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Adsorption behaviour of polar solvent and water vapours on Sorbonorit B4 activated carbon

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In this work, the affinity of the heterogeneous Sorbonorit B4 (SB4) activated carbon toward methyl ethyl ketone (MEK), isopropyl alcohol (IPA), n-propyl alcohol (NPA) and isobutyl alcohol (IBA), and water vapours was examined. Adsorption equilibrium measurements demonstrate a higher adsorption capacity of water vapour than organic compounds at relative pressures above 0.4. The adsorption capacities of SB4 at the same vapor pressure followed the order: NPA> IPA> MEK> IBA. The Langmuir, Dubinin-Radushkevich, Dubinin-Astakhov, and Toth isotherm models were chosen to describe experimental results. Based on the multi-temperature isotherms, the values of the isosteric heat of adsorption were determined for various adsorbate loading. The results indicate a strong influence of VOC molecule structures and the surface heterogeneity of SB4 on the adsorption efficiency. For IPA-SB4 pair, the maximum temperature rise in a fixed-bed bed in the adsorption process and the energy requirement for regeneration were calculated and experimentally verified.

Keywords: adsorption, activated carbon, isotherms, isosteric heat, column studies.

INTRODUCTION

One of the environmental problems is the release of volatile organic compounds (VOCs) into the atmosphere, that are substances with a vapor pressure of 0.01 kPa or more at 20 °C. VOCs are commonly used in both industrial and household chemical applications as solvents and ingredients in products such as antiseptics. Industrial waste gases may contain compounds with different adsorption affinities, which depend on the strength of the adsorbate-adsorbent interaction[1].

Activated carbon (AC) fixed bed adsorption is used to remove and recover VOCs from the polluted streams. AC is classified as a non-polar adsorbent with a strong affinity for non-polar compounds. Various functional groups containing oxygen may be present on the carbon surface. They may significantly hinder the adsorption of nonpolar molecules and may act as polar active sites for specific interactions with polar molecules[2]. Hydroxyl and carbonyl functional groups can act as the hydrogen-bonding donor or acceptor for polar VOCs, respectively. As the content of the oxygen functional groups on the carbon surface increases, it becomes more hydrophilic, which increases its affinity toward polar molecules[3]. In addition, the process can be problematic in the presence of water vapor, which also adsorbs on the adsorbent, reducing its VOC capture capacity[4–6].

In cyclic adsorption processes, the service life of the adsorbent depends on operating conditions at the adsorption stage (temperature, inlet concentration, gas flow velocity) and the degree of regeneration of the exhausted AC. In the case of a strong affinity of the adsorbent toward the adsorbed components, it is not possible to restore the original adsorption capacity of activated carbon at a moderate temperature of regeneration. Regeneration conditions should be optimized to enable rapid desorption with minimal adsorbate decomposition and coke formation. Due to heel formation, some adsorptive sites remain occupied by the adsorbate, which caused a change in the surface chemistry and adsorption capacity of AC[7–9]. Insufficient regeneration efficiency of the adsorbent in a given adsorption cycle shortens the adsorption time in the subsequent cycle[7, 10]. Adsorption equilibrium measurements for individual adsorbate-adsorbent systems are necessary to determine the adsorption capacity of air pollutants at operating temperature and pressure, and to select the appropriate adsorbent and the method of adsorbent regeneration. In addition, the isotherm is used to determine the relationship between the adsorption capacity and the affinity of VOCs for adsorbents, which is necessary to understand the adsorption mechanism. These factors are important for designing an adsorption plant[11].

In this study the affinity of the heterogeneous Sorbonorit B4 (SB4) activated carbon toward polar VOCs was examined. Isopropyl alcohol (IPA), n-propyl alcohol (NPA), isobutyl alcohol (IBA), and methyl ethyl ketone (MEK) were selected for the research. Molecules of aliphatic alcohols and ketone contain hydroxyl and carbonyl groups, respectively, that can interact with different types of oxygen functional groups on AC surface via hydrogen bonds. In addition, they differ in the structure and size of carbon chains and the arrangement of their functional groups, which may affect the adsorption behaviour of heterogeneous AC and the regeneration efficiency in cyclic adsorption processes. Despite the growing demand for polar solvents, only a few studies have addressed this issue to data[12–15].

The aims of this paper are (i) assessment of the adsorption capacity of SB4 carbon for VOCs of different polarity (ii) estimation of bed temperature increase in a well-insulated column for safety process, (iii) determination of the amount of energy necessary for the regeneration of the adsorbent saturated with VOC vapours.

EXPERIMENTAL SECTION

Materials

The extruded activated carbon Sorbonorit B4 (SB4) was used as an adsorbent. It was produced from peat by Norit Nederland B.V. The adsorbent consists of cylindrical pellets with a diameter of 3.7 mm. Owing to its favourable adsorption properties (total surface area B.E.T. 1250 m^2/g, particle porosity 0.44 cm^3/g, apparent

density 400 kg/m^3), it is designed for use in solvent recovery applications[14, 16].

