

Adsorption of dyes on mesoporous carbons*

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Mesoporous carbonaceous materials were synthesized by applying the method of impregnation of mesoporous silica being the pore creating template. The isotherms of adsorption of methylene blue and methyl orange were measured from aqueous solutions. The kinetics of methylene blue adsorption was studied. The adsorption isotherms and kinetic dependence were discussed.

1. INTRODUCTION

Dyes widely utilized in many branches of industry belong to toxic pollutants exerting harmful effect on the environment. Thus, the process of treatment of dye-containing sewage is studied by many research groups. With regard to their stability to light and oxidizing agents, and resistance to biodegradation, usefulness of some traditional methods for dye removal from wastewaters is limited [1]. The processes of flocculation and coagulation with metallic compounds result in producing sludge and in increasing concentration of metallic contaminants. Thus, the adsorption techniques seem to be the alternative effective methods for dye removal. Various adsorbents, like zeolites, alumina dioxide, clays or carbons were investigated in order to estimate their effectiveness in purification of waters from such contaminations.

Activated carbons are adsorbents widely applied for purification of waters and wastewaters from inorganic and organic substances of differentiated

* Dedicated to Professor Emil Chibowski on his 65th birthday

properties [2,3]. Several studies on dyes adsorption were conducted in order to investigate the influence of carbon structural and surface properties on adsorption effectiveness [4-13]. Activated carbons are characterized by high specific surface areas and pore volumes, chemical stability, low costs and high affinity towards different solutes. Microporous granular activated carbons belong to the most popular materials. However, their utility may be limited by slow solute diffusion in the pore system of microporous carbon granules which results in slow establishing of adsorption equilibria. Moreover, the microporous carbons can not be used for removing substances of larger molecular sizes.

In the present paper the process of methylene blue and methyl orange adsorption on two mesoporous carbons is studied. The carbon samples were synthesized by using mesoporous silicas as pore structure templates and their impregnation with carbon precursor followed by carbonization. The adsorption isotherms were measured for aqueous solutions of methylene blue and methyl orange by using the static method. The kinetic measurement was conducted by using UV-Vis spectrophotometer with a flow cell. The experimental adsorption data were analyzed by applying the theory of adsorption on energetically heterogeneous surfaces.

2. EXPERIMENTAL

Silica and Carbon Synthesis. In the synthesis of mesoporous silicas two non-ionic triblock poly-(ethylene oxide)-poly-(propylene oxide)-poly-(ethylene oxide) copolymers (Pluronic): PE9400 – (EO)₂₁(PO)₄₇(EO)₂₁ and PE6800 – (EO)₇₁(PO)₃₀(EO)₇₁ (BASF, Poland) were applied as pore-creating agents. The synthesis followed a procedure being a modification of the method described in the papers [14,15]. It was conducted in strong acidic conditions (1.6M HCl), tetraethylorthosilicate (TEOS) was used as silica source, and 1,3,5-trimethyl benzene (TMB) was introduced to a reacting mixture as pore expanding agent. The composition of reacting mixtures and the synthesis conditions were as follows: the polymer concentration $c_{pol} \approx 2,7\%$, the mass ration of polymer to TMB, Pol/TMB=1:1, the mass ration of polymer to TEOS, Pol/TEOS=1:3,4. After the first stage of synthesis the reacting mixtures were aged in autoclaves for 24 hrs at 343 K. The synthesized products were washed with bi-distilled water, dried and calcined at 873 K for 6 hrs in order to remove the silica template.

