

## Study of adsorption of differently charged dyes by carbon adsorbents

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### ABSTRACT

The article investigates the adsorption of basic (Methylene blue) and acidic (Congo red) dyes by three types of industrial activated carbon synthesized from natural raw materials. Using the method of isothermal adsorption/desorption of nitrogen, the porous structure of all types of carbon was studied, and the effect of the size of the adsorbent particles on the adsorption capacity was shown. It was established that the adsorption isotherms of both dyes can be described using the Langmuir model. It is assumed that dye molecules are weakly bound to the surface of the carbon material due to van der Waals and hydrophobic interactions. It is shown that the adsorption of Methylene blue is significantly greater than the adsorption of Congo red. This is due to the peculiarities of the dissociation of the functional groups of dye molecules, as well as the almost twice the length of Congo red molecules compared to Methylene blue molecules. It is shown that the boundary amount of adsorbed Methylene blue allows us to estimate the specific surface area of microporous activated carbon with high accuracy if the hydrophilicity of the surface of this carbon is taken into account.

*Keywords:* Activated carbon; Porous structure; Methylene blue; Congo red; Adsorption isotherm; Maximum adsorption

### 1. Introduction

The industrial production of food, pharmaceuticals and textiles uses thousands of names of dyes of various origins. In addition to the dyes of natural origin, the chemical industry offers new and improves existing synthetic substances, providing them with the necessary properties – from smell and colour to extending the shelf life of products. Synthetic dyes are more stable and often cheaper than natural ones, so they are widely used as additives in the pharmaceutical and food industries [1,2].

Dyes are divided into anionic (direct, acid and reactive dyes), cationic (basic dyes) and nonionic (disperse dyes). Chromophores in anionic and nonionic dyes mainly consist of azo groups or anthraquinones. Anthraquinone-based dyes are more resistant to degradation due to their linked aromatic structures. Metal-complex dyes are mostly synthesized based on chromium compounds. It should be added that most often azo dyes are used. They make up 60% of the total number of used dyes [3].

However, in addition to the useful properties and improvement of product quality, the production and use of

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dyes are accompanied by the formation of significant volumes of wastewater. The synthetic origin and complex aromatic structures of dyes make them stable and difficult to biodegrade [3,4]. A study of the ecotoxicity of various dyes, which was conducted by the Environmental Toxicology Association of the Dye Industry, found that  $\geq 90\%$  of the dyes used in the fabric dyeing process have a lethal dose value of  $50\% \text{ LD}_{50} \geq 2,000 \text{ mg/kg}$  [5]. The large amount of dyes used, their properties and low degradability pose a significant threat to the environment and require the development of methods for efficient wastewater treatment in industries that use dyes. Such wastewater is usually treated by physical or chemical methods. These include flocculation combined with flotation, electro flocculation, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion exchange, irradiation, precipitation, ozonation, and others [6–10]. The choice of the appropriate treatment process is of key importance from the point of view of the efficiency and economic feasibility of its application for wastewater treatment [11].

Among conventional treatment methods, adsorption processes are widely used to achieve the efficient removal of dyes from industrial wastewater [12–15]. The use of traditional activated carbon (AC) turned out to be efficient, but quite expensive. Many studies have been conducted investigating the adsorption properties of low-cost adsorbents such as peat, bentonite, metallurgical slag, china clay, corn processing waste, wood shavings, and silica [3]. However, these inexpensive adsorbents have, as a rule, low adsorption capacity and require the use of a large amount of adsorbent for efficient wastewater treatment. In this regard, there is a need to find such types of AC that would be economically attractive, synthesized from readily available raw materials, and at the same time possess high efficiency as adsorbents. The most attractive raw material for such carbon is the raw material of plant origin, which allows the synthesis of AC with a wide range of applications both in industry and for solving environmental safety problems [16–19].

Among the dyes used as marker substances, the main ones are Methylene blue (MB) and Congo red (CR) [20]. MB in solution is in cationic form, that is, it is positively charged and has a hydrophobic aromatic fragment. MB is used to model the adsorption of positively charged low-molecular-weight substances (alkaloids, histamine, diphenhydramine, novocaine hydrochloride, promedol, etc.) on negatively charged surfaces. CR belongs to anionic dyes, it is used to study the adsorption of negatively charged low- and medium-molecular substances (sodium diclofenac, salicylates, analgin, asparkam, salts of barbituric acid, salts of fatty and bile acids, etc.) on positively charged surfaces [20].

AC producers often point to a specific application of their carbon in a certain narrow field. This is due both to the limitations of the research carried out by the manufacturer and to the binding of researchers to the specific recommendations of the manufacturer. For example, AC Norit DLC Super 30 and Norit DLC Supra 30 (Cabot Norit Nederland B.V., The Netherlands) are used in scientific publications as an active material for the manufacture of supercapacitor electrodes [21–25]. You will not find any examples of how these types of AC are used as adsorbents because there are no such studies. Therefore, we studied the adsorption properties

of microporous industrial carbon Norit DLC Super 30 and Norit DLC Supra 30, which are synthesized from a natural raw material – coconut shell, concerning the differently charged dyes – MB (basic dye) and CR (acid dye).

## 2. Experiment set-up

### 2.1. Characterization of activated carbons

To compare the adsorption behaviour of new types of carbon, the necessary conclusions can be drawn by comparing the obtained results with the results demonstrated by such types of AC that have already been previously studied. In our case, to compare the adsorption of MB and CR dyes, AC brand BAU-A (Khimprom, Ukraine) was chosen, which is also obtained from natural raw materials (birch wood) and is widely used in adsorption studies of dyes [26–28].