The high-purity (99,7%) organic compounds, IPA, MEK, NPA, and IBA, supplied by Chempur (Poland) were selected as adsorbates. They are commonly used in industrial applications as solvents and ingredients in products[17].

Apparatus and procedure

Adsorption isotherm study

Adsorption isotherm measurements were conducted using an intelligent gravimetric analyser IGA-002 (Hiden Isochema Ltd, UK). It is a precise microbalance system with a resolution of 0.1 μg and an uncertainty of ± 1 μg. A sample of activated carbon with a mass of ca. 85 mg was placed in the thermostated reactor chamber with accurate temperature control ($\pm$0.1 K). Before the isotherm measurements, the SB4 was outgassed to a constant weight at a high vacuum level (10^{-6} Pa) at 120 °C for 2 hours. A real time sample weight change, temperature, and pressure were measured and recorded using the IGASwin software. The process was terminated when the weight change approached 1 μg. A comprehensive description of the methodology of isotherm determination with IGA-002 is presented elsewhere[2]. The measurements were conducted at 20, 40, 60, 75, and 100 °C. The selected temperatures are within the temperature range of column studies. The equilibrium points were collected and plotted as an isotherm. The adsorption capacity was calculated as the ratio of the mass of the adsorbed substance to the mass of the adsorbent sample after degassing.

Column studies

IPA was selected as the adsorbate for the column studies, that were carried out in adsorption installations with a glass adsorption column (internal diameter 0.055 m) with SB4 fixed bed with a mass of 0.26 kg and height of 0.27 m. A comprehensive description of the experimental setup can be found elsewhere[8]. Cyclic column adsorption-desorption tests consisted of adsorption, regeneration, and cooling stages. During the adsorption stage, the dynamic tests at ambient temperature were performed. All experiments were carried out under the following operating conditions: inlet concentration of IPA vapour C_0 = 5–16 g/m^3, gas flow rate 1.8 m^3/h (superficial gas velocity 0.21 m/s). The experiments were conducted until the bed reached saturation, indicated by a stable concentration at the column outlet. After each adsorption stage, the saturated adsorbent was regenerated using the direct resistive heating method. The regeneration experiments were performed in the following invariability range of parameters: 30 V voltage, 0.02 m^3/h nitrogen flow and 150 °C temperature. The procedure for carbon regeneration by direct resistive heating method was described elsewhere[18].

Methodology for determining isotherm parameters

Four adsorption isotherm models were chosen to describe the equilibrium data. The Langmuir isotherm model was developed for adsorption on a homogeneous adsorbent, all adsorptive sites of which have the same affinity towards the adsorbate. It is based on the concept of a monolayer that is filled with non-interacting molecules and the assumption about constant adsorption energy, which is independent of the surface coverage of the adsorbent. The isotherm model predicts a monotonically increasing function of pressure, which tends to a constant value of q_m. The isotherm equation is as follows[19]:

$$q = q_m \frac{b\,p}{1 + b\,p} \tag{1}$$

where q is the adsorption capacity (mol/kg), p the equilibrium pressure (Pa), q_m the monolayer adsorption capacity (mol/kg), and b a parameter (1/Pa).

The Dubinin-Radushkevich (D-R) isotherm is derived based on Polanyi's theory of adsorption potential, assuming that the adsorption of vapours is to fill the pore volume of microporous adsorbents[20], not to cover the adsorbent surface layer by layer. It is well suited to describe adsorption systems in which only van der Waals forces are present and is particularly useful to describe adsorption on activated carbon[21]:

$$W = W_0 \exp\left[-\frac{RT}{E_0 \beta} \ln\left(\frac{p_s}{p} \right)^2 \right] \tag{2}$$

where W is the volume of liquid-like adsorbate within the pore structure (cm^3/g) and W_0 is the overall micropore volume (cm^3/g), W is calculated by $W = q\,V$, where V is the liquid molar volume of adsorbate (cm^3/mol), E_0 is the characteristic adsorption energy (J/mol) which is a function of the adsorbent, β is the dimensionless affinity coefficient, which was calculated as the ratio of the molar specific volume of the adsorbate and benzene as the reference substance, R is the gas constant (8.314 J/mol K) and T is the temperature (K).

According to Polanyi's sorption potential theory, at each point of the sorption space, there is a sorption potential generated mainly by the intermolecular forces of adsorbate and adsorbent. Adsorption in micropores is much stronger than on the same flat surface, and more atoms of the adsorbate interact closely with the adsorbate[22]. The Dubinin-Astakhov (D-A) equation, a more general form of the D-R one, is described as follows:

$$q = q_{\max} \exp\left\{ -\left[\frac{RT}{E} \ln\left(\frac{p_s}{p} \right) \right]^m \right\} \tag{3}$$

where q_{max} is the maximum adsorption capacity (mol/kg), E is the characteristic energy (kJ/mol) and exponent m is a measure of the surface heterogeneity[19, 22].

