

Hierarchically porous carbon monolithic column for efficient methyl orange adsorption under flow conditions

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Abstract

This work presents a nanocasting fabrication method for highly porous carbon monoliths and their performance in a continuous-flow adsorption process of methyl orange from aqueous solutions. The monoliths were obtained using sucrose as a carbon precursor and a silica scaffold with exceptionally large macropores of approximately 100 μm as a hard template. The materials were characterised by nitrogen adsorption, SEM, thermogravimetry, and FTIR spectroscopy. Highly porous carbon monoliths with good mechanical stability were obtained by using a three-step impregnation process. The monoliths were characterised by a large specific surface area of 1399 m^2/g , a total pore volume of 6.1 cm^3/g , and a three-modal pore size distribution. They showed excellent adsorption properties under flow conditions. Regardless of the flow rate and the initial methyl orange concentration, the sorption capacity was close to the equilibrium capacity determined in the batch process, i.e. approximately 450 mg/g . The experimental breakthrough curves were well described by both the Thomas and Yoon–Nelson models. The sorption capacity in the monolithic column was 35 times greater than that in the packed-bed column with commercial microporous carbon grains under the same flow conditions.

Keywords

carbon monoliths, hierarchical porosity, methyl orange adsorption

1. INTRODUCTION

The increasing contamination of water bodies by synthetic dyes, particularly textile and industrial effluents, poses a significant risk to both aquatic ecosystems and human health. Azo dyes, such as methyl orange, are of particular concern due to their widespread use, high solubility, and resistance to biodegradation (Aider et al., 2023; Alghamdi et al., 2019; Kumar et al., 2023). Adsorption is one of the most effective methods for the removal of these contaminants. It has been used for many years because of its simplicity, low cost, and high efficiency (Abdoul et al., 2023; Asouhidou et al., 2009; Gabelman, 2017). Carbon materials have attracted considerable attention due to their large surface area, tuneable surface chemistry, and environmental stability (Bulavová et al., 2018; Kueasook et al., 2020; Xie et al., 2024). However, the adsorption performance is closely related to their structural properties, particularly their specific surface area and pore size.

Hierarchically porous carbon materials, which feature interconnected macro-, meso- and micropores, offer distinct advantages for adsorption applications. Macropores facilitate mass transport, mesopores enhance accessibility to active sites, and micropores provide a large surface area, thus ensuring a high concentration of adsorption centres. Such multimodal pore architectures are especially beneficial under dynamic flow-through conditions, where fast and efficient contaminant removal is required. Porous carbon materials with a well-defined hierarchical structure can be effectively synthesised through a templating approach in which a sacrificial scaffold directs the morphology and porosity of the resulting carbon.

Various hard templates, including silica-based materials such as SBA-15 and KIT-6, as well as colloidal silica spheres, have been found to be particularly advantageous due to their controllable pore sizes and structural stability (Díez et al., 2021; Liu et al., 2019; Lu and Schüth, 2006; Sobrinho et al., 2019). In the nanocasting method, a carbon precursor, such as resorcinol, formaldehyde, sucrose, or phenol, is introduced into the pores of the template and subjected to polymerisation. After carbonisation, the silica template is removed, usually by etching using a solution of hydrofluoric acid or sodium hydroxide (Lu et al., 2004; Sharma et al., 2018). This process results in the formation of a porous carbon replica which can be used in dynamic adsorption systems as monolithic columns for wastewater treatment.

In this study, silica monoliths with exceptionally large macropores of about 100 μm and developed mesoporosity were used as a hard template to create hierarchically porous carbon replicas. We focused on the synthesis and characterisation of mechanically stable, rod-shaped materials with high porosity for the use in adsorption under flow conditions. In particular, our goal was to develop monolithic materials that combine fast kinetics, high adsorption capacity, and low pressure drop. Materials were examined in the adsorption of methyl orange from aqueous solutions. The results were fitted with the Thomas and Yoon–Nelson models. Moreover, the sorption properties of highly porous carbon monolithic materials were compared with those obtained for the microporous commercial carbon beds in batch and flow processes as well. The presented results contribute to the development of advanced carbon-based adsorbents for water purification and environmental remediation.



2. MATERIALS AND METHODS

2.1. Materials

Nitric acid (65%, Stanlab), tetraethoxysilane (99%, ABCR), polyethylene glycol 100000 (Thermo Scientific), hexadecyltrimethylammonium bromide (98%, Roth), ammonia solution (25%, Chempur), table sucrose, sulphuric acid (96%, Stanlab) and sodium hydroxide (Chempur) were used for material synthesis, methyl orange (POCH) was used for adsorption studies. All chemicals were used as received.