Although industrially obtained types of AC have appropriate quality certificates, many important indicators are not provided. For example, the specific surface area is not indicated in the BAU-A carbon certificate. This indicator is provided for carbon brands Norit DLC Super 30 and Norit DLC Supra 30 (1,600 and 1,900  $\text{m}^2/\text{g}$ , respectively). Pohlmann et al. [29], the specific surface area determined for Norit DLC Super 30 carbon is 1,618  $\text{m}^2/\text{g}$ , which is close to the parameter declared by the manufacturer Rodriguez-Romero et al. [25], the specific surface area determined for Norit DLC Supra 30 carbon is only 1,700  $\text{m}^2/\text{g}$ , which is a lower value than the declared value. Therefore, the characteristics of the porous structure of these types of carbon were determined using the standard method of isothermal adsorption/desorption of nitrogen at the boiling temperature of ( $T = 77 \text{ K}$ ) with the help of an automated Quantachrome Autosorb Nova 2200e analyzer. Before measurements, samples of all materials were pre-degassed in a vacuum at 453 K for 20 h.

Activated carbon was photographed using a scanning electron microscope with a low-vacuum camera and a REMMA-102-02 energy dispersive microanalysis system. This microscope is intended for direct investigation of the surface relief of various materials in the solid phase and the determination of their elemental composition by X-ray microanalysis based on the energies of characteristic X-ray quanta in low and high vacuum conditions. Particle sizes were estimated using a composite image in backscattered electrons. This mode allows obtaining images with phase contrast, where each phase of the sample has a luminescence brightness, which is proportional to its averaged atomic number.

The total volume of pores accessible to liquid was determined by long-term soaking in heptane that well wets the surface of activated carbon. The proportion of hydrophilic pores was determined by the amount of water absorbed during soaking. Calculation of hydrophilic–hydrophobic properties was carried out according to the method [30].

### 2.2. Adsorption experiments

The study of the adsorption of dyes was carried out according to the spectrophotometric methods described by the study of Bestani et al. [31] for MB and Paška et al. [32] for CR, using a single-beam spectrophotometer SF-46 with a built-in microprocessor, the limit of absolute errors when

measuring transmission coefficients in the spectral range of 400–750 nm is not more than 0.5%. Cuvettes with an optical path length of 10 mm were used for measurements.

To study the adsorption of dyes by industrial AC and to construct calibration graphs, control solutions with a known concentration were prepared. The calibration graph was constructed as follows: a set of aqueous solutions of dyes with known concentrations was prepared, and then the dependence of the optical density of these solutions on the concentration of the dye in the solution was determined. The measured data were modelled by a linear dependence, and equations with corresponding coefficients were obtained.

Studying adsorption properties of carbon materials, one has to deal with dispersion, where a dye solution acts as a dispersed medium, and carbon particles act as a solid dispersed phase. To reduce the negative impact of particles, which are additional scattering centres, on the final determination of the dye concentration, the additional separation of such a heterogeneous system was carried out using an OPn-8 centrifuge for 10 min.

### 3. Results and discussion

#### 3.1. Activated carbons characterization

When considering AC obtained by an industrial method, we have a list of selected parameters. These parameters are standardized by various organizations around the world, such as the American Society for Testing and Materials (ASTM), the American Water Works Association (AWWA), the Food and Drug Administration (FDA) in the USA, the Japanese Industrial Standards (JIS) in Japan, and the European Federation of Chemical Manufacturers Council (CEFIC) in Europe [33]. Based on these parameters, AC can be characterized by physical and active properties. Both types of properties become important factors in the specification of industrial carbon. Physical properties include specific surface area, density, particle size, mechanical strength, and ash content. Activity characteristics are the key indicators

of the potential effectiveness of AC to remove contaminants from water. The activity can be determined using several standard methods, which include the determination of iodine number, molasses number and MB adsorption. The iodine number provides information about the micropores (<2 nm) in AC, and therefore reflects its ability to adsorb small molecules. The molasses number characterizes macropores (>50 nm) and is used as a relative reference for measuring the capacity of AC for large molecules [33].

However, when we compare the adsorption properties of AC with different particle sizes, the results may be incorrect. This is because adsorption by large AC particles proceeds more slowly and is less than by small particles [33–36]. Therefore, there is a need to reduce the studied types of industrial AC to the same conditions.

AC brands Norit DLC Super 30 and Norit DLC Supra 30 are visually quite finely dispersed. The technical parameters in the accompanying documentation for these types of carbon indicate an average particle size of 30  $\mu\text{m}$  in both these brands.

However, the scanning electron microscopy (SEM) images of these AC types in Fig. 1 show that Norit DLC Supra 30 is more monodisperse, and Norit DLC Super 30 carbon has larger particles.

The other situation is with AC brand BAU-A. More than 95% of this carbon consists of 1–3.6 mm particles. Therefore, it is possible to compare the adsorption properties with Norit carbon only with definite grinding of BAU-A carbon particles. For a preliminary assessment of the adsorption capacity, the particles of this carbon were crushed mechanically and sifted on sieves with the selection of 7 fractions with an average particle size of  $d = 30, 42, 54, 72, 85, 145$  and 200  $\mu\text{m}$ . Carbon of each fraction weighing 2.5 mg was placed in 20 mL of an aqueous dye solution and kept for 24 h. After that, the residual concentration of the dye in the solution was determined. The results of the study are shown in Figs. 2 and 3.

