(C_0 - C) \cdot V}{m_{\text{adsorbent}}} \quad (2)$$

where: C_0 and C are toluene vapours concentration, initial and at equilibrium, [mg/m^3] or [ppm]; V is the volume of gas in the headspace vial, [m^3]; $m_{\text{adsorbent}}$ is the mass of adsorbent, [g].

The adsorption capacity of adsorbents for water vapour, % *water adsorbed*, was calculated using (Eq. (3)):

$$\% \text{ water adsorbed} = \frac{m_{\text{adsorbed}}^{\text{water}}}{m_{\text{adsorbent}}} \cdot 100 \quad (3)$$

where: $m_{adsorbed}^{water}$ is mass of water adsorbed by adsorbent at equilibrium, [g] and $m_{adsorbent}$ is the mass of adsorbent use in test, [g].

3. Results and Discussion

3.1. The Influence of Toluene Vapours Concentration

The influence of initial toluene vapours concentration on the adsorption retention efficiency (R , %) and on the adsorption capacity (q , mg/g) of MN 202 and MN 250 polymers and of AC 20 – GAC was examined using 0.01 g of adsorbent, at room temperature and at different concentration of toluene in the vials, in the range 0-56550 ppm.

The experimental results are illustrated in Fig. 1a-c.

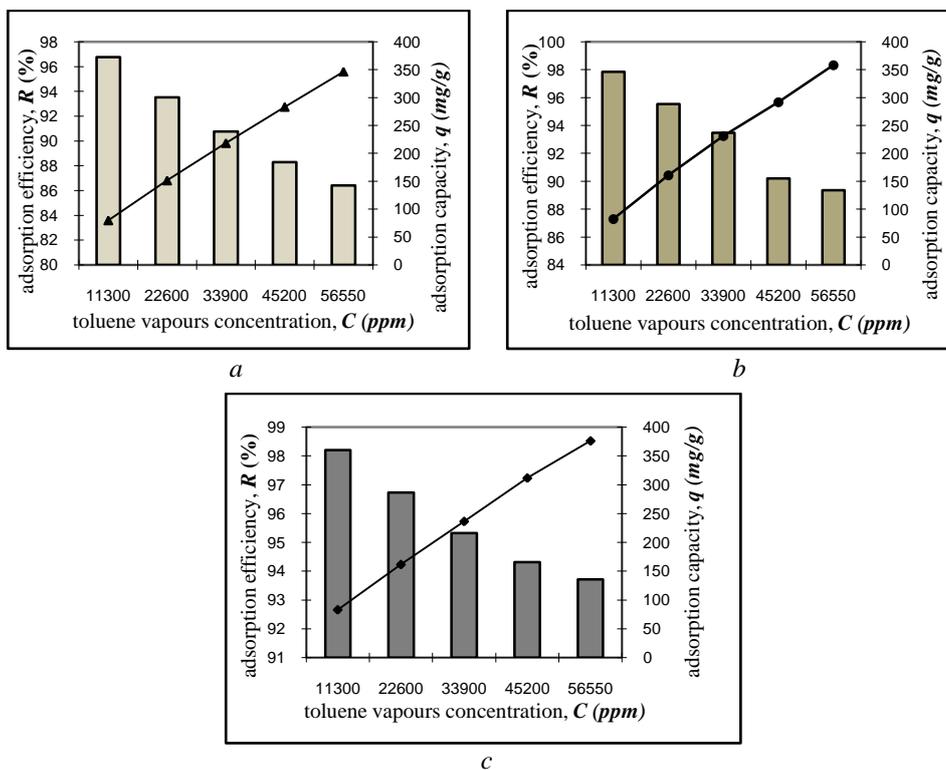


Fig. 1 – Effects of toluene vapours concentration on the adsorption efficiency (R , %) and on the adsorption capacity (q , mg/g) for MN 202-(a), MN 250-(b) and AC 20-(c).