2.2. Synthesis of silica monolith

The synthesis of silica monoliths (M-S) was carried out according to a procedure published by [18]Småt et al. (2003) with some modifications. Briefly: polyethylene glycol (PEG 100000) was dissolved in nitric acid (1 mol/dm³). The solution was cooled in an ice bath, and tetraethoxysilane (TEOS) was added dropwise. After 30 min, CTAB was added and the mixing was continued for an additional 30 min. The mixture was then transferred to polypropylene tubes, sealed, and aged for 8 days. The mass ratio of the reaction composition TEOS:HNO₃:CTAB:PEG was 1:1.21:0.046:0.1. Synthesised silica monoliths were removed from moulds, washed with water, treated with ammonia solution (1 mol/dm³, 6 hours, 90 °C), washed again, and dried. The organic template was removed by calcination at 550 °C for 8 hours.

2.3. Synthesis of carbon materials

The silica monoliths were soaked with a 20 wt.% sucrose solution in water (acidified with a 0.75 wt.% H₂SO₄) under vacuum. Samples were dried sequentially at ambient temperature, 40 °C, and 110 °C, each step for 24 hours and finally at 160 °C for 5 hours. The impregnation procedure was repeated one, two, or three times. Subsequently, the samples were carbonised at 950 °C (nitrogen atmosphere, 5 hours, heating rate 4 °C/min). Monoliths were denoted as M-SC1, M-SC2 and M-SC3 for 1, 2, 3 – step impregnation, respectively.

Silica was removed from M-SC materials by etching in a 3 M NaOH solution at room temperature for 3 days, followed by washing in excess water until neutral pH was achieved. Finally, the samples were rinsed with a 0.1 M HCl, washed with water, and dried at 200 °C. The materials were denoted as M-C1, M-C2 or M-C3.

2.4. Characterisation of materials

The low-temperature nitrogen adsorption method was used to characterise the porous texture of the materials. Nitrogen isotherms were obtained at −196 °C using the Micrometrics 2020 instrument. The samples prior to analysis

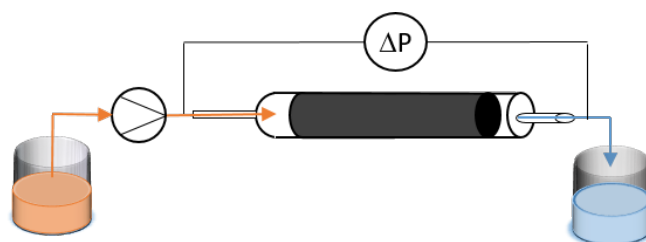
were outgassed at 200 °C for 24 hours. The specific surface area S_{BET} was calculated from the linear part of the isotherm, and the BJH method was applied to determine the pore size distribution. The Dubinin-Astakhov model was used for micropore analysis. The scanning electron microscopy images were obtained using a Phenom Pure instrument (BDS detector, 5 kV, Thermo Scientific). The total pore volume was calculated using the formula:

$$V_t = \frac{1}{\rho_a} - \frac{1}{\rho_s} \quad (1)$$

The apparent density was calculated from the volume and mass of the monolith, and the skeleton density was determined by helium pycnometry (Micromeritics). Thermogravimetric analysis (TGA/SDTA851e, Mettler Toledo) was performed to determine the carbon content of the M-SC materials. The samples were heated to 800 °C in an air atmosphere with a heating rate of 10 deg/min. FTIR spectroscopy was used to identify the surface functional groups. The spectrum was obtained using the transmission technique (Nicolet 6700, Thermo Scientific). The sample concentration in KBr was 0.002%.

2.5. Adsorption studies

The carbon monolithic rods of 3 cm in length, 0.4 cm in diameter, and a mass of 0.06 g were embedded in a heat-shrinkable tube, equipped with connectors, and tested in a continuous flow adsorption process using the setup shown in Scheme 1.



Scheme 1. Setup for adsorption studies.

The adsorption of methyl orange (MO) was studied for the initial dye concentration, C_0 equals to 250, 500, 750 mg/dm³. Experiments were conducted at a flow rate, F of 0.25, 0.5, and 0.75 cm³/min. The constant flow rate was maintained with a syringe pump (KDS200, KD Scientific) and continuously monitored at the column outlet. The effluent was collected at regular time intervals and the MO concentration was determined using a spectrophotometer (Cecil CE 2020, Cecil Instruments) at a wavelength of 462 nm. The experiments were carried out at 22 °C, without any pH adjustment. Commercial carbon material (C_B) in the form of cylindrical particles with a diameter of 1 mm and a length of 1 to 3 mm was used as a benchmark material. The adsorption of MO on the C_B was carried out in a packed-bed column of 3 cm in length and 1.5 cm in diameter using the same residence time as in the monolithic column.

The total amount of methyl orange adsorbed was determined using the formula:

$$q = \frac{C_0 F}{m} \int_0^{t_s} \left(1 - \frac{C}{C_0}\right) dt \quad (2)$$

The q was calculated by integrating the area above the experimental breakthrough curve over the adsorption time and then normalised by the mass of the adsorbent.