Having analyzed the graphical dependencies in Figs. 2 and 3, it is easy to see that the carbon with the smallest particle size has the best adsorption properties. This result is

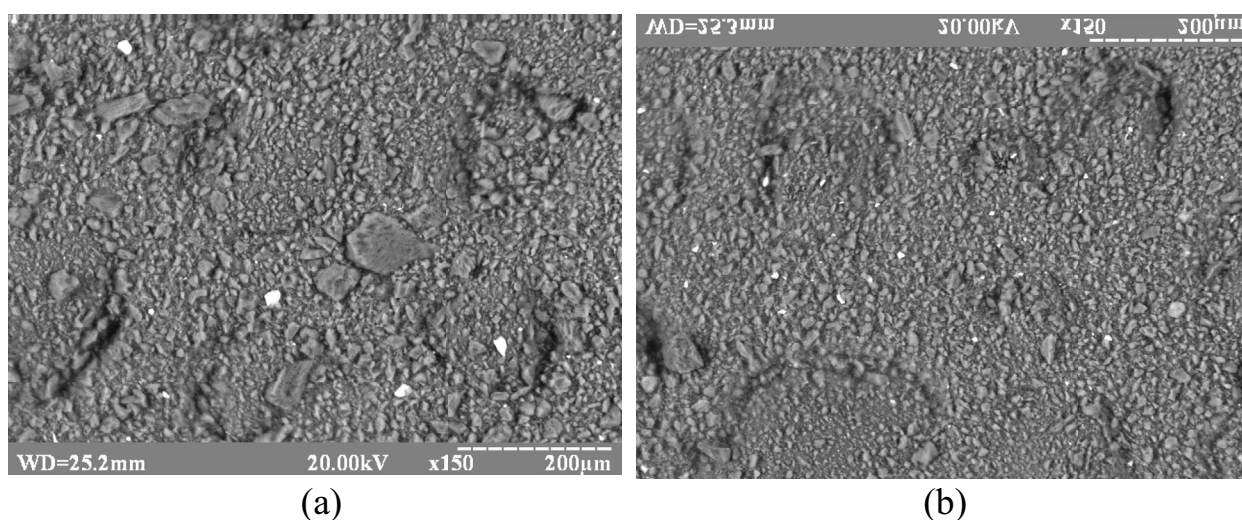


Fig. 1. SEM image of AC particles of Norit DLC Super 30 (a) and Norit DLC Supra 30 (b) brands.

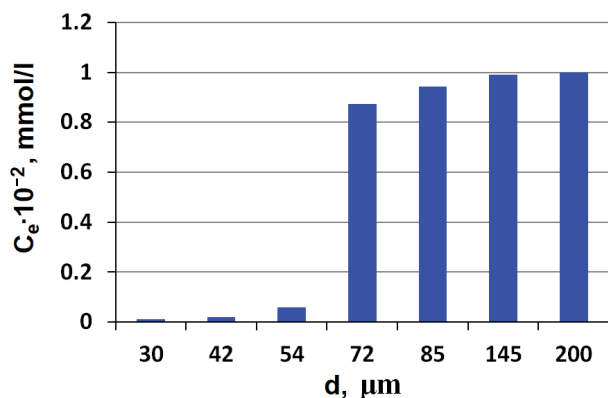


Fig. 2. Dependence of the residual concentration of the MB dye solution after the establishment of adsorption equilibrium depending on the average particle size of AC BAU-A ( $C_0 = 1.5 \times 10^{-2}$  mmol/L).

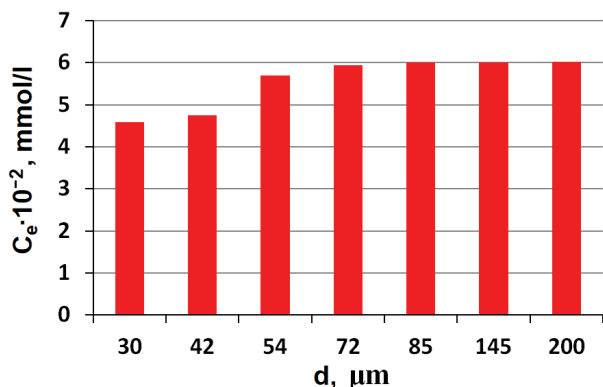


Fig. 3. Dependence of the residual concentration of the CR dye solution after establishing the adsorption equilibrium depending on the average particle size of AC BAU-A ( $C_0 = 6.5 \times 10^{-2}$  mmol/L).

understandable, because with the smallest size of the fraction, the surface of the carbon material, which has contact with the aqueous solution, is larger. Even though carbon with an average particle size of 30 μm exhibits the best adsorption properties, further studies of this type of carbon were carried out using a fraction with an average size of 42 μm. This is because, as a result of the grinding/separation processes, a very small amount of carbon material with a fraction size of 30 μm was obtained, which did not allow conducting a full range of research. Therefore, all the following results were carried out with the fraction of BAU-A crushed carbon with an average particle size of 42 μm since it was obtained in much larger quantities.

The characteristics of the porous structure of AC, especially the open pores that make it possible to effectively adsorb pollutants from the water environment, can be established based on simple and reliable methods, among which the nitrogen adsorption/desorption method is the most common. At the first stage of such research, adsorption/desorption isotherms are obtained, which are shown in Fig. 4. According to the shape of the curves, all isotherms

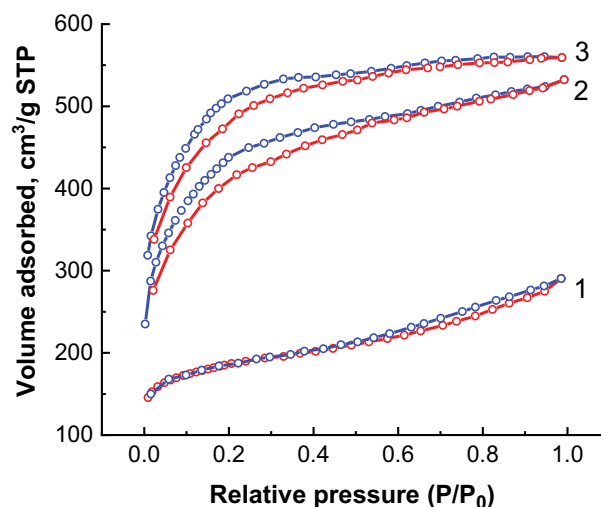


Fig. 4. Nitrogen adsorption/desorption isotherms of AC brands BAU-A (1), Norit DLC Super 30 (2) and Norit DLC Supra 30 (3), red curves correspond to adsorption and blue curves to the desorption of nitrogen.

can be roughly classified as type II according to the IUPAC classification [37], which are characteristic of adsorbents with slit-like pores.