The Toth isotherm model is an empirical equation that was developed to improve the description of monolayer adsorption by the Langmuir isotherm. In the model, an asymmetric quasi-Gaussian energy distribution is assumed, where most sites have lower adsorption energy than the energy peak of maximum adsorption[19]. The model is best suited for heterogeneous systems in which multiple adsorption layers occur. The multitemperature Toth model developed by Taqvi et al.[6] is given by:

$$q = q_T \frac{p}{\left(b_T + p^t \right)^{1/t}} \tag{4}$$

$$b_T = b_{0T} \exp\left(-\frac{Q_{st}\, t}{RT} \right) \tag{4a}$$

where q_T is the maximum adsorption capacity (mol/g), b_T is the parameter (Pa^t), t is the parameter that indicates the heterogeneity of the adsorbent (–), and Q_{st} is the isosteric heat of adsorption (J/mol). In this model, the exponential term of equation (4a) contains the heterogeneity parameter t, and the parameter Q_{st} is independent of adsorbate loading and temperature. It can be applied both in the low- and high- pressure ranges, thus the Clausius-Clapeyron equation is satisfied[6].

The parameters of the adsorption isotherm equations were estimated with non-linear regression method using the Statistica 13.3 program (Statsoft). Two methods of error measurement were used to assess the quality of fit of the adsorption isotherm models: the coefficient of determination R^2 (Eq. 5) and the average relative error δ (Eq. 6). The value of R^2 ranges from 0 to 1, where 1 denotes an ideal linear relationship. For the average relative error δ, the smaller the calculated value, the better the model provides. The error definitions are as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(q_{cal\,i} - q_{exp\,i}\right)^2}{\sum_{i=1}^{N}\left(q_{exp\,i} - \frac{1}{N}\sum_{i=1}^{N} q_{exp\,i}\right)^2} \quad (5)$$

$$\delta = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\left(q_{exp\,i} - q_{cal\,i}\right)}{q_{exp\,i}}\right| \cdot 100\% \quad (6)$$

where q_{exp} and q_{cal} are respectively the experimental and calculated from the model adsorption capacity.

RESULT AND DISCUSSION

Adsorption isotherms at ambient temperature

Figure 1 presents experimental isotherm curves of MEK, IPA, NPA, IBA and water vapours on SB4 at 20 °C in the relative pressure p/p_s range from 0.01 to 0.97, where p and p_s are the current and saturation vapour pressures, respectively. As can be seen from Table 1, the compounds differ in physical properties[23], molecular size, and structure. As can be seen from Fig. 1, the isotherm curves for VOCs have a similar course. There are convex-upward-shaped curves that can be classified as Type I(b) in the IUPAC scheme[24]. In the pressure range of $p/p_s < 0.07$, the highest growth in the adsorption loading was observed. It shows that the adsorption of VOCs occurs mainly in micropores accessible to their molecules. However, in high-pressure range, the isotherm at 20 °C shows some deviations from

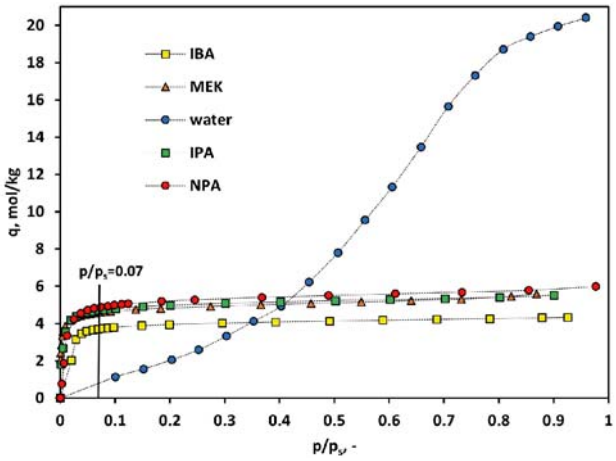


Figure 1. Experimental isotherms for MEK, IPA, NPA, IBA and water vapor on Sorbonorit B4 at 20 °C

monolayer adsorption. This phenomenon is typical for adsorbents with a large porosity. Water vapor adsorption isotherms differ from the others. It can be classified as Type V in the IUPAC scheme, which indicates that the water-water interactions are stronger than that of water--adsorbent and the filling of the main pore volume of SB4 occurs at high relative humidity[25]. This results in greater adsorption capacity of SB4 for water vapour than that for VOC vapours at $p/p_s > 0.4$. Pre-adsorbed water molecules can occupy part of the VOC adsorption site, resulting in lower affinity of AC for VOCs adsorption and hindering the diffusion of VOCs into micropores. As a result of competitive adsorption between water and VOC molecules on AC water vapour can also displace VOC from AC and slow down the adsorption kinetics[25–27].