The performance of the monolithic column was modelled using the Thomas (Eq. (3)) and Yoon–Nelson (Eq. (4)) models. These models can be expressed as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(k_{Th} q_{Th} \frac{m}{F} - k_{Th} C_0 t\right)} \quad (3)$$

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp(k_{YN} \tau - k_{YN} t)} \quad (4)$$

Furthermore, the adsorption capacity of the powdered monolith M-C3 and the commercial carbon material was determined in a batch process using 10 mg of sorbent and 100 cm³ of methyl orange solution in water with a concentration of 100 mg/dm³. The particle size was ca. 0.1 mm in all experiments.

3. RESULTS AND DISCUSSION

3.1. Properties of the materials

Carbon monoliths with a hierarchical three modal micro-, meso- and macroporous structure were obtained using the well-known nanocasting method (Lu et al., 2004; Lu et al., 2005; Taguchi et al., 2003; Wang et al., 2005), with sucrose applied as the carbon source and silica monoliths as a hard template (Fig. 1).

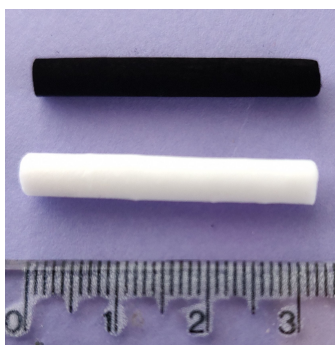


Figure 1. Silica M-S and carbon M-C3 monoliths.

The silica monoliths were characterised by the presence of large, interconnected macropores of approximately 100 μm and a bimodal mesopore structure with dominant pore diameters of 2.5 and 20 nm. The surface area and the mesopore

volume were equal to 350 m²/g and 1.13 cm³/g, respectively (Table 1). Figure 2 shows SEM images of the scaffold monolith (M-S), composite silica-carbon material (M-SC3), and carbon sample (M-C3) after three cycles of impregnation and carbonisation. The macrostructure of all samples is almost identical. Impregnation with a sucrose solution, followed by carbonisation, resulted in a homogeneous coating on the surface of the macropores, and their pristine structure was preserved. After removal of the silica template, a highly porous carbon monolith was obtained. Therefore, it can be concluded that carbon was primarily located in the mesopores of the scaffold. This finding is consistent with Lu's observations on carbon monoliths, which were obtained by impregnation of the silica monoliths with small macropores using furfuryl alcohol at various concentrations (Lu et al., 2005).

Table 1. Properties of carbon-silica monoliths.

Monolith	S_{BET} [m ² /g]	V_{N_2} [cm ³ /g]	d_{meso} [nm]	Carbon content [%]
M-S	350	1.13	2.5/20	—
M-SC1	346	0.57	3.9/18.5	15.6
M-SC2	336	0.43	4/17	26.9
M-SC3	362	0.22	3/18	33.5

The micro/mesostructure of the monoliths was analysed by nitrogen adsorption after each preparation step. Figure 3 shows the nitrogen adsorption–desorption isotherms and pore size distributions of the silica monolithic scaffold and carbonised composite samples. All samples exhibit type IV isotherms. The well-developed mesoporosity in the silica scaffold changed significantly after subsequent impregnation cycles. The complete filling of small mesopores with diameters of around 2.5 nm was observed in all composite materials, and the gradual decrease in volume of large mesopores with a dominant diameter of around 20 nm was recorded. Small mesopores with a diameter of 3 – 4 nm, which appeared in the composite samples, probably formed as a result of the gaps that developed between the carbon material and the shrinking silica during the carbonisation process at 950 °C (Table 1). The total mesopore volume decreased from 1.13 cm³/g in M-S to 0.22 cm³/g in the M-SC3 composite material. The values of specific surface area of the silica material and the composites were similar, although they were the result of the presence of pores of various origins.

The carbon content in the composite materials was determined by thermogravimetry. TG curves (Fig. 4) showed a sharp mass loss that occurred above 500 °C attributed to the combustion of carbon deposited within the silica matrix. The amount of carbon introduced in three subsequent cycles was 16, 27, and 34 wt.%, respectively (Table 1). The increase in carbon content correlates well with the decrease in mesopore volume in the materials, which were gradually filled with the carbon precursor.

