Perspectives for use of technological waste to obtain carbon-mineral sorbents

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Abstract. Carbon-mineral materials were obtained by mixing of clay mineral (montmorillonite) with aqueous solutions of cationic dye "methylene blue" and anionic dye "direct clean-blue" (a component of wastewater of dyeing enterprises) and subsequent drying and carbonization in an atmosphere of water vapor. It is shown that the specific surface area of the synthesized carbon materials depends on the nature of the modifying organic compound, its content in the sample and the influence of ultrasound. It is found that the preliminary activation of the initial clay increases the surface area, but does not have a significant effect on the adsorption of phenol, compared with materials obtained without activation. Hydrophobic surface properties of materials are confirmed by the results of studies on the adsorption of phenol from aqueous solutions. Adsorption capacity of obtained carbon-mineral materials with respect to phenol is 4-8.5 mg \cdot g^{-1}, which is 15-30 times higher than that of the original clay. Synthesized sorbents are comparable to the adsorption capacity with respect to phenol with carbon material obtained by direct pyrolysis.

1. Introduction

Currently, much attention is attracted to research on the development of carbon-mineral materials (CMM), which can serve as an alternative to expensive carbon sorbents – activated carbons. Activated carbons are characterized by a high specific surface area (more than 1000 m^2 \cdot g^{-1}) and are used in the purification of gas and liquid media from various pollutants, but have low mechanical strength [1]. In the development of carbon-mineral materials, preference is given to resource saving and energy saving methods, allowing them to be synthesized from cheap natural raw materials at low temperatures. These may include materials obtained by carbonization of bottom sediments [2-5], waste from the processing of plant raw materials (shells, oil cakes, etc.), as well as technological waste sewage water treatment from organic pollutants using natural and synthetic porous matrices. Spherical aluminum oxides support of the Al_2O_3 type are most often used as a synthetic matrix [6], but the great disadvantage of such sorbents is their high cost, which makes it economically unprofitable to use them in the treatment of industrial wastewater. The use of natural matrices such as zeolites, clay minerals leads to a significant reduction in the cost of production of carbon-mineral materials. The obtained carbon-mineral sorbents combine the hydrophilic and hydrophobic properties of mineral and coal sorbents, as a result of which they can exhibit high adsorption properties with respect to both inorganic and organic substances that cannot be sorbed on the surface of the original mineral matrix. In work [7], palygorskite-montmorillonite clay from the Cherkassy deposit was used as a sorbent, which was
used to purify aromatic concentrates from unsaturated hydrocarbons. In another work, the authors also used palygorskite as a mineral base sorbent for the production of carbon-mineral sorbent, while plant waste (tomato squeeze and bran) followed by carbonization at 500-850 °C was used as a modifier [8]. The obtained materials were used in the adsorption of tannin from its model solutions and in the purification of wine materials. It is shown that the sorption properties of the materials used to clean the syrups from dyes in the sugar industry are close to the properties activated carbon AGS-4, although the organic content in carbon-mineral materials is only 14.5-20.5%. At the same time, the authors work [9-11] have obtained a carbon-containing material able to adsorb large organic anions of dyes using sucrose. It is established that glucose and sucrose, penetrating into the interlayer space of the clay mineral, form the so-called organoclays. Subsequent calcination transform organic matter into coke, which fills the interlayer space. Clay is a good cation exchanger due to excess negative charge on the surface of montmorillonite, which arises due to isomorphic substitution [12,13]. Due to the fact that the organic cations are included into the interlayer space of the clay particles, it is difficult to recover them after carrying out the processes of adsorption. Clay minerals that were used in wastewater treatment from cationic dyes can be used to obtain carbon-mineral sorbents, which can be re-used in water purification technologies. However, this problem requires a more detailed study [14].

The purpose of this work is the synthesis of carbon-mineral materials based on a clay mineral montmorillonite and organic substances (dyes), as well as the study of their adsorption properties with respect to phenol.