By using mesopore silicas as pore structure templates two mesoporous carbons of divergent porosity were synthesized. The method of silica impregnation with carbon precursor followed by its carbonization was applied [16]. In the used procedure the calcined mesoporous silicas were impregnated

with aqueous solution of sucrose containing sulfuric acid as catalyst (1 g of silica + 1.25 g of sucrose + 0.14 g of H_2SO_4 + 5 g of water). The mixtures were placed in vacuum dryer at 373 K to evaporate the solution, then the temperature was elevated to 433 K and the samples were kept in such conditions for 6 hrs. Then the procedure of impregnation was repeated (0.8 g of sucrose + 0.09 g of H_2SO_4 + 5 g of water), the materials were again carbonized at 373 and 433 K. Finally the samples were carbonized at 1073 K in nitrogen atmosphere, and the silica skeleton was removed in KOH solution to produce the mesoporous carbons.

Gas Adsorption Experiments. Nitrogen adsorption/desorption isotherms at 77 K were determined volumetrically using ASAP 2405N analyzer (Micromeritics Corp., USA). Before the experiment the adsorbents were degassed (10^{-4} mmHg) at 493 K.

The linear BET plots of adsorption data were used to evaluate the BET specific surface area, S_{BET} , and from the adsorption at the relative pressure $p/p_o=0.98$ the total pore volume, V_t was estimated [17]. By using the α_s method with the graphitized carbon black Carbopack F as a reference non-porous adsorbent [18] the values of the external surface area, S_{ext} , and the primary mesopore volume, V_p were estimated. The calculations of pore size distributions (PSD) followed the Barrett, Joyner and Halenda (BJH) procedure [17]. The mean hydraulic pore diameters were calculated from the BET surface areas and pore volumes $D=4V_p/S_{BET}$.

Liquid Adsorption Experiments. The adsorption isotherms were measured for aqueous solutions of methylene blue and methyl orange (in Table 1 the physicochemical properties of both adsorbates are given). First, the weighted amounts of synthesized carbons were contacted with 5 cm³ of water and degassed under vacuum. Then, the solutions of both dyes of defined concentrations were added and the samples were placed in thermostated shaker. After attaining the adsorption equilibrium the spectrophotometric method was used to estimate the equilibrium concentrations (UV-Vis spectrophotometer, Cary 100, Varian). Next, to each sample a certain portion of concentrated adsorbate was added and after attaining adsorption equilibrium the dye concentration was measured. The procedure was repeated eleven times in order to measure the adsorption isotherms over a wide range of concentrations [19]. For the analysis of experimental data for adsorption of dyes from aqueous solutions the Langmuir-Freundlich (LF) isotherm equation, taking into account the energetic heterogeneity of solids was chosen [20]:

$$a = a_m \frac{(Kc)^m}{1 + (Kc)^m} \quad (1)$$

In the above, a is the adsorption of organic solute over the whole surface phase, a_m is the adsorption capacity, c is the solute equilibrium concentration, the heterogeneity parameter m characterizes the shape (width) of adsorption energy distribution function, and the equilibrium constant, K , describes the position of distribution function on the energy axis.

Tab. 1. The physicochemical properties of methylene blue and methyl orange.

Dye	Chemical formula	Molecular weight [g/mol]	Ionization constant pK_a	Water solubility [%]
methylene blue	$C_{16}H_{18}N_3ClS$	319.85	>12	3.55
methyl orange	$C_{14}H_{15}N_3O_3S$	327.34	3.4	0.15

Kinetic Experiment. Kinetic curve for methylene blue adsorption on the carbon W-1 was measured by applying the UV-Vis spectrophotometer Cary 100 (Varian, Australia) with a flow cell to estimate a solute concentration [20]. The aqueous solution of methylene blue of established initial concentration was contacted with a known amount of carbon in a specially constructed vessel. The solution was stirred during the experiment by applying a magnetic stirrer. At definite time intervals the solution sample was collected to the flow cell, the UV-Vis spectrum was recorded and the solution was returned to the vessel. The concentration vs. time and the adsorption vs. time profiles were calculated from the obtained spectra. In the adsorption and kinetic experiments the 0.1 – 0.315 mm grain fractions were used.