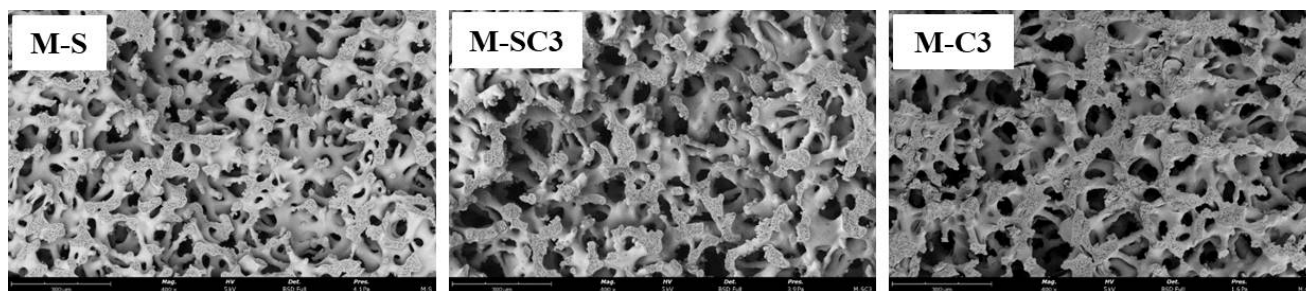


Figure 2. SEM images of silica, carbon-silica, and carbon monoliths.

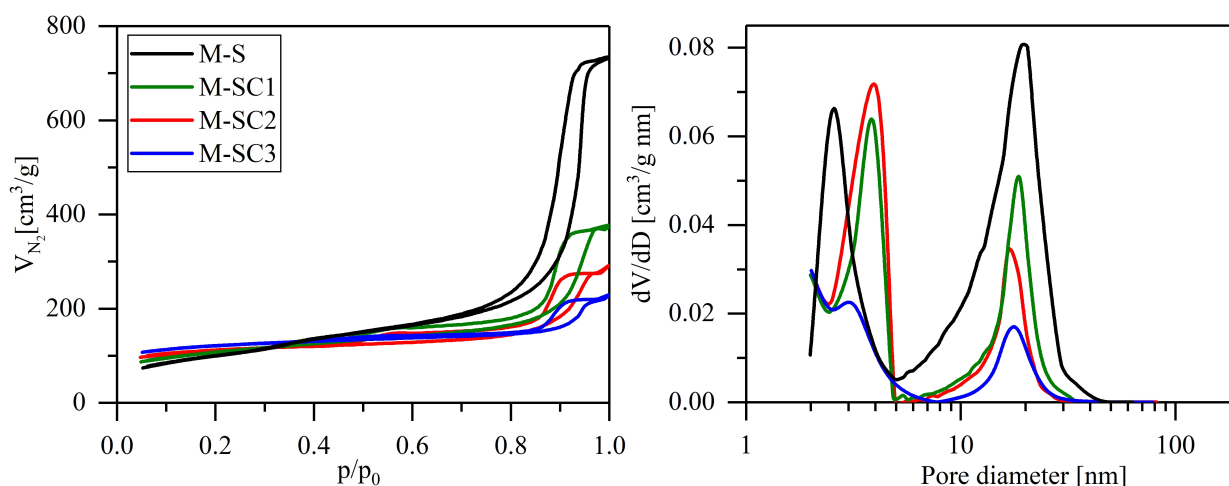


Figure 3. Nitrogen adsorption/desorption isotherms and pore size distribution of silica and carbon-silica monoliths.

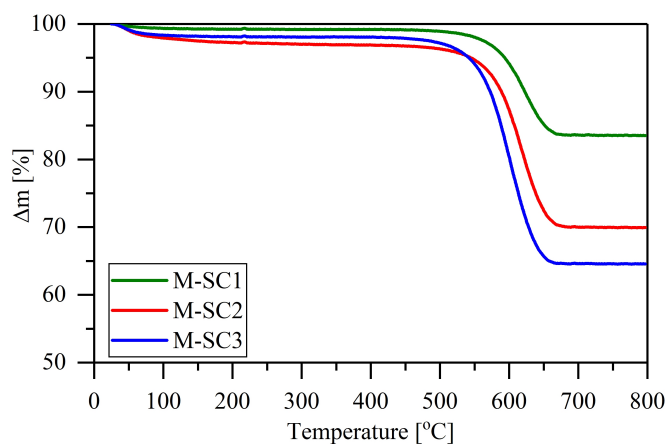


Figure 4. TG curves of carbon-silica monoliths.

the carbon content. Moreover, all materials had macropores with a diameter of ca. 100 μm that formed a continuous network, and their volume in the M-C3 monolith was equal to 4.38 cm^3/g . The total pore volume in the monolith M-C3, equal to 6.1 cm^3/g , was determined from the apparent and skeletal density, which were 0.162 g/cm^3 and 2.178 g/cm^3 , respectively. The highly porous structure and carbon content had a strong influence on the mechanical properties of M-C materials, which increased in the order M-C1 < M-C2 < M-C3. However, it should be emphasised that only the M-C3 monolith, despite its very high porosity (92.5%), was characterised by a sufficient mechanical strength to be used as a monolithic column under flow conditions. Furthermore, it was not possible to determine the apparent density and macropore volume in the monoliths M-C1 and M-C2 due to the very low mechanical strength.