From Fig. 1a-c it is observed that the retention efficiency of each adsorbent decrease with increasing initial concentration of toluene vapours in the headspace vials. The highest value for adsorption efficiency is achieved at a low concentration of toluene vapours, *i.e.*: at 11300 ppm, the values for R are

96.7% for MN 202, 97.8% for MN 250 and 98.2% for AC 20. At greater concentrations of toluene in the vials (56550 ppm), the adsorption efficiency decrease for each adsorbents studied (with 10% for MN 202, 8% for MN 250 and 4% for AC 20) but still recording a very high retention for VOCs vapours. From this point of view, the performance of toluene vapours adsorption is performed in order $AC\ 20 > MN\ 250 > MN\ 202$.

Regarding the adsorption capacity (q , mg/g), this increases with the increase in toluene vapours concentration. Thus, at 56550 ppm the values of q recorded for the adsorbents studied are 346.5 mg/g for MN 202, 358.4 mg/g for MN 250 and 375.8 mg/g for AC20. With respect to adsorption capacity, the performance of toluene vapours adsorption in static conditions is realized in order $AC\ 20 > MN\ 250 > MN\ 202$. It is observed that polymeric resins MN 202 and MN 250 records high efficiencies for toluene vapours adsorption comparable to those recorded by granular activated carbon.

3.2. The Influence of Relative Humidity

In Fig. 2 the adsorption capacities of the AC 20, MN 202 and MN 250 adsorbents for water vapour are presented, after reaching equilibrium (after 24 h), at the RH studied, namely 33%, 75%, 84 % and 97%.

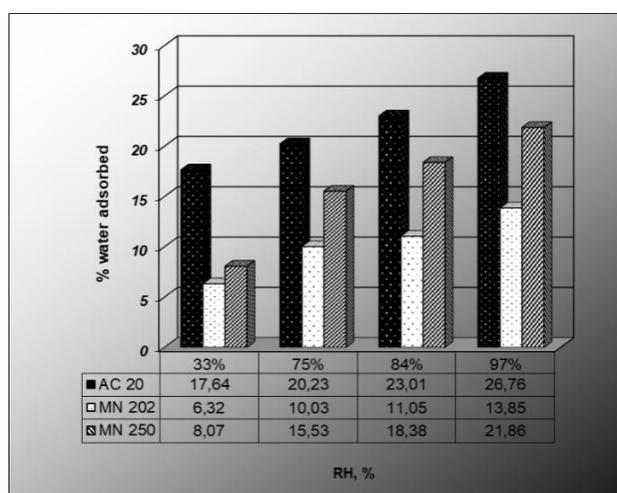


Fig. 2 – Comparison of the maximum adsorption capacities for water vapours of AC 20, MN 202 and MN 250 adsorbents.

As can be seen from Fig. 2, granular activated carbon AC 20 adsorbed most water at each relative humidity studied, followed by MN 250 and MN 202 polymeric adsorbents. This is one of the advantages of hyper-crosslinked polymeric adsorbents MN 202 and MN 250 over GAC-AC 20, which will

materialize in a very small amount of water co-desorbed in the regeneration phase of polymeric adsorbents.

The experimental data obtained for the adsorption efficiency, R , [%], of toluene vapour by MN 202, MN 250 and AC 20 adsorbents under static conditions, at different relative humidities, RH , [%] and at different concentration are presented in Fig. 3a-c.