The experimental kinetic data were analyzed by multi-exp equation corresponding to a series of parallel first order processes [21-23]:

$$\frac{c_t}{c_o} = \sum_{i=1}^s A_i \exp(-k_i t) + A_0 \quad \text{where} \quad \sum_{i=1}^s A_i = 1 - A_0 \quad (2)$$

$$a = \frac{c_o V}{m} \left[(1 - A_0) - \sum_{i=1}^s A_i \exp(-k_i t) \right] \quad \text{and} \quad a_{eq} = \frac{c_o V}{m} (1 - A_0) \quad (3)$$

In the above, c_t is the temporary concentration, c_o is the initial one, a is the adsorbed amount, m is the adsorbent mass, V is the solution volume, A denote the total concentration change, k describes the adsorption rate. The value A_0 allows to calculate (extrapolate) equilibrium concentration and adsorption, and a_{eq} corresponds to the equilibrium adsorption.

If parameter $s=1$ then this equation becomes identical to the well known Lagergren dependence corresponding to the first order and pseudo-first order kinetics [24-26].

$$\frac{dc}{dt} = -k_1(c - c_{eq}) \quad \text{and} \quad \frac{da}{dt} = k_1(a_{eq} - a) \quad (4)$$

$$\ln(c - c_{eq}) = \ln(c_o - c_{eq}) - k_1 t \quad \text{and} \quad \ln(a_{eq} - a) = \ln a_{eq} - k_1 t \quad (5)$$

However, one of the most successful kinetic equations is the pseudo 2nd order kinetic equation introduced by Ho and McKay [25-26]:

$$\frac{t}{a} = \frac{1}{k_2 a_{eq}^2} + \frac{t}{a_{eq}} \quad (6)$$

where k_2 is the rate coefficient.

This equation usually describes experimental data better than the simple Lagergren equation (5), moreover, it is supposed to take into account various factors, e.g. surface heterogeneity [27].

3. RESULTS AND DISCUSSION

In Figure 1 the nitrogen adsorption/desorption isotherms are compared for two synthesized carbon samples. Both isotherms have similar course in the range of high values of relative pressures evidencing similar total pore volumes. However, for lower pressures the course of nitrogen isotherms measured for the carbons W-1 and W-2 is quite different. In the case of the carbon W-1 high increase of nitrogen adsorption for very low pressures means that the pore diameters are smaller for this adsorbent than for W-2. Moreover, the shape of isotherm obtained for the sample W-1 suggests that this material has mesopores of small sizes close to micropore region. In Table 2 the values of structure parameters characterizing both carbonaceous materials are presented. One can find that the carbons W-1 and W-2 are characterized by identical pore volumes,

however, the specific surface area is higher for W-1 and its pore size is almost two times smaller than for W-2.

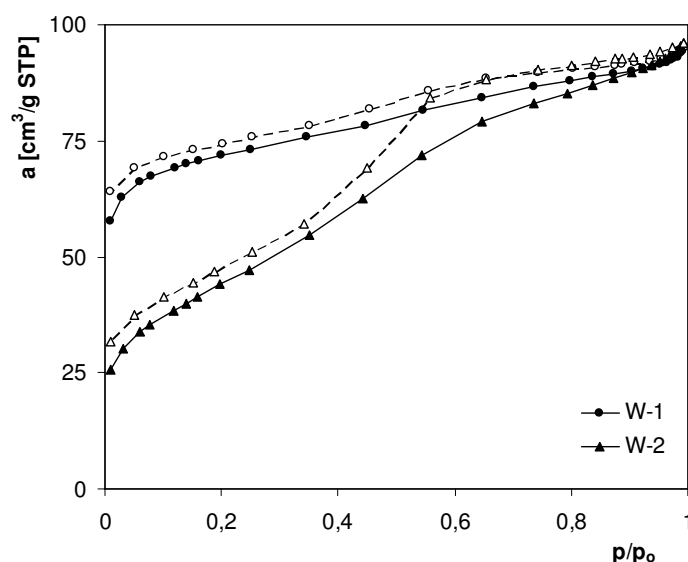


Fig. 1. The nitrogen adsorption/desorption isotherms for the carbons W-1 and W-2.