A small hysteresis loop at higher relative pressures on the curve of nitrogen adsorption/desorption by BAU-A carbon is associated with capillary condensation. In open pores, the delayed condensation is the result of the metastability of the adsorbed multilayer coating. It follows that in the aggregate of such pores, the adsorption branch of the hysteresis loop is not in thermodynamic equilibrium. From Fig. 4, curve 1, we can conclude that we have a hysteresis loop of type H4. H4 loops are often found in aggregated zeolite crystals, some mesoporous zeolites, and micro-mesoporous carbon [37]. Rouquerol et al. [38] in monograph also established that H4-type hysteresis loops are obtained on AC and other adsorbents with slit-like pores – mainly in the micropores range. Isotherms in Fig. 4, curves 2 and 3, are characterized by the divergence of the adsorption and desorption lines, especially in the region of low relative pressure. This behaviour of isotherms is called low-pressure hysteresis, and its causes, according to Rouquerol et al. [38], can be:

- Irreversible retention of gas molecules in pores, the sizes of which are close to the sizes of these molecules;
- Irreversible chemical adsorbate–adsorbent interaction;
- Swelling of the spatial high-molecular framework of the adsorbent.

In the case of AC brands Norit DLC Super 30 and Norit DLC Supra 30, the most likely reason may be the first one.

To calculate AC parameters, the obtained isotherms were analyzed using the Quantachrome TouchWin programme. The specific surface area was determined by the multipoint Brunauer–Emmett–Teller (BET) method, the parameters of the microporous structure – by the t-method, and the mesoporous structure – by the BJH (Barrett–Joyner–Halenda)

method on the desorption line of the isotherm. The results of the calculations of the parameters of the porous structure with the predetermined hydrophilicity are given in Table 1.

3.2. Adsorption isotherms

Adsorption isotherms of dyes from aqueous solutions are of great importance for describing how adsorbates will interact with carbon and for optimizing the use of AC as an adsorbent.

The amount of adsorption of dyes was calculated by the difference in concentrations before and after contact with the carbon adsorbent. Knowing the initial concentration  $C_0$ , the equilibrium residual concentration of the solution  $C_e$ , the volume of the solution  $V$  and the mass of the adsorbent  $m$ , it is possible to calculate the adsorbed amount of the substance. The amount of adsorption was calculated according to the formula [38]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where  $q_e$  is the amount of adsorbate on carbon at equilibrium, in units of mg/g;  $C_0$  is the initial concentration of the initial solution, mg/L;  $C_e$  is the residual concentration of the equilibrium solution, mg/L;  $V$  is the volume of the aqueous solution, L;  $m$  is the amount of used carbon, g.

Based on the obtained adsorption values, the dependences  $q_e = f(C)$ , that is, adsorption isotherms, which are shown in Figs. 5 and 6 were constructed.

Analyzing Figs. 5 and 6, we can say that all isotherms belong to type II adsorption isotherms, which indicates a weak connection of dye molecules with the surface mainly due to electrostatic van der Waals interaction and the formation of hydrogen bonds. It allows us to use the Langmuir model to analyze all isotherms, which is the best for this type of isotherm [19,39].

The Langmuir equation can be used to describe experimental adsorption isotherms in the form [38]:

$$q_e = q_m \frac{K_L (C / C_0)}{1 + K_L (C / C_0)} \tag{2}$$

where  $q_e$  is the adsorption value,  $q_m$  is the maximum adsorption value,  $C$  is the equilibrium concentration,  $C_0$  is the standard concentration,  $K_L$  is the equilibrium constant of the process of interaction of the adsorbate with the adsorbent (Langmuir constant).

For the analysis of experimental adsorption isotherms, it is convenient to use the linear form of the Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \frac{C_0}{C} \tag{3}$$

After constructing the adsorption isotherms in the coordinates  $1/q_e = f(1/C)$ , we obtain a straight line that cuts off a segment equal to  $1/q_m$  on the ordinate axis. Therefore,

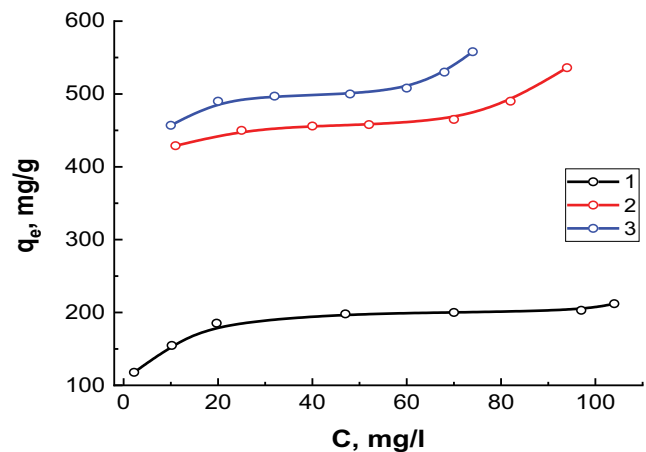


Fig. 5. Adsorption isotherms of MB of AC brands BAU-A (1), Norit DLC Super 30 (2) and Norit DLC Supra 30 (3).