The adsorption equilibrium of VOCs and water vapor on activated carbon at 20 °C was analysed using isotherms Langmuir, Dubinin-Astakhov and Dubinin-Radushkevich, respectively. The isotherm parameters and error values are summarized in Table 2. It shows that Langmuir isotherm gave poor fit, which shows that adsorption did not occur at identical and equivalent adsorptive sites, and lateral interaction and steric hindrance between the adsorbed polar molecules, may took place. By contrast, the D-A model gave the best fit to the equilibrium data for all VOC-SB4 systems (δ = 2.60–3.75%) except for the IBA-SB4 (δ = 5.3%). The situation is different for the water vapor-SB4 equilibrium (δ = 16.4%), which represents the different type of isotherm and none of the selected isotherms describes it well. As can be seen in Figure 1, for the value of $p/p_s > 0.49$, the amount of water vapor adsorption on activated carbon exceeded its capacity towards all VOCs, for which it decreases

Table 1. Physical properties of adsorbates at 20 °C

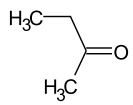
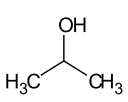
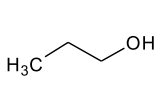
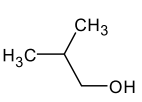
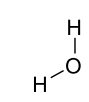
Parameter	MEK	IPA	NPA	IBA	water
					
Molecular mass (kg/kmol)	72.11	60.10	60.10	74.12	18.02
Boiling point (°C)	79.64	82.50	97.20	107.66	100
Dipole moment (D)	2.76	1.66	1.68	1.79	1.86
Saturation pressure (kPa)	10.04	4.41	1.99	0.96	2.34
Minimum projection radius, Å	2.8	2.95	2.67	3.14	1.73
Maximum projection radius, Å	3.97	3.36	3.89	3.9	1.97
Enthalpy of evaporation (kJ/mol)	35.5	44.6	49.1	55.6	40.7

Table 2. Parameters of MEK, IPA, NPA, IBA and water vapor adsorption model isotherms on Sorbonorit B4 activated carbon at 20 °C

Parameter	MEK	IPA	NPA	IBA	water
Langmuir isotherm					
q_m (mol/kg)	4.8726	5.1488	5.6761	4.3101	66.3651
b (1/Pa)	0.0740	0.0523	0.0468	0.0793	0.000164
R^2 (–)	0.9598	0.9887	0.9927	0.9853	0.9185
δ (%)	7.45	4.21	5.97	3.74	68.56
Dubinin-Radushkevich isotherm					
W_0 (cm^3/g)	0.4664	0.4152	0.4265	0.3767	0.3647
E_0 (kJ/mol)	19.737	18.338	19.326	19.401	6.574
β (–)	1.006	0.857	0.836	1.039	0.203
R^2 (–)	0.9886	0.9949	0.9957	0.9936	0.9865
δ (%)	2.49	4.3	5.52	2.66	49.85
Dubinin-Astakhov isotherm					
q_{max} (mol/kg)	5.2429	5.2583	5.5005	4.1123	21.7084
E (kJ/mol)	20.1983	15.6962	12.3591	10.5656	1.7446
m (–)	1.8683	2.5725	3.6134	5.0843	1.3538
R^2 (–)	0.9890	0.9907	0.9860	0.9566	0.9953
δ (%)	2.60	2.37	5.26	3.75	16.40

as follows NPA>IPA>MEK>IBA. This sequence is reflected in the q_m values (Table 2). The characteristic energy E of the adsorbate-adsorbent interaction is the lowest for the system with water and increases for VOC in the order IBA<NPA<IPA<MEK, respectively. This may be caused by different adsorbate-adsorbent interactions due to differences in the structure and size of adsorbate molecules[25].

The W_0 values determined from the D-R isotherm are lower than the total pore volume determined by nitrogen adsorption method at –196 °C which equals to 0.48 cm^3/g[16]. This may be due to molecular packing restrictions of VOC molecules in narrow micropores. Most micropore sizes should be slightly larger than the VOC molecular size to minimize unused porosity. The accessibility of the adsorbate molecules to the pores can be assessed based on the projection area of each compound, i.e., the area occupied by a separate molecule on the flat surface of the adsorbent. Table 1 shows the minimum and maximum projection radiuses of individual compounds. They were determined for the lowest energy conformers using ChemAxon Marvin Pro software. As can be seen, the minimum projection radius of the NPA molecule is 0.94 Å greater than that of water, but it is smaller than that of other solvents. By contrast, the maximum projection radiuses of MEK, NPA, and IBA are almost the same, while water and IPA molecules are smaller than them. The results of the pore size distribution analysis using the Barrett–Joyner–Halend method (BJH) presented elsewhere[16] revealed that SB4 contained three groups of pores: micropores (ca. 70%), mesopores (ca. 29%), and macropores (0.01%). Micropore diameters from 6 to 10 Å were dominant and were close to VOC molecule sizes, which affects the adsorption affinity of SB4. Moreover different interactions of the alcohol molecules with surface functional groups located at micropore entrances may reduce the adsorption capacity of SB4.