Table 2. Structure parameters of carbon materials.

Sample	S_{BET} [m^2/g]	V_t [cm^3/g]	V_{N_2} [cm^3/g]	V_{meso} [cm^3/g]	S_{micro} [m^2/g]	V_{micro} [cm^3/g]	d_{micro} [nm]
M-C1	1642	N/A	2.53	1.87	1529	0.66	1.53
M-C2	1499	N/A	1.84	1.20	1498	0.64	1.52
M-C3	1399	6.1	1.72	1.12	1424	0.60	1.50
C _B	848	—	0.49	0.10	939	0.39	1.38

The shape of the hysteresis loop of carbon materials (M-C) indicated a wide distribution throughout the entire range of mesopores, which is clearly visible in Fig. 5, which shows the cumulative distribution curves calculated from the adsorption isotherms. After removal of the silica skeleton, new mesopores with a diameter of ca. 8.5 nm appeared in the materials. The microstructure parameters of carbon skeleton were similar in all samples, regardless of the number of the impregnation stages (Fig. 5, Table 2). However, a significant reduction in the mesopore volume was observed with an increase in

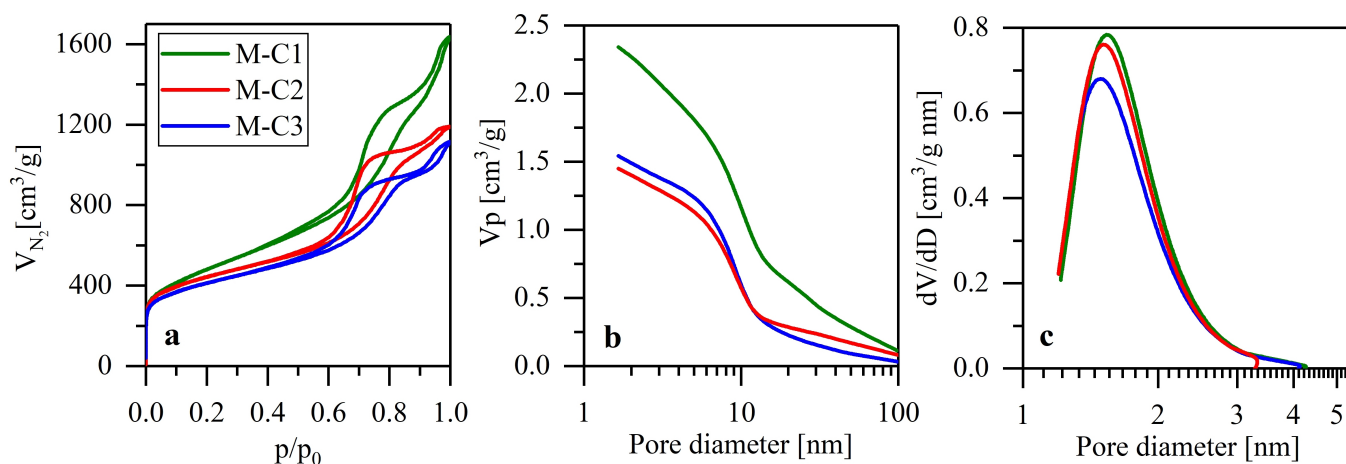


Figure 5. Nitrogen adsorption/desorption isotherms and pore size distributions of carbon monoliths.

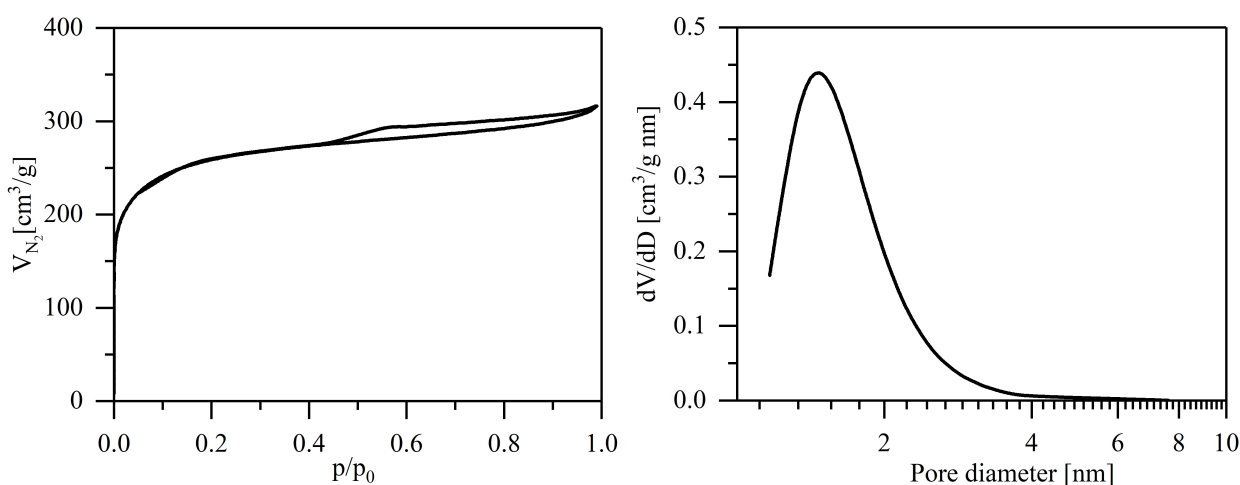


Figure 6. Nitrogen adsorption/desorption isotherms and pore size distribution of commercial carbon.