Tab. 2. The values of parameters characterizing porous structure of synthesized carbons calculated from nitrogen adsorption/desorption isotherms.

Resin	S_{BET} [m ² /g]	V_t [cm ³ /g]	V_p [cm ³ /g]	S_{ext} [m ² /g]	D [nm]
W-1	255	0.14	0.13	7	2.0
W-2	155	0.15	0.13	11	3.7

The isotherms of adsorption of methylene blue from aqueous solutions on both synthesized carbons are compared in Figure 2 in the coordinates: adsorption a vs. equilibrium concentration c . Much stronger adsorption is observed on the sample W-2, what is a surprising conclusion because this material has lower specific surface area. This relative decrease of methylene blue adsorption on W-1 may be explained by small pore sizes (2 nm) of this carbon. Some of the smallest pores are not accessible for large dye molecules reducing the total amount of adsorbed methylene blue. Presenting the adsorption data as the dependence of adsorbate surface concentration (adsorption divided by specific

surface area) vs. equilibrium concentration one can find even greater difference between the isotherms on both carbons confirming the inaccessibility of the smallest pores for dye molecules. It means that the pore diameters and probably their shapes are very important structural factors which determine the effectiveness of adsorption process in the case of adsorbates of larger molecular sizes.

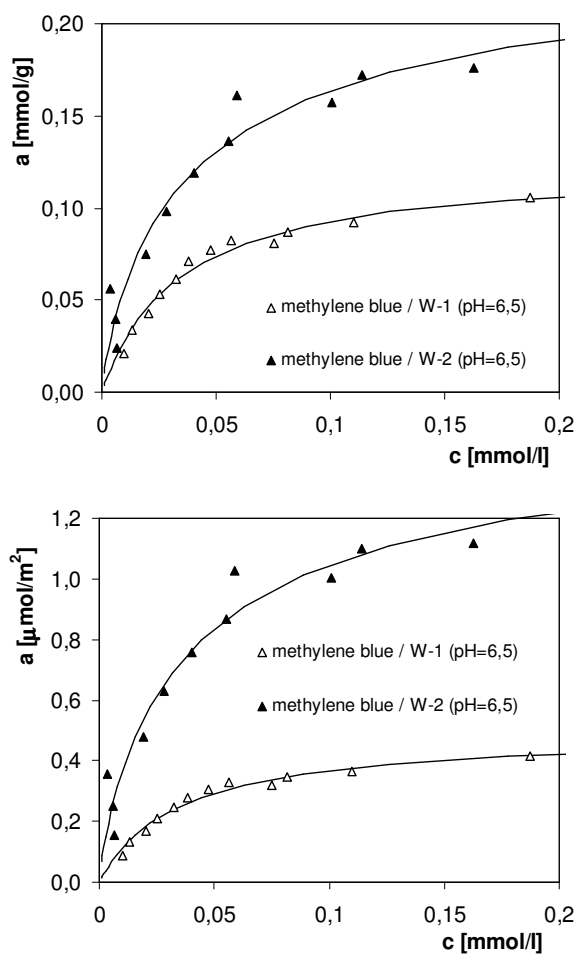


Fig. 2. The isotherms of methylene blue adsorption from aqueous solutions on the mesoporous carbons W-1 and W-2.

Consequently, these factors should also influence the rate of establishing adsorption equilibria. Thus, kinetics of adsorption process may be a critical

factor while regarding the usefulness of the adsorption technique on a large scale in technological or environmental applications.