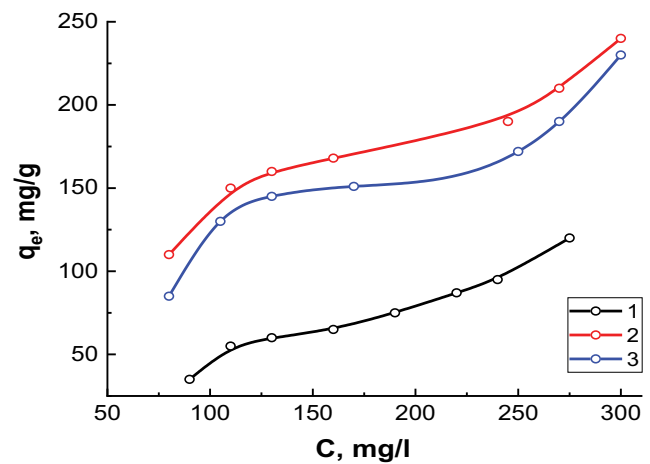


Fig. 6. Adsorption isotherms of CR of AC brands BAU-A (1), Norit DLC Super 30 (2) and Norit DLC Supra 30 (3).

Table 1  
Parameters of the porous structure of the studied AC types

AC type	Hydrophilicity, %	$S_{BET}$ , m <sup>2</sup> /g	$S_{micro}$ , m <sup>2</sup> /g	$V_{total}$ , cm <sup>3</sup> /g	$V_{micro}$ , cm <sup>3</sup> /g	$V_{mezo}$ , cm <sup>3</sup> /g	$d$ , nm
BAU-A	53	683	510	0.45	0.21	0.22	2.63
Norit DLC Super 30	69	1,580	1,410	0.82	0.62	0.19	2.08
Norit DLC Supra 30	63	1,865	1,695	0.865	0.73	0.093	1.86

the maximum amount of absorbed dye  $q_m$  by the porous structure of carbon can be determined from the analysis of the linear approximation of the adsorption isotherms. Table 2 provides the values of the maximum adsorption of dyes by the investigated types of AC, as well as the data of the maximum adsorption for other types of AC from organic raw materials, which are found in the literature.

The comparison of adsorption values depending on the type of dye shows that for all studied types of AC, this indicator significantly decreases during the transition from MB to CR. High values of adsorption of the basic dye MB and much smaller values of adsorption of the acid dye CR indicate a significant effect on the adsorption of functional oxygen groups on the AC surface. These include carboxyl, carbonyl, phenolic and lactone surface groups, which are generated during the synthesis of AC [45]. The presence of two  $\text{SO}_3\text{Na}$  groups in the CR, which dissociate in water, causes the molecules of this dye to have a negative electric charge. And this leads to electrostatic repulsion from the particles of carbon material with the same electrical charge and, accordingly, a decrease in adsorption.

The difference between AC adsorption of Norit DLC Super 30 and Norit DLC Supra 30 brands of differently charged MB and CR dyes is due to the peculiarities of the porous structure of these types of carbon. It is known that the MB molecule is almost twice as short as the CR molecule. The length of the MB molecule is 1.382 nm [46] or 1.447 nm [47], and the width is approximately 0.95 nm. The CR molecule is 2.3 nm [48] or 2.6 nm [49] long. The width of the CR molecule is almost the same – 0.93 nm. If we take into account the features of the micro- and mesoporous structure of Norit carbon presented in Table 1, we can see that Norit DLC Super 30 carbon has a smaller specific surface area than Norit DLC Supra 30 carbon, but its mesopore volume is almost twice as large. This makes most of the pore space of Norit DLC Super 30 available for large molecules of the CR compared to the more microporous Norit DLC Supra 30.

If we compare the maximum adsorption indicators of Norit DLC Super 30 and Norit DLC Supra 30 with these indicators for other types of AC (Table 2), we can note that the selected industrial carbon has very good adsorption properties concerning MB, but they are a little lower

concerning CR. This means that industrial carbon Norit DLC Super 30 and Norit DLC Supra 30 can be not only efficient AC for the manufacture of supercapacitor electrodes but also an efficient adsorbent of positively charged low-molecular-weight substances from aqueous solutions.

Some data on the adsorption of MB dye on AC are contradictory and ambiguous. Güzel and Tez [50], it is stated that the maximum value of MB adsorption at 298 K in AC can be used to indicate developed microporosity. Pittman et al. [51] found that the surface area determined by the BET method from nitrogen adsorption/desorption isotherms can be compared with the results obtained from the adsorption of MB dye on carbon fibres and activated carbon materials. However, Hourieh et al. [52] came to the opposite conclusion and indicated the inaccessibility of the microporous AC structure for the MB molecule, which leads to underestimated values of the specific surface area calculated from the adsorption value.

Since the data in Table 2 indicate the efficient adsorption of MB by the AC surface of Norit DLC Super 30 and Norit DLC Supra 30, it is possible to estimate the specific surface area of the studied types of AC based on the maximum adsorption index of this dye according to the formula [53]:

$$S = \frac{\omega q_m N_A}{M} \quad (4)$$

where  $\omega$  is the area on the surface of the carbon material occupied by one MB molecule ( $\text{nm}^2$ ),  $q_m$  is the maximum amount of absorbed dye ( $\text{mg/g}$ ),  $N_A$  is Avogadro's number,  $M$  is the molar mass of MB ( $319.85 \text{ g/mol}$ ).