The commercial carbon material (C_B) was characterised by a microporous structure typical of conventional carbon sorbents (Fig. 6 and Table 2). The specific surface area of the micropores and their volume were 35% and 40% lower, respectively, than the corresponding values of the M-C3 carbon monolith. In this material, the slit mesopores occupied only $0.1 \text{ cm}^3/\text{g}$, and no macropores were found.

Infrared spectroscopy was performed for identification of surface functional groups (Fig. 7). A broad band centred at 3400 cm^{-1} can be attributed to O-H stretching vibrations of surface hydroxyl groups and/or adsorbed moisture. The absorption peaks at $3000 - 2800 \text{ cm}^{-1}$ arise from the C-H stretching (CH , CH_2 , CH_3), indicating the presence of residual aliphatic moieties, which may originate from incomplete sucrose carbonisation, despite the fact that the process was carried out at a high temperature. A small band centred at 1698 cm^{-1} can be assigned to $\text{C}=\text{O}$ stretching of carbonyl or carboxyl groups, while the band observed at 1600 cm^{-1} is assigned to aromatic $\text{C}=\text{C}$ vibrations, reflecting the formation of sp^2 carbon domains during carbonisation. A strong

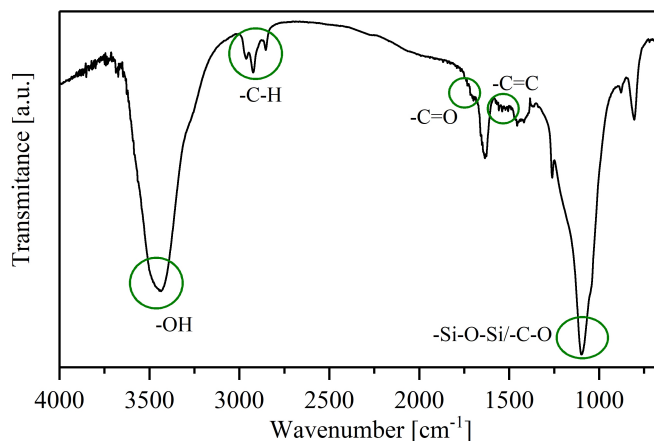


Figure 7. FTIR spectrum of M-C3 material.

absorption peak centred at 1100 cm^{-1} is characteristic of Si-O-Si vibrations, indicating incomplete removal of the silica template. Moreover, C-O vibrations from carboxyl groups also occur in the same wavelength range. The spectrum confirmed

the successful formation of a carbonaceous framework with dominant aromatic C = C structures, in line with high temperature carbonisation, and the presence of some surface oxygen functionalities. The latter may enhance the hydrophilic character of the carbon surface and provide potential adsorption sites for polar molecules (Wembabazi et al., 2015; Fauziyah et al., 2020; Ruz et al., 2024).

3.2. Adsorption of methyl orange

The breakthrough curves were obtained for the adsorption of methyl orange at different initial concentrations and flow rates (Fig. 8). For all flow rates, an increase in the initial dye concentration led to a reduction in breakthrough times and sharpening of breakthrough fronts.

The shape of the breakthrough curves was generally sigmoidal, which is characteristic of fixed-bed adsorption processes. In the initial phase, the concentration of methyl orange in the effluent was zero due to the presence of unoccupied active sites that could adsorb all the molecules. As these active sites became saturated, methyl orange appeared in the effluent mixture until the outlet concentration of the column was equal to the inlet concentration. The breakthrough region was relatively narrow, indicating fast adsorption kinetics and minimal axial dispersion (Al Mesfer et al., 2020). Most likely, the adsorption process was also influenced by favourable hydrodynamic conditions, such as the absence of channelling and uniform fluid distribution in the monolith.

The experimental data were compared with those predicted by the Thomas and Yoon–Nelson models (Thomas, 1944; Yoon and Nelson, 1984). The aim of this study was to assess the effect of the inlet dye concentration and flow rate on the column's dynamic behaviour and to evaluate the predictive capability of both models under varying operating conditions. The results are presented in Tables 3 and 4.

Table 3. Thomas model parameters for the monolithic column M-C3.