2. Experimental
Bentonite clay containing more than 80% montmorillonite (MM) the chemical composition of which was described in work [15] served as the starting material for the synthesis of carbon mineral materials (CMM). Synthesis of carbon-containing materials were carried out using a cationic dye - “Methylene Blue” (MB) and anionic type “Direct Pure Blue” dye (DCB) in two ways. Formula dyes are presented in Table 1.

| Organic dye               | The structural formula of dye | Molecular weight (g·mol⁻¹) |
|---------------------------|--------------------------------|---------------------------|
| Methylene blue            | ![Methylene Blue structure](image) | 320                       |
| Direct clean-blue         | ![Direct Clean-blue structure](image) | 992                       |

2.1. Preparation of carbon-mineral materials
The first method of obtaining CMM is as follows: to 3 g of clay added 24 ml of water for obtaining 10% aqueous suspension of bentonite clay then to the resulting clay suspension added 30 ml solution of the dye (10%), after which the mixture was shaken for 4 hours at a stirring speed of 170 rpm, 25 °C. Next, the aqueous suspension of clay and dye was left to stand at room temperature until complete evaporation of water. In contrast to the first method, when preparing CMM by method II the suspension of bentonite clay was previously (before mixing with dye solutions) treated with ultrasonic vibrations at a frequency of 22 kHz for 3 min to better disperse the clay particles, which can contribute to greater penetration dye molecules in the interlayer space of clays. The subsequent stages were performed as in method I. Next, the dried samples of the organoclay were treated in an
atmosphere of water vapor at 500 °C for 30 min to form a carbon-containing coat on the surface of
the mineral matrix. The materials obtained by method I were named as C(MB)-MM-I, C(DCB)-MM-I,
and by method II were named as C(MB)-MM-II, C(DCB)-MM-II (table 2).

2.2. Methods
The specific surface area \( S_{sb} \) of the materials was determined by the method of low-temperature
nitrogen adsorption/desorption on a TermoSorb LP unit (Katakon, Novosibirsk, Russia). The values of
the specific surface of the materials are presented in the table 2.

Electron microscopic images were taken with an NEOSCOPE II JCM-6000 electron scanning
microscope (JEOL Company, Japan) in the Scientific Instruments Collective Medical Center of the
Buryat State University.

The adsorption properties of the obtained carbon-mineral materials were studied by the limited
volume method with an initial phenol concentration of 47.1 mg \( \text{l}^{-1} \); sorbent loading 5.0 g \( \text{l}^{-1} \); temperature 25 °C . Loading of the materials was added into an aqueous solution of phenol and
suspension was mixed on the device LAB-PU-01 (LOIP, St. Petersburg, Russia). After 24 and 48
hours, a sample was taken, the liquid phase was separated from the sorbent by centrifugation and
analyzed for phenol content. The residual concentration of phenol in the solution was determined by a
colorimetric method by reaction with 4-aminoantipyrine [16]. The amount of phenol adsorbed on
carbon-mineral materials \( q_t \) \( \text{mg g}^{-1} \) was calculated by the formula:

\[
q_t = \frac{(C_o - C_t) \cdot V}{m}
\]

where \( C_o \) is the initial concentration of phenol in solution, \( \text{mg g}^{-1} \); \( C_t \) is the concentration of phenol
in solution at the moment of time \( t \), \( \text{mg g}^{-1} \); \( V \) is the volume of phenol solution, l; \( m \) is the weight
adsorbent, g.

3. Results and discussion

3.1. Characteristics of sorbents
The synthesis conditions and the values of specific surface of carbon-containing materials obtained
using MB and DCB dyes are given in table 2.

| Organic dyes | Method     | \( S_{sb} \) (m²·g⁻¹) |
|--------------|------------|-----------------------|
| C(MB)-MM-I   | I          | 5.8                   |
| C(MB)-MM-II  | II         | 6.3                   |
| C(DCB)-MM-I  | I          | 9.3                   |
| C(DCB)-MM-II | II         | 11.7                  |