Multitemperature adsorption isotherm

Figure 2 presents the experimental and simulated adsorption isotherms of MEK vapor onto SB4 at five temperatures. The scatter plots represent experimental data, whereas the line plots represent the results determined from the Toth isotherm model. As can be seen, the adsorption capacity decreased with temperature increases, which caused by the exothermal nature of the

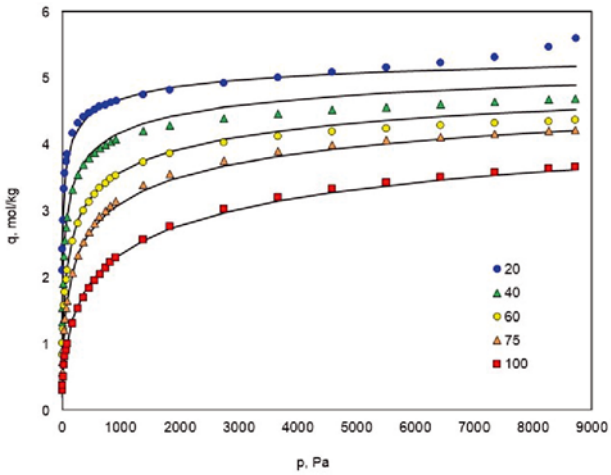


Figure 2. Experimental and correlated isotherms for MEK vapor adsorption onto SB4 at 20, 40, 60, 75, and 100 °C

vapor adsorption. The same effect was observed for both propanol isomers and IBA on SB4. The experimental data for these alcohols can be found in[14] and[28], respectively.

The Toth model parameters were estimated using nonlinear regression method using the Statistica 13.3 program. They are presented in Table 3. As can be seen, for all adsorbate-adsorbent systems, the Q_{st} values are lower than 80 kJ/mol, and therefore the process can be classified as physical adsorption, which favours the regeneration of the adsorbent[9]. They are higher than the enthalpy of VOC evaporation at 20 °C (Table 1), which means that adsorption is favourable. In addition, the value of exponent t deviated from the unity, which denotes the heterogeneity of AC surface.

Table 3. Parameters of Toth model and error coefficients

Parameter	MEK	IPA	NPA	IBA
q_T (mol/kg)	5.664	5.576	6.126	4.253
b_{0T} (Pa^t)	1720	877.105	172.846	35.734
n_T (–)	0.348	0.548	0.479	0.444
Q_{st} (kJ/mol)	54.175	56.978	60.224	61.373
R^2 (–)	0.9967	0.9979	0.9940	0.9980
δ (%)	5.21	8.23	6.99	3.42

In the Toth model, it was assumed that the isosteric heat of adsorption is independent of the adsorbate loading (Eq. 6a), so that there is no interaction between the adsorbate molecules. The validity of this assumption was verified by calculating the Q_{st} value using the Clausius-Clapeyron equation[29]:

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q = -R\left(\frac{\partial \ln p}{\partial \frac{1}{T}}\right)_q \quad (7)$$

where: Q_{st} is the isosteric heat of adsorption (J/mol), R = 8.314 J/(mol K) is the universal gas constant, T is the temperature (K), p is the pressure (Pa). The values of Q_{st} were determined from the slopes of the $lnp - 1/T$ plots for selected q values. As can be seen from Figure 3, the values of Q_{st} change with increasing adsorbate loading q, which indicates that the process takes place at adsorptive sites with different binding energies. They affect both the strength of electrostatic and dispersive interactions between adsorbents and polar adsorbates. This is due to the SB4 surface heterogeneity, which was confirmed by results of X-ray photoelectron spectroscopy (XPS) presented in our earlier work[14]. The analysis shows that non-functionalised carbons (aromatic and aliphatic carbons) are the main surface components of SB4. It also revealed the presence of surface oxygen groups such as C-OH, C=O and COOH, that may act as primary active sites and create the same specific interactions with alcohol and ketone molecules, especially at low relative pressures[25].

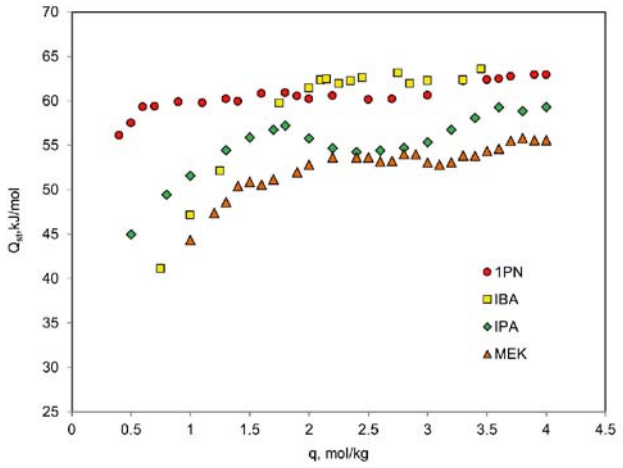


Figure 3. Isosteric heat of adsorption of VOCs on SB4

Different interactions may be responsible for the adsorption behaviour of polar VOCs which is dependent on the participation of the dispersion interaction (alkyl group) and hydrogen bonding (hydroxyl or carbonyl groups). The straight chain of NPA molecules can arranged parallel along the pore walls and joined closely, which results in stronger dispersion forces between them and the adsorbent, and higher Q_{st} values in the q value range from 0.7 to 3 mol/kg. As can be seen from Fig. 3, the plots for NPA, IPA, IBA, and MEK have increasing trends up to the adsorbate loading of 0.7, 1.8, 2.1, and 2.3 mol/kg, respectively. This initial increase in the isosteric heat of adsorption indicates that intermolecular interactions between the VOC molecules are dominant over adsorbate-adsorbent interactions[26]. At high surface coverage, the Q_{st} values are almost constant for all VOCs and are close to the Q_{st} values in the Toth equation (Table 3). They are higher for NPA and IBA than for IPA and MEK, which is caused by the greater affinity of the adsorbent for alcohols with longer and straight carbon chains[6, 25].