Flow rate [cm ³ /min]	C ₀ [mg/dm ³]	q [mg/g]	q _{Th} [mg/g]	k _{Th} [cm ³ /(mg·min)]	R ²
0.25	250	445	444	0.20	0.99
0.50	250	454	448	0.22	0.98
0.75	250	449	440	0.24	0.99
0.25	500	440	434	0.16	0.98
0.50	500	443	444	0.21	0.99
0.75	500	448	447	0.23	0.99
0.25	750	427	432	0.14	0.98
0.50	750	430	451	0.15	0.96
0.75	750	455	454	0.16	0.98

Table 4. Yoon–Nelson model parameters for the monolithic column M-C3.

Flow rate [cm ³ /min]	C ₀ [mg/dm ³]	t _{Y-N exp.} [min]	t _{Y-N model} [min]	k _{Y-N} [1/min]	R ²
0.25	250	419	425	0.052	0.99
0.50	250	195	197	0.056	0.98
0.75	250	133	130	0.061	0.99
0.25	500	199	200	0.080	0.98
0.50	500	112	107	0.105	0.99
0.75	500	78	77	0.113	0.99
0.25	750	132	135	0.104	0.98
0.50	750	67	74	0.115	0.96
0.75	750	52	53	0.122	0.98

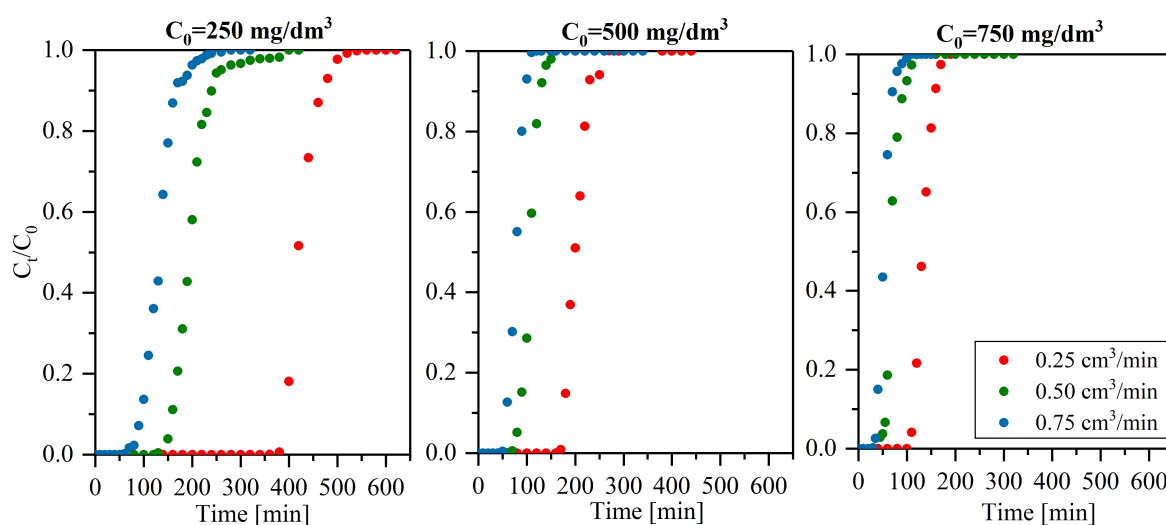


Figure 8. Breakthrough curves for methyl orange adsorption on the M-C3 monolith.

The adsorption capacity calculated from the Thomas model was in the range of 432 to 454 mg/g for all conditions and was almost the same as that determined experimentally. The slight increase in k_{Th} at higher flow rates can be attributed to an improved external mass transfer and a reduction in the thickness of the boundary layer on the adsorbent surface, which facilitates the transport of methyl orange molecules from the solution to the active adsorption sites. As a result, the adsorption process appears to be kinetically more favourable. The k_{Th} rate constant also decreased slightly with increasing adsorbate concentration at the column inlet, reflecting slightly slower adsorption kinetics and the increasing influence of diffusion on the process rate. The high values of R^2 , ranging from 0.96 to 0.99, indicate that the model fits the experimental data well.

The Yoon–Nelson model demonstrated that the half-breakthrough time τ significantly decreased from 425 to 53 min with higher flow rates and larger inlet concentrations. These results showed that under more intensive operating conditions the adsorption process was eight times shorter. The R^2 values in the range of 0.96 to 0.99 confirm the good description of the process by this model.

The adsorption process of the methyl orange was performed in a packed-bed column filled with commercial carbon grains to compare its efficiency with the data obtained in the monolithic column. The breakthrough time in the fixed-bed column was very short, ca. 2 min (Fig. 9), and the adsorption capacity was only 12.3 mg/g, while in the monolithic column it was 430 mg/g under the same process conditions, i.e. $C_0 = 750 \text{ mg/dm}^3$ and residence time equal to 44 s.