\( S_{sb} \) – specific surface area of sorbents, m²·g⁻¹

In figures 1 and 2 are presented photos and SEM images of the original clay and sample C(DCB)-
MM-II. It can be seen that, unlike the image of natural clay, the sample is characterized by black color,
which is caused by the formation of carbon on the surface of clay particles (figure 1). This is also
confirmed by SEM images in which carbon is represented by flaky inclusions (figure 2).
Heat treatment of organoclay “MM-dye” in the atmosphere of water vapor leads to the formation of carbon-containing materials with rather low specific surfaces, which are 5.8 - 11.7 $m^2 \cdot g^{-1}$ depending on the synthesis conditions, compared to the original clay with a surface area of 83 $m^2 \cdot g^{-1}$. This is because in the process of heat treatment, carbonization of the organic mass is occurred, as a result of which the formed carbon covers the entire surface of the mineral matrix and materials with a lower porosity compared to the original MM are formed. The specific surface of the obtained materials depends not only on the chemical nature of the modifier used, but also on the size of the dye molecules ($M_{MB} = 320 \ g \cdot mol^{-1}$ and $M_{DCB} = 992 \ g \cdot mol^{-1}$).

At the initial stage of obtaining samples of C(MB)-MM-I dye adsorption occurs. Methylene blue, being a cationic dye, is sorbed not only on the basal surface of montmorillonite particles having an excess negative charge, but also in its interlayer gaps, forming a monolayer or multilayer coating. The MB molecule, having a more compact structure with a molecular area of 1.35 nm² [17], forms a denser packing of the adsorption layer, and during carbonization, a less porous carbon layer ($S_{cb} \approx 5.8 \ m^2 \cdot g^{-1}$) is formed. The effect of ultrasound on the suspension of clay (method II) leads to dispersion of clay particles up to elementary packages, which contributes to a greater adsorption of the dye on the basal surfaces of MM particles. Its further heat treatment leads to the formation of a carbon-mineral material with a surface area of 6.3 $m^2 \cdot g^{-1}$ (table 2).

During the synthesis of materials C(DCB)/MM-I and C(DCB)/MM-II, the DCB anionic dye is sorbed on the OH groups of the montmorillonite octahedral network, which are located on the lateral surfaces of the clay particles. The molecule of this dye has a flatter and branched structure (table 1), as
a result of which the slit-like pores of MM remain unoccupied by dye molecules. This results in a CMM with a higher specific surface area than when using the MB dye. The difference in the values of the specific surface of the samples obtained by the first and second method using the DCB dye is due to the same reasons as when CMM were obtained by using the MB dye.

3.2. Adsorption properties of sorbents

To study the hydrophobic properties of the obtained carbon-mineral materials, we carried out test adsorption studies in aqueous solutions with respect to phenols. Phenols are found in wastewater associated with the thermal processing of wood, shale, peat, brown and black coal; in wastewater from refineries, plastic factories, artificial resins, forest chemical plants, organic dye plants, chipboard, processing plants of non-ferrous metallurgy, etc. It is known that phenols are characterized by high toxicity and low biodegradability [18-19].

Figure 3 presents the results of studies on the adsorption of phenol. The amount of sorbed phenol on the initial clay for 48 hours of sorption is only 0.29 mg·g⁻¹, which is due to the hydrophilic nature of the surface of montmorillonite. Phenol adsorption is on carbon mineral sorbents 15-30 times higher (4.32-8.49 mg·g⁻¹), due to the fact that, a large amount of carbon is formed on the surface of clay particles as a result of heat treatment of organoclays. This increases the sorption of phenol due to the interaction of the benzene ring of phenol with the hydrophobic carbon surface of sorbent particles. The results of phenol adsorption on carbon-mineral materials show that their sorption properties depend on the nature of the organic dye and the method of obtaining of materials. When comparing materials C(MB)/MM-I and C(DCB)/MM-I, obtained by the first method, but differing in the nature of dyes, sample C(DCB)/MM-I having a specific surface of 9.3 m²·g⁻¹ has a higher sorption capacity (7.26 mg·g⁻¹), while the sorption capacity of sample C(MB)/MM-I with a surface area of 5.8 m²·g⁻¹ is 4.32 mg·g⁻¹. A similar dependence is observed for carbon-mineral materials obtained by the second method: C(MB)/MM-II, C(DCB)/MM-II (with a specific surface area of 6.3 and 11.7 m²·g⁻¹) have adsorption capacity 4.49 mg·g⁻¹ and 8.49 mg·g⁻¹, respectively. It is seen that the preliminary dispersion of clay particles upon the synthesis of materials increases the specific surface and, accordingly, the sorption capacity of materials with respect to phenol. The obtained carbon-mineral materials by their phenol adsorption capacity are superior to carbon-mineral sorbents obtained by direct pyrolysis of bleaching lands, the adsorption capacity of which is 3 mg of phenol per gram of sorbent [19]. They also exceed carbon materials obtained by pyrolysis of rice husks, the adsorption capacity of which according to phenol is 3.87 mg·g⁻¹, while their specific surface area is 344.7 m²·g⁻¹ [20].