As we mentioned-above, the maximum amount of dye  $q_m$  absorbed by the porous structure of carbon can be determined from the analysis of the linear approximation of adsorption isotherms, but the issue of the area occupied by one MB molecule on the surface of the carbon material is also ambiguous. For example, the value of  $0.69 \text{ nm}^2$  was used by the study of Khokhlova and Hien [26], the value of  $1.06 \text{ nm}^2$  was substantiated Pahovchysin et al. [39], the area of the MB molecule was chosen to be  $1.3 \text{ nm}^2$  Bestani et al. [31], and  $1.97 \text{ nm}^2$  Pittman et al. [51]. Therefore, in various studies, areas that differ by almost three times are calculated. A value of  $1.3 \text{ nm}^2$  was chosen for the analysis of our data. This value has the most complete physical substantiation from the point of view of the adsorption process, namely the charge of the MB molecule, its orientation on the surface, as well as the Coulomb repulsion between the MB molecules are taken into account. Based on this value, the specific surface areas of AC brands Norit DLC Super 30 and Norit DLC Supra 30 were calculated. The results are shown in Table 3.

As can be seen from the data in Table 3, taking into account hydrophilicity, it is possible to estimate the value of the specific surface area of microporous carbon materials with fairly good accuracy. Of course, the deviation of the value of the calculated surface areas can be either larger or smaller. This can be attributed to the fact that the hydrophilicity was calculated from the volumetric absorption of the wetting liquid and water, as well as the different content of the total number of surface oxygen-containing groups.

Table 2  
Adsorption properties of the studied AC types

AC type	Value of the maximum adsorption $q_m$ , mg/g	
	MB	CR
BAU-A	235.3	76.9
Norit DLC Super 30	467.3	208.3
Norit DLC Supra 30	507.6	188.7
AC, Palm shell [40]	243.9	–
AC ( $\text{ZnCO}_3$ )-800, Date pits [41]	194.73	35.21
PAC (Norit) [42]	400.0	312.5
AW AC, Ashitaba waste [43]	289.25	345.17
WS AC, Walnut shell [43]	314.19	281.45
AC2, Beet pulp [44]	169.3	–

Table 3  
Results of calculations of the specific surface area of the studied AC

AC type	Norit DLC Super 30	Norit DLC Supra 30
Hydrophilicity, %	69	63
Maximum amount of absorption $q_m$ , mg/g	467.3	507.6
Surface area $S$ , calculated by Eq. (4), m <sup>2</sup> /g	896.8	974.4
Surface area $S$ , taking into account hydrophilicity, m <sup>2</sup> /g	1,594.3	1,896.8
Surface area $S$ by BET, m <sup>2</sup> /g	1,580	1,865

The last fact is particularly important because, in an aqueous solution, MB has a positive charge and three main amino groups, which must be attracted by oxygen-containing surface groups on the AC surface [39]. AC brands Norit DLC Super 30 and Norit DLC Supra 30 are manufactured according to the same technology using potassium hydroxide as an activator, so the calculated areas have a “shift” in the same direction relative to the value obtained by the BET method.

#### 4. Conclusions

Thus, the study of the porous structure of industrial AC brands Norit DLC Super 30 and Norit DLC Supra 30, produced from natural raw materials, showed its significant influence on the adsorption capacity of carbon during the adsorption of dyes. But the type of dye molecules (basic or acidic) and the size of these molecules are also important. It was determined that AC brands Norit DLC Super 30 and Norit DLC Supra 30 have very good adsorption properties concerning MB molecules, but they are a little lower concerning CR. Therefore, industrial carbon Norit DLC Super 30 and Norit DLC Supra 30 can be used as efficient adsorbents of positively charged low-molecular-weight substances from aqueous solutions.

It was established that all dye adsorption isotherms can be described within the framework of the Langmuir model. Based on the simulation results, the specific surface areas were calculated by the maximum amount of absorbed dye. The analysis of literature data made it possible to use the value of the area occupied by one MB molecule on the surface of the carbon material at 1.3 nm<sup>2</sup>. It was established that the method of determining the specific surface area of various types of carbon using the absorption of MB from aqueous solutions is quite consistent with the results obtained using the standard method of nitrogen adsorption/desorption if the hydrophilic properties of the AC surface are taken into account. This method can be used as a simple method to estimate the surface area of carbon materials.

For a deeper understanding of the processes of adsorption of differently charged dyes by carbon adsorbents, it is planned to investigate the kinetics of adsorption and the influence of the parameters of the solution – dye concentration, temperature, and hydrogen pH.