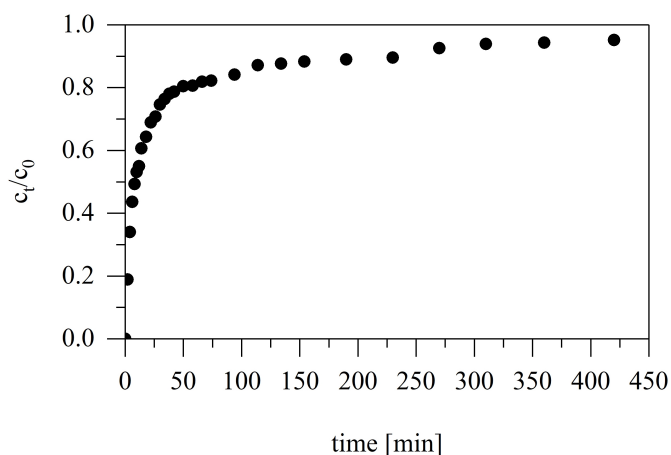


Figure 9. Methyl orange adsorption onto C_B material under flow conditions.

The adsorption capacity determined in the batch process was found to be very well correlated with the microporous surface area of the sorbents ($1399 \text{ m}^2/\text{g}$ vs. $848 \text{ m}^2/\text{g}$) and was equal to 455 mg/g and 285 mg/g for M-C3 and C_B materials, respectively. However, the adsorption equilibrium of the M-C3 material was obtained after 40 min, while that of the C_B material after 10 hours.

The comparative study of the methyl orange adsorption process in M-C3 and C_B materials showed that the sorption capacity in the batch process depended solely on the specific surface area and was proportional to its size, but the time to reach the adsorption equilibrium was significantly longer for microporous carbon. However, in a continuous process, the transport of molecules within the material skeleton is of primary importance. In the M-C3 monolithic material, which contains mesopores over a wide range of sizes, the sorption capacity was 35 times greater than that of the C_B material under the same flow conditions. Moreover, the smaller thickness of the carbon skeleton compared to the size of C_B grains significantly reduces diffusion resistance. The macropores in monoliths play the same role as the spaces between grains in a packed-bed column. This clearly demonstrates the advantages of using highly porous monolithic columns in adsorption processes. Furthermore, the excellent structural and transport properties of monoliths open up possibilities for other applications, particularly in catalysis as microreactors.

4. CONCLUSIONS

The structural and mechanical properties of the carbon monoliths synthesised by the nanocasting method strongly depended on the number of impregnation steps of the carbon precursor solution. The monoliths' porosity and specific surface area decreased with increasing carbon content, but their mechanical stability improved significantly. Triple impregnation resulted in the material with a large specific surface area of $1399 \text{ m}^2/\text{g}$, transport macropores with a diameter of approximately $100 \mu\text{m}$, mesopores over a wide range of sizes, and micropores of approximately 1.5 nm . The total pore volume was $6.1 \text{ cm}^3/\text{g}$. This monolithic material appeared to be an excellent adsorbent in the continuous-flow process of methyl orange sorption. The threefold increase in flow rate and initial methyl orange concentration was shown to result in eight times shorter time required to reach 50% of the breakthrough curve, while maintaining the same sorption capacity, which was close to the equilibrium capacity determined in the batch process, i.e. 450 mg/g . This confirms that within the applied range of column operating parameters, its efficiency is determined solely by the kinetics of sorption. In the packed-bed column, equipped with microporous carbon grains, the sorption capacity was 23 times smaller than that reached at equilibrium in the batch process. In that case, the rate of the process was determined by very slow diffusion in the micropores. Furthermore, the experimental data are well described by the Thomas and Yoon–Nelson models, and the high values of the correlation coefficient ($R^2 \geq 0.96$) were obtained. This clearly demonstrated the advantages of using highly porous monolithic columns in adsorption from liquids.

SYMBOLS

C_0 inlet MO concentration, mg/dm^3

C_t MO concentration in the effluent at time t , mg/dm^3

d_{meso}	mesopore diameter, nm
d_{micro}	micropore diameter, nm
F	flow rate, cm^3/min
k_{Th}	Thomas model rate constant, $\text{cm}^3/(\text{mg} \cdot \text{min})$
k_{YN}	Yoon–Nelson model constant, min^{-1}
m	mass of adsorbent, g
q	adsorption capacity, mg/g
q_{Th}	maximum adsorption capacity, mg/g
S_{micro}	micropore surface area from Dubinin–Astakhov model, m^2/g
S_{BET}	specific surface area, m^2/g
t_s	saturation time, min
V_{micro}	micropore volume, cm^3/g
V_{N_2}	mesopore volume, cm^3/g
V_t	total pore volume, cm^3/g
w	flow velocity, cm/s

Greek symbols:

ρ_a	apparent density, g/cm^3
ρ_s	skeletal density, g/cm^3
τ	time required to reach 50% of the breakthrough curve, min

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