Column studies

In the dynamic adsorption studies, the adsorbate vapour concentration in the air stream at the column outlet and temperature at six heights of the SB4 bed were measured. The tests were carried out on regenerated activated carbon at an initial temperature (20 °C). Fig. 4 presents both time-temperature profiles and breakthrough curves (BTCs) determined at the outlet of the fixed bed for three IPA inlet concentrations. BTCs describe the relationship between the outlet-to-inlet IPA vapour concentration (C/C_0) and adsorption time. As can be seen, the higher the inlet concentration of IPA, the faster the breakthrough and the steeper the breakthrough curve. This affects the lifetime of the bed in the adsorption step.

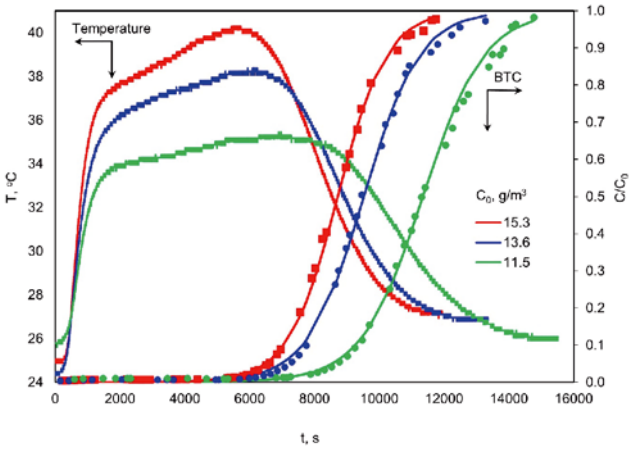


Figure 4. Temperature profiles and breakthrough curves (BTCs)

The shape of the time-temperature profiles indicates that the adsorption process was exothermic. Due to the heat transfer from the solid phase to the gas phase along the gas flow direction, the temperature gradually increased to the maximum value and then decreased to ambient temperature. The maximum value on the temperature profile corresponds to the breakthrough point, i.e., the time when the outlet concentration of the adsorbate is 5% of the inlet concentration. Due to the exothermic heat of adsorption, a truly isothermal process never occurs in fixed bed adsorbers. The heat of adsorption combined with the gas flow creates a temperature wave that propagates with the concentration wave. For simplification of the solution of adiabatic or nearly adiabatic adsorption issue, the constant pattern approach can be used[30], from which the condition that the thermal wave cannot pull ahead of the mass transfer zone whenever the solid/gas heat capacity ratio exceeds the inlet equilibrium ratio of (q/Y). Assuming that concentration and thermal waves propagated at the same velocity, the energy balance under equilibrium conditions allows to determine the maximum bed temperature[31]. The maximum temperature increase ΔT_{max} can be estimated based on the isosteric heat of adsorption, the specific heat capacity of the adsorbent and the gas mixture, and operating parameters[5]. It can be calculated using the equation (8) which was developed for an adiabatic fixed bed[31]:

$$\Delta T_{max} = T_{max} - T_{in} = \frac{\frac{Q_{st}}{M}\frac{q_{in}}{C_{pf}}}{\frac{q_{in}}{C_0} - \frac{C_{ps}}{C_{pf}}} \quad (8)$$

where T_{in} (K) is the initial temperature, Q_{st} (kJ/mol) is the isosteric heat of adsorption which depends on the adsorbent loading q, M (kg/mol) is the molar mass of adsorbate, C_0 (kg/m^3) is the initial adsorptive concentration related to pressure p, q_{in} is the equilibrium adsorption capacity (kg/m^3) related to the initial adsorptive concentration, C_{pf} is the specific heat capacity of the gas phase, and C_{ps} is the specific heat capacity of the adsorbent in (kJ/kg K).

Due to the low concentration of VOC, the value of C_{pf} was assumed as the specific heat capacity of air at the temperature of 20 °C (1.02 kJ/kg K). The specific heat capacity of the SB4 carbon was determined experimentally in the temperature range from 25 to 200 °C using the SETARAM TG/DSC 111 calorimeter. As shown in Fig. 5, the C_{ps} value increases with increasing temperature up to 60 °C, then it is almost constant up to 100 °C. An increase in temperature to 200 °C caused an increase in the C_{ps} value from 0.9 to 1.24 J/g K. The following fourth-order polynomial equation was used to correlate the experimental data:

$$C_{ps} = -4.22 \cdot 10^{-9} T^4 + 2.01 \cdot 10^{-6} T^3 - 3.28 \cdot 10^{-4} T^2 + 2.36 \cdot 10^{-2} T + 0.259 \quad (9)$$

The relative error of approximation δ was 1.5%.