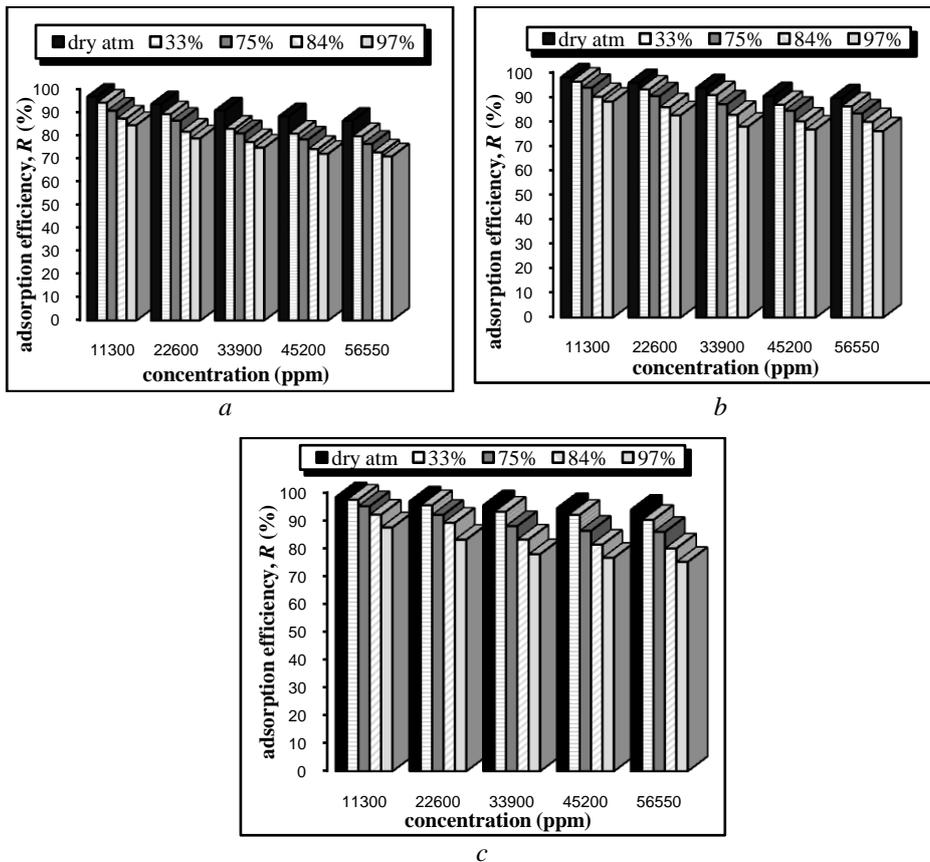


Fig. 3 – Effects of relative humidity (RH , %) on the adsorption efficiency (R , %) for MN 202-(a), MN 250-(b) and AC 20-(c).

It can be seen from Fig. 3a-c that the relative humidity of atmosphere influences the adsorption performances of toluene vapours for each of the studied adsorbents. Their adsorption efficiency decreased with the increase of relative humidity in the atmosphere which implies that the adsorption capacity of the adsorbents is progressively diminished. Similar results were reported in the literature (Li *et al.*, 2020b). The decrease in the adsorption efficiency of toluene vapours is all the more pronounced as the initial concentration of

toluene vapours in the vials is higher. Also, it is observed that the adsorption efficiency of toluene vapour is more affected for AC 20 compared to polymeric adsorbents MN 250 and MN 202. Thus, under conditions of high atmospheric humidity, the performance of the toluene vapours adsorption is higher for polymeric adsorbents MN 250 and MN 202 than for AC 20 – GAC.

3.3. The Influence of the Type of Adsorbent

In Fig. 4 are presented comparatively the adsorption efficiencies achieved by MN 202 and MN 250 hyper-crosslinked polymers and by AC 20 granular activated carbon for toluene vapours, under static conditions and the temperature of 298 K, in dry atmosphere (Fig. 4a) and at a relative humidity of 97% (Fig. 4b), for the toluene concentration range from 11300 ppm to 56550 ppm.

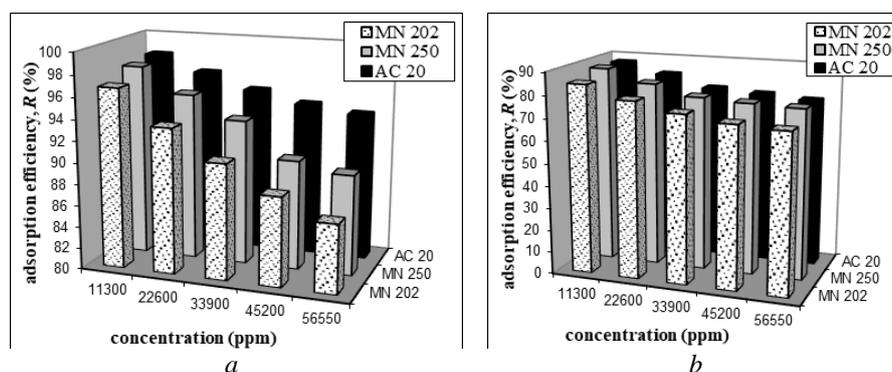


Fig. 4 – Comparisons of adsorption efficiency of AC 20, MN 250 and MN 202 adsorbents on toluene vapours in dry atmosphere – (a) and at RH = 97% – (b).