In Figure 3 methylene blue kinetics is presented. In the left figure, the non-linearity of the data in Lagergren coordinates (5) is shown (the value of a_{eq} is a multi-exp extrapolated value), however it is clear that this equation may well describe the data after 1000 min. when the kinetic process becomes stationary. This suggests that other equations should be used. In the right part of the figure, the results of the LSQ fitting of the multi-exp equation (2,3) (Table 3) and 2nd order kinetic equation (6) are compared with experimental data. Excellent fit is obtained for the multi-exp equation (2,3), whereas the fit quality for the pseudo 2nd order equation is very good, but not excellent. One may conclude that while the equation (6) approximates this kinetic experiment very well, it is too simple to be able to describe more complicated systems; however, the multi-exp equation (2,3) may describe kinetic data in the widest possible range of times at the cost of increased complexity.

Analyzing the affinity of organic substances towards carbon surface the properties of the whole adsorption system should be regarded: solute, adsorbent, solution pH, ionic strength and temperature. In the case of adsorbate, its molecular size, number and properties of functional groups, solubility, and tendency to dissociation should be taken into account. Generally, adsorption is a result of electrostatic and non-electrostatic interactions between the adsorbent active sites and the solute molecules. Aromatic, non-dissociated compounds are adsorbed mainly by dispersion interactions between the π -electrons of the aromatic rings and the graphene layers of carbonaceous material. This mechanism may be disturbed when there appear the ionized forms of solute molecules; in such a case a certain share of the electrostatic interactions should be regarded depending on the dissociation degree. Apart from the adsorbate properties, the surface characteristics of carbons are very important factors in adsorption mechanism. The surface oxygen groups can form the H-bonds with water molecules reducing adsorption of organic substances and can attract and localize the electrons of the basal planes influencing interactions between adsorbate and adsorbent [2,3]. Similarly as for the carbon surface groups also the substituents of the aromatic rings of solute molecules affect the dispersion interactions between the graphene layers of carbon and the aromatic ring of solute by changing the electron density. In the case of some compounds stronger electron donor-acceptor interactions or charge-transfer mechanism should be regarded.

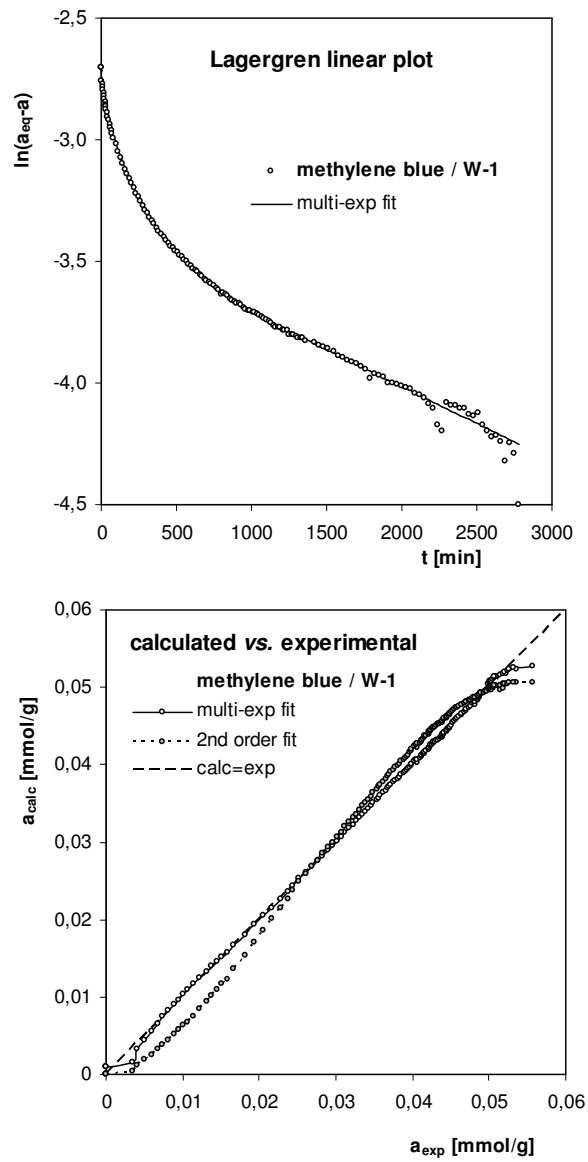


Fig. 3. Kinetic curves of methylene blue adsorption from aqueous solutions on the mesoporous carbon W-1.