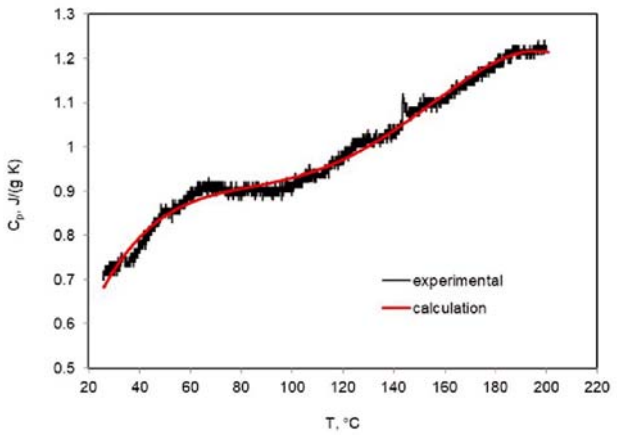


Figure 5. Dependence of specific heat of SB4 carbon on temperature

Figure 6 shows the calculated ΔT_{max} values obtained for different inlet concentrations C_0 for all selected VOC vapours. As can be seen, equation (8) provided well agreement between the experimental and computational results for IPA vapor adsorption in the insulated adsorbent bed, which works almost adiabatically[5].

According to[31], the temperature effects can be negligible when temperature changes in the fixed-bed are smaller than 1 to 2 °C, then, it can be assumed that the process is conducted in near-isothermal conditions. As can be seen, this condition is not met in this case, so the VOC adsorption column process for concentrations above 5 g/m^3 cannot be considered isothermal. The calculated values of the maximum temperature rise in the fixed bed were consistent with the relevant experimental data. At

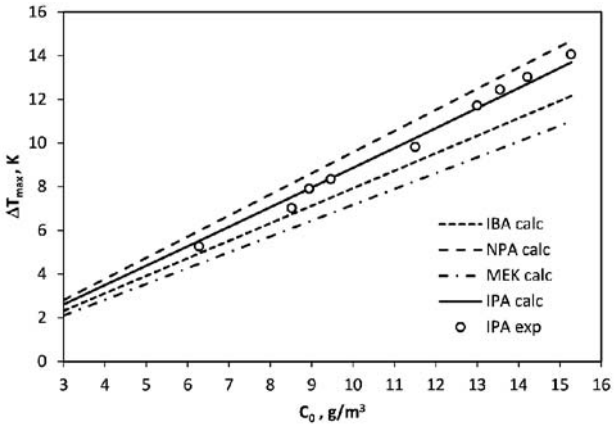


Figure 6. Effect of VOC vapours concentration on the increase in SB4 bed temperature (o – experimental points for IPA, line – values calculated from Eq. 8)

high concentrations of adsorbate in the air, the increase in bed temperature may be so large that the process cannot be treated as isothermal, which should be taken into account when designing the fixed-bed adsorber.

Energetic requirements for regeneration processes

The temperature of the adsorbent bed has a significant impact on the energy efficiency of the cyclic adsorption-desorption process. An increase in temperature causes a decrease in the adsorption capacity of AC, which improves the regeneration efficiency and increases the amount of recovered adsorbate. However, this requires the supply of the appropriate amount of thermal energy (Q_{reg}) which is used to heat up the adsorbent bed (Q_{bed}) and to desorb an adsorbate (Q_{des}) and is lost to the surroundings (Q_{loss}). The heat balance for the regeneration process can be written as:

$$Q_{reg} = Q_{bed} + Q_{des} + Q_{loss} \quad (10)$$

The sensible heat Q_{bed} required to raise the temperature of the adsorbent bed from the adsorption temperature T_{ads} to the desorption temperature T_{des} is calculated by multiplying the adsorbent mass m_s (kg) by the specific heat capacity C_{ps} (kJ/kg K) and the change in temperature:

$$Q_{bed} = m_s C_{ps} (T_{des} - T_{ads}) \quad (11)$$

where C_{ps} is defined as:

$$C_{ps} = C_s + q\, C_{p\,liq} \quad (12)$$

where: $C_{p\,liq}$ (kJ/mol K) is the specific heat capacity of the liquid adsorbate, C_s (kJ/kg K) is heat capacity of the pure adsorbent.

Heat duty required to desorb the IPA vapour from the saturated SB4 is calculated using Eq. (13). Assuming that Q_{des} (kJ) is equal to the adsorption energy released in the adsorbent during the adsorption process, it can be calculated by multiplying the change in adsorbate loading by the isosteric heat of adsorption Q_{st} (kJ/mol):

$$Q_{des} = q_{ads} m_s Q_{st} \quad (13)$$

where q_{ads} (mol/kg) is the adsorption capacity representing the amount of adsorbed compound in relation to the weight of the adsorbent.