As can be seen from Fig. 4a, for the toluene vapour adsorption under static conditions, in dry atmosphere and the temperature of 298 K, all three adsorbents studied achieve high toluene vapour adsorption efficiency, more than 90%. The exception is for MN 202 whose retention efficiency decreases to 87%, for a toluene concentration of 56550 ppm. Instead, at a high relative humidity, RH = 97%, the adsorption efficiency for toluene vapours for GAC - AC 20 greatly decreases compared to the adsorption efficiencies of polymeric adsorbents MN 250 and MN 202 (Fig. 4b). Thus, under high relative humidity conditions, the MN 250 polymeric adsorbent achieves toluene vapour adsorption efficiencies greater than granular activated carbon AC 20, throughout the concentration range studied. The hyper-crosslinked polymeric resins MN 202 and MN 250 have rather a hydrophobic character than a hygroscopic one and thus adsorb less water than granular activated carbon AC 20. Consequently, the adsorption capacities of these adsorbents for toluene vapours are less affected by the relative humidity of the

gaseous stream, and the competitive effect between VOCs molecules and water is less intense compared to granular activated carbon AC 20.

4. Conclusions

In this study, the possibility of using hyper-crosslinked polymeric resins MN 202 and MN 250 for toluene vapours adsorption was analyzed, under static conditions. All the experiments were performed in comparison with adsorption of toluene vapours on granular activated carbon AC 20 at different conditions. The results show that:

- The adsorption efficiency (R , %) of toluene vapours by the studied adsorbents is dependent on the initial concentration of toluene in the system and its increase has the immediate effect of decreasing their adsorption efficiency, but still very high (*i.e.*: at 56550 ppm R is over 87%).

- The adsorption capacity (q , mg/g) increases with the increase in toluene vapours concentration from system and the values of q recorded by polymeric adsorbents MN 202 and MMN 250 are very close to those recorded by GAC-AC 20 in the same conditions.

- In the humid environments, AC 20 has a much higher adsorption capacity for water vapour compared to polymeric adsorbents MN 202 and MN 250, at each of RH studied.

- The increase of the relative humidity (RH , %) in the system has a negative effect on the efficiency of toluene vapours adsorption, leading to a reduction of the toluene retention efficiency (R , %), this being more pronounced for the GAC-AC 20 than for MN 202 and MN 250 polymeric adsorbents.

- The adsorption capacities of MN 202 and MN 250 polymeric adsorbents for toluene vapours are less affected by the relative humidity from the environment, and the competitive effect between VOCs molecules and water is less intense compared to granular activated carbon AC 20.

The results of this study indicate that the hyper-crosslinked polymeric adsorbents MN 202 and MN 250 could be successfully used for toluene vapour removal and can be better adsorbents than activated carbon for toluene vapours removal in humid environments.

REFERENCES

- Gill R.R., Ruiz B., Lozano M.S., Martin M.J., Fuente E., *VOCs Removal by Adsorption onto Activated Carbons from Biocollagenic Wastes of Vegetable Tanning*, Chemical Engineering Journal, **245**, 80-88 (2014).
- Hu Q., Li J.J., Hao Z.P., Li L.D., Qiao S.Z., *Dynamic Adsorption of Volatile Organic Compounds on Organofunctionalized SBA-15 Materials*, Chemical Engineering Journal, **149**, 281-288 (2009).