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#### References

- [1] K. Venkataraman, Ed., *The Chemistry of Synthetic Dyes*, Vol. 5, Academic Press, New York and London, 1971.
- [2] R. Singh, *Synthetic Dyes*, Mittal Publications, New Delhi, 2002.
- [3] A. Srinivasan, T. Viraraghavan, Decolorization of dye wastewaters by biosorbents: a review, *J. Environ. Manage.*, 91 (2010) 1915–1929.
- [4] C.A. Fewson, Biodegradation of xenobiotic and other persistent compounds: the causes of recalcitrance, *Trends Biotechnol.*, 6 (1998) 148–153.
- [5] K. Vikrant, B.S. Giri, N. Raza, K. Roy, K. Kim, B.N. Rai, R.S. Singh, Recent advancements in bioremediation of dye: current status and challenges, *Bioresour. Technol.*, 253 (2018) 355–367.
- [6] I.M. Banat, P. Nigam, D. Singh, R. Merchant, Microbial decolorization of textile dye containing effluents: a review, *Bioresour. Technol.*, 58 (1996) 217–227.
- [7] D.A. Giannakoudakis, A. Hosseini-Bandegharaei, P. Tsafrakidou, K.S. Triantafyllidis, M. Kornaros, I. Anastopoulos, *Aloe vera* waste biomass-based adsorbents for the removal of aquatic pollutants: a review, *J. Environ. Manage.*, 227 (2018) 354–364.
- [8] S. Mishra, A. Maiti, The efficacy of bacterial species to decolourise reactive azo, anthroquinone and triphenylmethane dyes from wastewater: a review, *Environ. Sci. Pollut. Res.*, 25 (2018) 8286–8314.
- [9] A. Kumar, H. Gupta, Activated carbon from sawdust for naphthalene removal from contaminated water, *Environ. Technol. Innovation*, 20 (2020) 101080, doi: 10.1016/j.eti.2020.101080.
- [10] S. Mishra, I. Cheng, A. Maiti, The utilization of agro-biomass/by-products for effective bio-removal of dyes from dyeing wastewater: A comprehensive review, *J. Environ. Chem. Eng.*, 9 (2021) 104901, doi: 10.1016/j.jece.2020.104901.
- [11] K. Paździar, L. Bilińska, S. Ledakowicz, A review of the existing and emerging technologies in the combination of AOPs and biological processes in industrial textile wastewater treatment, *Chem. Eng. J.*, 376 (2019) 120597, doi: 10.1016/j.cej.2018.12.057.
- [12] Ü. Geçgel, O. Üner, G. Gökara, Y. Bayrak, Adsorption of cationic dyes on activated carbon obtained from waste *Elaeagnus* stone, *Adsorpt. Sci. Technol.*, 34 (2016) 512–525.
- [13] M.T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: a review, *Adv. Colloid Interface Sci.*, 209 (2014) 172–184.
- [14] M. Malovanyy, K. Petrushka, I. Petrushka, Improvement of adsorption-ion-exchange processes for waste and mine water purification, *Chem. Chem. Technol.*, 13 (2019) 372–376.
- [15] O.S. Bello, K.A. Adegoke, A.A. Olaniyan, H. Abdulazeez, Dye adsorption using biomass wastes and natural adsorbents: overview and future prospects, *Desal. Water Treat.*, 53 (2015) 1292–1315.
- [16] I.M. Lima, A.A. Boateng, K.T. Klasson, Physicochemical and adsorptive properties of fast-pyrolysis bio-chars and their steam activated counterparts, *J. Chem. Technol.*, 85 (2010) 1515–1521.
- [17] X.-F. Tan, Y.-G. Liu, Y.-L. Gu, Y. Xu, G.-M. Zeng, X.-J. Hu, S.-B. Liu, X. Wang, S.-M. Liu, J. Li, Biochar-based nanocomposites for the decontamination of wastewater: a review, *Bioresour. Technol.*, 212 (2016) 318–333.
- [18] X.-F. Tan, S.-B. Liu, Y.-G. Liu, Y.-L. Gu, G.-M. Zeng, X.-J. Hu, X. Wang, S.-H. Liu, L.-H. Jiang, Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage, *Bioresour. Technol.*, 227 (2017) 359–372.