Tab. 3. The parameters of multi-exp equation (2,3) fitted to adsorption kinetic data of methylene blue on W-1 carbon.

Sample	Fast stage	Slow stage		Equil.	Fast/Slow ratio
	A_1 / k_1	A_2 / k_2	A_3 / k_3	A_0	$A_1 / (A_2 + A_3)$
methylene blue / W-1	0.081 / 0.043	0.254 / 0.0042	0.330 / 0.00029	0.336	0.138

In Figure 4 the isotherms of methylene blue and methyl orange adsorption from aqueous solutions on the carbon W-1 are compared. Stronger adsorption of methylene blue evidences greater effectiveness of the process of its removing from solutions by adsorption on carbonaceous materials. Comparing solubility of both solutes (table 1) one can find that methyl orange is much less soluble substance, thus, its hydrophobic interactions with carbon should be stronger. On the other hand, in experimental conditions (aqueous solution, $\text{pH} \approx 7$) methyl orange is dissociated. Depending on the surface charge of carbon the ionic forms of organic solute may be repelled from adsorbent surface reducing adsorption. Another factors influencing adsorption uptake are: nature of substituents in aromatic rings of solutes and the molecule size and shape. The adsorption uptake is a result of all these parameters.

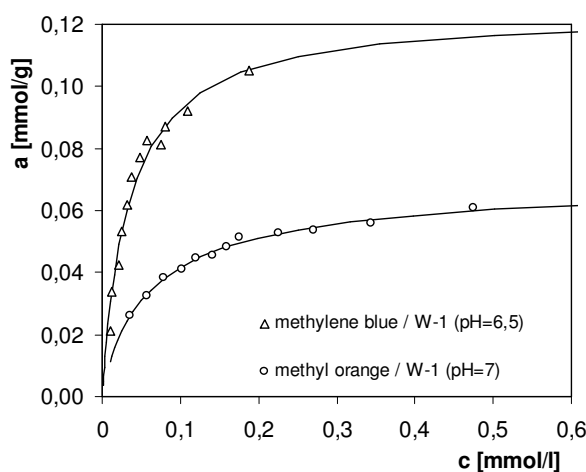


Fig. 4. The isotherms of methylene blue and methyl orange adsorption from aqueous solutions on the mesoporous carbon W-1.

Tab. 4. The parameters of Langmuir-Freundlich equation calculated by fitting procedure.

Adsorption system	a_m [mmol/g]	m	K	SD
methylene blue/W-1	0.12	1	29.2	0.0043
methylene blue/W-2	0.24	0.83	24.0	0.0140
methyl orange/W-1	0.07	0.88	15.1	0.0010

$$SD = \left[\sum_{i=1}^L (a_{i,\text{exp}} - a_{i,\text{theor}})^2 / (L-3) \right]^{1/2}, \quad L - \text{number of experimental points}$$

In Table 4 the parameters of Langmuir-Freundlich equation obtained by fitting procedure are presented for all experimental systems. In every case very good agreement is observed between the experimental points and fitted lines, confirmed by low SD values. All studied systems show only slight heterogeneity effects. The values of adsorption capacity correspond well to the differences between adsorption isotherms.

4. CONCLUSIONS

Two mesoporous carbons of differentiated structure were synthesized by impregnation of silicas with sucrose solutions. Both adsorbents are characterized by very similar values of pore volumes and different values of specific surface areas and pore diameters. Lower adsorption of methylene blue is found for the carbon characterized by higher specific surface area, because its small pores are not accessible for large dye molecules reducing the dye adsorption. Methylene blue is adsorbed stronger than methyl orange.

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