Figure 3. The values of the adsorption capacity of sorbents with respect phenol.
4. Conclusion

Carbon-mineral materials were obtained by mixing of the clay mineral (montmorillonite) with aqueous solutions of cationic dye "Methylene Blue" and anionic dye "Direct Clean-Blue" (a component of wastewater of dying enterprises) and subsequent drying and carbonization in an atmosphere of water vapor. The specific surface area and their sorption capacity with respect to phenol depends on the nature of the modifier (dyes) and the method of producing of materials. Among carbon mineral materials, sample C(DCB)/MM-II has the highest sorption capacity with respect to phenol, during the synthesis of which the Direct Pure Blue dye was used as the organic modifier and the initial clay was activated by ultrasonic vibrations.

References

[1] Balasubramani K and Sivarajasekar N 2014 Int J Innov Res Sci Eng Techn 3 10575–81
[2] Skubiszewska-Zieba J, Leboda R, Charmas B and Gun’ko V M 2012 Microporous and Mesoporous Mater 156 209–16
[3] Zhang J, Sequaris J M, Narres H D, Vereecken H and Klumpp E 2010 Chemosphere 80 1321–7
[4] Adeeva L N and Kovalenko T A 2012 Russ J Appl Chem 85 557–63
[5] Terekhova E N, Lavrenov A V, Shilova A V, Kireeva T V, Saveleva G G, Trenikhin M V and Bel’skaia O B 2017 Russ J Appl Chem 90 1663–70
[6] Leboda R and Dabrowski A 1996 Stud Surf Sci Catal eds A Dabrowski and V A Tertykh, vol 99 (Amsterdam: Elsevier) p 115
[7] Tarasevich Yu I and Rudenko V 1989 J Water Chemistry and Technology 11 568–9
[8] Dunets R V, Khrustuk R V and Dunets E G 2008 New Technologies 5 23–7
[9] Tarasevich Yu I, Doroshenko V E, Rudenko V M and Ivanova Z G 1988 J Water Chemistry and Technology 10 315–7
[10] Leboda R, Chodorowski S, Skubiszewska-Zieba J and Tarasevich Yu I 2001 Colloids Surf A 178 113–28
[11] Leboda R, Charmas B, Chodorowski S, Skubiszewska-Zieba J and Gun’ko V M 2006 Microporous and Mesoporous Mater 87 207–16
[12] Aripov E A and Agzamkhodzhaev A A 1983 Active Centers of Montmorillonite and Chemisorption (Tashkent: FAN) p 164
[13] Khankhasaeva S Ts, Dashinamzhilova E Ts, Bardamova A L and Ayurova O Zh 2019 Russ J Appl Chem 92 282–7
[14] Tarasevich Yu I 1988 Structure and Chemistry of the Surface of Layered Silicates (Kiev: Naukova Dumka) p 248
[15] Khankhasaeva S Ts, Dashinamzhilova E Ts, Badmaeva S V and Bardamova A L 2018 Colloid J 80 454–9
[16] Gomez J L, Bodalo A, Gomez E Bastida J, Hidalgo A M and Gomez M 2006 Enzyme Microb Technol 39 1016–22
[17] Chulkov A I, Denneka V N and Denneka L A 2011 Scientific statements: Natural Sciences Series 16 88–92
[18] Toxicological profile for phenol 2008 (Atlanta: Division of Toxicology and Environmental Medicine/Applied Toxicology Branch) p 269
[19] Leboda R, Skubiszewska-Zieba J, Charmas B, Chodorowski S and Pokrovskiy V A 2003 J Colloid Interface Sci 259 1–12
[20] Kennedy J L, Vijaya J J, Kayalvizhi K and Sekaran G 2007 Chem Eng J 132 279–87

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