- [19] M. Ahmad, R.T. Bachmann, M.A. Khan, R.G.J. Edyvean, U. Farooq, M.M. Athar, Dye removal using carbonized biomass, isotherm and kinetic studies, *Desal. Water Treat.*, 53 (2015) 2289–2298.
- [20] I.I. Gerashchenko, Physicochemical aspects of therapeutic effect of enterosorbents (theoretical research), *Chem. Phys. Technol. Surf.*, 9 (2018) 373–382.
- [21] A. Krause, P. Kossyrev, M. Oljaca, S. Passerini, M. Winter, A. Balducci, Electrochemical double layer capacitor and lithium-ion capacitor based on carbon black, *J. Power Sources*, 196 (2011) 8836–8842.
- [22] P. Ratajczak, K. Jurewicz, F. Béguin, Factors contributing to ageing of high voltage carbon/carbon supercapacitors in salt aqueous electrolyte, *J. Appl. Electrochem.*, 44 (2014) 475–480.
- [23] A.G. Berezhnaya, V.V. Chernyavina, A.L. Sinyavin, Electrochemical parameters of supercapacitors on a neutral aqueous electrolyte with various electrode materials, *Russ. J. Electrochem.*, 55 (2019) 802–806.
- [24] I. Bordun, P. Chabecki, M. Malovanyy, T. Pieshkov, K. Chwastek, Changes in the electrical charge accumulation ability of nanoporous activated carbon under ultrasonic radiation exposure, *Isr. J. Chem.*, 60 (2020) 615–623.
- [25] J. Rodríguez-Romero, I. Ruiz de Larramendi, E. Goikolea, Nanostructured manganese dioxide for hybrid supercapacitor electrodes, *Batteries*, 8 (2022) 263, doi: 10.3390/batteries8120263.
- [26] T.D. Khokhlova, L.T. Hien, Adsorption of dyes on activated carbon and graphitic thermal carbon black, *Moscow Univ. Chem. Bull.*, 62 (2007) 128–131.
- [27] L.M. Soldatkina, E.V. Sagaidak, Kinetics of adsorption of water-soluble dyes on activated carbons, *J. Water Chem. Technol.*, 32 (2010) 212–217.
- [28] Z.C. Kadirova, K. Katsumata, T. Isobe, N. Matsushita, A. Nakajima, K. Okada, Adsorption and photodegradation of Methylene blue by iron oxide impregnated on granular activated carbons in an oxalate solution, *Appl. Surf. Sci.*, 284 (2013) 72–79.
- [29] S. Pohlmann, B. Lobato, T.A. Centeno, A. Balducci, The influence of pore size and surface area of activated carbons on the performance of ionic liquid based supercapacitors, *Phys. Chem. Chem. Phys.*, 15 (2013) 17287–17294.
- [30] A.P. Baranov, G.V. Shteynberg, V.S. Bagotskiy, Study of the hydrophobized active layer of a gas diffusion electrode, *Elektrokhimiya*, 7 (1971) 387–390.
- [31] B. Bestani, N. Benderdouche, B. Bestaali, M. Belhakem, A. Addou, Methylene blue and iodine adsorption onto an activated desert plant, *Bioresour. Technol.*, 99 (2008) 8441–8444.
- [32] O. Paşka, R. Ianoş, C. Păcurariu, A. Brădeanu, Magnetic nanopowder as effective adsorbent for the removal of Congo red from aqueous solution, *Water Sci. Technol.*, 69 (2013) 1234–1240.
- [33] F. Raposo, M.A. de La Rubia, R. Borja, Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: influence of adsorbate/adsorbent mass ratio and particle size, *J. Hazard. Mater.*, 165 (2009) 291–299.
- [34] S. Mitra, M. Muttakin, K. Thu, B.B. Saha, Study on the influence of adsorbent particle size and heat exchanger aspect ratio on dynamic adsorption characteristics, *Appl. Therm. Eng.*, 133 (2018) 764–773.
- [35] Y. Matsui, S. Nakao, A. Sakamoto, T. Taniguchi, L. Pan, T. Matsushita, N. Shirasaki, Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol vary with activated carbon particle size: effects of adsorbent and adsorbate characteristics, *Water Res.*, 85 (2015) 95–102.
- [36] N. Saeidi, M.N. Lotfollahi, Effects of powder activated carbon particle size on adsorption capacity and mechanical properties of the semi activated carbon fiber, *Fibers Polym.*, 16 (2015) 543–549.
- [37] M. Thommes, K. Kaneko, A. Neimark, J. Rodríguez-Reinoso, J. Rouquerol, K. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.*, 87 (2015) 1051–1069.
- [38] J. Rouquerol, F. Rouquerol, P. Llewellyn, G. Maurin, K. Sing, *Adsorption by Powders and Porous Solids: Principles, Methodology and Applications*, Elsevier/Academic Press, Oxford, 2014.
- [39] S.V. Pahovchyslin, I.G. Chernych, V.F. Gritsenko, Some restrictions on the use of the indicator method in studying the surface of graphite particles, *Colloid J. USSR*, 3 (1991) 245–249.
- [40] K.Y. Foo, B.H. Hameed, An overview of dye removal via activated carbon adsorption process, *Desal. Water Treat.*, 19 (2010) 255–274.
- [41] N. Bouchemal, F. Addoun, Adsorption of dyes from aqueous solution onto activated carbons prepared from date pits: the effect of adsorbents pore size distribution, *Desal. Water Treat.*, 7 (2009) 242–250.
- [42] M. Szlachta, P. Wojtowicz, Adsorption of Methylene blue and Congo red from aqueous solution by activated carbon and carbon nanotubes, *Water Sci. Technol.*, 68 (2013) 2240–2248.
- [43] Z. Li, H. Hanafy, L. Zhang, L. Sellaoui, M.S. Netto, M.L.S. Oliveira, M.K. Seliem, G.L. Dotto, A. Bonilla-Petriciolet, Q. Li, Adsorption of Congo red and Methylene blue dyes on an Ashitaba waste and a walnut shell-based activated carbon from aqueous solutions: Experiments, characterization and physical interpretations, *Chem. Eng. J.*, 388 (2020) 124263, doi: 10.1016/j.cej.2020.124263.
- [44] Ch. Soloviy, M. Malovanyy, I. Bordun, F. Ivashchyslyn, A. Borysiuk, Yu. Kulyk, Structural, magnetic and adsorption characteristics of magnetically susceptible carbon sorbents based on natural raw materials, *J. Water Land Dev.*, 47 (2020) 160–168.
- [45] V. Jr. Strelko, D. Malik, M. Streat, Characterisation of the surface of oxidised carbon adsorbents, *Carbon*, 40 (2002) 95–104.
- [46] M.J. de Souza, N.B. da Costa Júnior, L.E. Almeida, E.F. da Silva Vieira, A.R. Cestari, I. de Fátima Gimenez, N.L. Villarreal Carreno, L.S. Barreto, Kinetic and calorimetric study of the adsorption of dyes on mesoporous activated carbon prepared from coconut coir dust, *J. Colloid Interface Sci.*, 298 (2006) 515–522.
- [47] G.L. Dotto, J.M.N. Santos, I.L. Rodrigues, R. Rosa, F.A. Pavan, E.C. Lima, Adsorption of Methylene blue by ultrasonic surface modified chitin, *J. Colloid Interface Sci.*, 446 (2015) 133–140.
- [48] Q. Wu, H. Liang, M. Li, Hierarchically porous carbon membranes derived from PAN and their selective adsorption of organic dyes, *Chin. J. Polym. Sci.*, 34 (2016) 23–33.
- [49] R.W. Dapson, Amyloid from a histochemical perspective. A review of the structure, properties and types of amyloid, and a proposed staining mechanism for Congo red staining, *Biotech. Histochem.*, 93 (2018) 1–14.
- [50] F. Güzel, Z. Tez, The characterization of the micropore structures of some activated carbons of plant origin by N<sub>2</sub> and CO<sub>2</sub> adsorptions, *Sep. Sci. Technol.*, 28 (1993) 1609–1627.
- [51] C.Ú. Pittman Jr., G.-R. He, B. Wu, S.D. Gardner, Chemical modification of carbon fiber surfaces by nitric acid oxidation followed by reaction with tetraethylenepentamine, *Carbon*, 35 (1997) 317–331.
- [52] M.A. Hourieh, M.N. Alaya, A.M. Youssef, Carbon dioxide adsorption and decolourizing power of activated carbons prepared from Pistacia shells, *Adsorpt. Sci. Technol.*, 15 (1997) 419–427.
- [53] S. Lowell, J.E. Shields, *Powder Surface Area and Porosity*, Chapman & Hall, London, 1998.