Figure 7 shows, that the increase in the adsorbate loading caused an increase in the Q_{des} value. For the

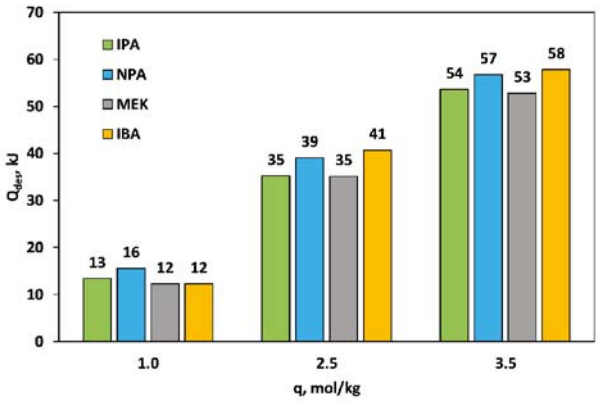


Figure 7. Comparison of heat Qdes for three adsorption capacities of SB4

adsorption capacity q equal to 1 mol/kg, the highest energy amount must be provided for the desorption of NPA. On the other hand, for q equal to 2 and 3 mol/kg, the values of Q_{des} are higher for IBA than for NPA by 7.3 and 1.5%, respectively. Due to the larger dimensions of the IBA molecules (Table 1), access to the narrowest micropores is limited, so the strength of the adsorbate-adsorbate interaction is lower than for NPA. As the value of q increases, the influence of dispersion interactions increases. They are the weakest for IPA and MEK at high adsorbate loadings, as evidenced by lower Q_{des} values.

In the electrothermal regeneration process, the thermal energy is generated in the fixed-bed by Joule effect[18]. According to the Joule-Lenz law, it is directly proportional to electrical power P (W) and the process time t (s):

$$Q_{reg} = \int_0^{t_{des}} P\,dt \tag{14}$$

The regeneration efficiency increases with increasing values of voltage, temperature and process duration[18]. Figure 8 shows a comparison of the energy consumption determined experimentally with the one calculated from

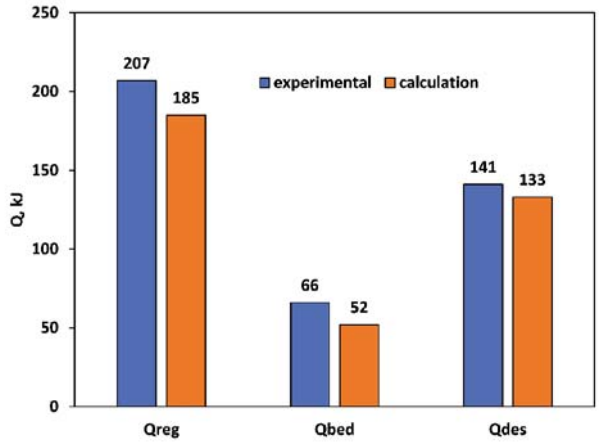


Figure 8. Energy balance for IPA vapor adsorption onto SB4 (q = 4.9 mol/kg)

the heat balance equations (10–13) for the same constant IPA adsorption loading on SB4 (q = 4.9 mol/kg).

As can be seen, the particular Q values determined experimentally were larger that calculated from equations (10–13). It is the result of omitting heat losses in the heat balance calculations, which account for about 22% of the heat energy generated electrothermally. It was consumed to heat the adsorption plant equipment (column, pipes, fittings) and was lost from the bed to the surroundings.

CONCLUSIONS

In this paper, equilibrium and dynamic adsorption tests were used to the evaluation of polar solvent vapour adsorption efficiency of the Sorbonorit B4 (SB4) activated carbon.

Adsorption equilibrium measurements at 20 °C showed that in the pressure range $p/p_s > 0.4$, SB4 adsorbs more water vapor than VOC. In addition, the Dubinin-Astakhov equation provided a good agreement with VOC-SB4 experimental data of adsorption (δ = 2.37–5.26%), which indicates a microporous structure of applied adsorbent.

The isosteric heat of adsorption varies as a function of the SB4 surface coverage which indicates that the adsorption mechanism of VOC vapours on heterogeneous SB4 is complex. It depends on the chemical structure and polarity of the adsorbed compounds. They are particularly visible for alcohols with a branched structure (IPA, IBA) at adsorbate loading less than 1.5 mol/kg. This is the result of specific interactions between the adsorbate molecules and the surface oxygen groups of SB4.

Column studies of IPA adsorption on SB4 showed that the maximum temperature increase in the bed during the adsorption process and the energy demand for desorption can be estimated on the basis of the isosteric heat of adsorption. However, according to the calculations of the heat balance, for the full regeneration of SB4, it is necessary to supply almost twice as much energy as the isosteric heat of adsorption. The additional amount of energy is necessary to heat the fixed-bed column and to cover heat losses to the environment.

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