- Li X., Zhang L., Yang Z., Wang P., Yan Y., Ran J., *Adsorption Materials for Volatile Organic Compounds (VOCs) and the Key Factors for VOCs Adsorption Process: a Review*, Separation and Purification Technology, **235**, 116213 (2020a).
- Li X., Zhang L., Yang Z., He Z., Wang P., Yan Y., Ran J., *Hydrophobic Modified Activated Carbon using PDMS for the Adsorption of VOCs in Humid Condition*, Separation and Purification Technology, **239**, 116517 (2020b).
- Liu S., Chen J., Peng Y., Hu F., Li K., Song H., Li X., Zhang Y., Li J., *Studies on Toluene Adsorption Performance and Hydrophobic Property in Phenyl Functionalized KIT-6*, Chemical Engineering Journal, **334**, 1991-197 (2018).
- Rodríguez-Mirasol J., Bedia J., Cordero T., Rodríguez J.J., *Influence of Water Vapor on the Adsorption of VOCs on Lignin-Based Activated Carbon*, Separation Science and Technology, **40**, 3113-3135 (2005).
- Shafiei M., Alivand M. S., Rashidi A., Samimia S., Mohebbi-Kalhari D., *Synthesis and Adsorption Performance of a Modified Micro-Mesoporous MIL-101(Cr) for VOCs Removal at Ambient Conditions*, Chemical Engineering Journal, **341**, 164-174 (2018).
- Valderrama C., Cortina J.L., Farran A., Gamisans X., Lao C., *Kinetics of Sorption of Polyaromatic Hydrocarbons onto Granular Activated Carbon and MacronetHyper-cross-linked Polymers (MN 200)*, Journal of Colloid and Interface Science, **310**, 35-46 (2007).
- Zang M., Zhao C., Wang Y., Chen S., *A Review of Recent Advances in Catalytic Combustion of VOCs on Perovskite-Type Catalysts*, Journal of Saudi Chemical Society, **23**, 645-654 (2019).
- Zhou B., Sun B., Qiu W., Zhou Y., He J., Lu X., Lu H., *Adsorption/Desorption of Toluene on a Hypercrosslinked Polymeric Resin in a Highly Humid Gas Stream*, Chinese Journal of Chemical Engineering, **27**, 863-868 (2019).
- Zhu L., Shen D., Luo H.K., *A Critical Review on VOCs Adsorption by Different Porous Materials: Species, Mechanisms and Modification Methods*, Journal of Hazardous Materials, **389**, 122102 (2020).
- * Purolite Technical Bulletin – Hypersol-MacronetTMSobent Resins (1999).

PERFORMANȚA DE ADSORBȚIE A RĂȘINILOR POLIMERICE HIPER-
RETICULATE COMPARATIV CU CĂRBUNELE ACTIV GRANULAR PENTRU
VAPORII DE TOLUEN, ÎN CONDIȚII STATICE ȘI ÎN MEDIU UMED

(Rezumat)

Scopul acestui studiu este de a evalua performanțele de adsorbție pentru două rășini polimerice hiper-reticulate MN 202 și MN 250 față de vaporii de toluen, în condiții statice. Experimentele au fost realizate în comparație cu adsorbția vaporilor de toluen pe cărbunele activ granular AC 20, în aceleași condiții experimentale. Deoarece umiditatea este unul dintre parametrii cruciali care dictează eficiența procesului de adsorbție, s-a avut în vedere și studiul influenței umidității relative asupra eficienței de

reținere a vaporilor de toluen, la diferite concentrații. Rezultatele obținute în urma acestui studiu au pus în vedere faptul că performanțele de adsorbție înregistrate de adsorbantii polimerici MN 202 și MN 250 față de vaporii de toluen din sistem sunt foarte apropiate de cele înregistrate de cărbunele activ AC 20. Mai mult decât atât, în condiții de umiditate ridicată, adsorbantii polimerici MN 202 și MN 250 se comportă mult mai bine decât cărbunele activ AC 20, înregistrând eficiențe de reținere a vaporilor de toluen mai ridicate. Astfel, atunci când umiditatea relativă crește în sistem de la 0% la 97%, capacitatea de adsorbție pentru vaporii de toluen descrește pentru AC 20 cu 80%, în timp ce pentru adsorbantii polimerici MN 202 și MN 250 descrește cu 40% și respectiv 50%. Rezultatele obținute indică faptul că adsorbantii polimerici MN 202 și MN 250 pot fi utilizați cu succes pentru reținerea vaporilor de toluen, și pot fi considerați adsorbantii mai eficienți decât cărbunele activ AC 20 în condiții de umiditate ridicată.