Extraction of methylene blue coloring agent from model solutions with a plant-origin sorbent

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Abstract. The production output of dyes and pigments in chemical industry is constantly increasing. Sewage waters, which contain synthetic and organic coloring agents, produce toxic effect, which is preconditioned by their low MAC values - below 0.001 mg/dm². The most promising method of the pigmented wastewater treatment, which allows reducing the pollutants' content to the regulated permissible amount, is the adsorption method. This work presents research findings concerning sorption purification of test water media, containing methylene blue coloring agent, by using crop farming waste – chopped sunflower (Heliánthus ánnus) stalks – as a sorption material. It has been determined that the maximum sorption capacity of chopped sunflower stalks biomass for this coloring agent is 0.245 mmol/dm². The processing of the received data has demonstrated that the obtained adsorption isotherm of methylene blue belongs to Type V isotherms according to classification by Brunauer-Deming-Deming-Teller (BDDT) or to the S-type, according to Giles’ classification. This adsorption process is the most accurately described by the Brunauer–Emmett–Teller model (BET), based on the concept of multilayer adsorption.

1. Introduction

At present the problem of fresh water pollution and depletion is rather acute all over the world. Water for drinking and for industrial use becomes less and less available in some countries or regions. Industrial enterprises discharge their sewage waters to rivers, lakes and water reservoirs [1]. The production volumes of dyes in chemical industry are constantly growing and amount to 7 mln tons per year [2]. The most widely spread are synthetic and organic dyes. The hazard of such wastewaters is conditioned by the high toxicity of dyes, as their maximum allowable concentration is less than 0.001 mg/dm² [3]. The coloring agents can also cause various allergic reactions, irritation of skin and mucous membranes, and produce other ecological risks both for aquatic organisms, and for people [4]. Due to this, the development of efficient and environmentally friendly methods of wastewater purification from synthetic and organic coloring agents is a topical problem.

There are many various methods of purifying wastewaters from dyes [5], namely:

- oxidation-reduction methods: treatment with oxidizing agents, electrochemical or electrocatalytic effects [6, 7, 8].
- physical-chemical methods: coagulation, flotation and electro-coagulation [9], reverse osmosis, ultrafiltration [10], and sorption by means of activated carbons or other sorption materials [11].

The colleagues from Moscow State University of Civil Engineering have carried out experimental research in ozone treatment of sewage waters, containing coloring agents. A generalized methodology of determining ozone consumption for oxidation of pollutants in wastewaters and a technological
parameter "chemical ozone demand" were suggested. The method is rather universal and by means of

test ozone treatment of water it allows receiving the relation of ozone consumption for pollutants’
decomposition processes and determining the required specific dose of ozone [12].

Center for Environmental Risk Assessment and Remediation, South Australia University, has
developed a method of textile industry sewage waters purification from dyes by means of
heterogenous photocatalysis with titanium dioxide ($\text{TiO}_2$) [13]. This technology looks rather
promising, but it is costly and complicated.

Among all the methods, used nowadays for wastewater treatment, adsorption process shows the
most promising results. Besides, the adsorption processes can be implemented by using both natural
materials as sorbents, as the most available and environmentally friendly, and industrial or agricultural
production waste, as the most low-cost raw stuff.

 Earlier the model laboratory studies of three low-cost adsorbents for removing methylene blue
coloring agent from sewage waters were studied: banana fiber, coconut fiber and sawdust. From the
findings of the research we can make a conclusion, that the coconut fiber has shown the highest
sorption capacity in comparison with other adsorbents and can be efficiently used for removing
complex dyes, contained in sewage waters in large amounts [14].

A method has been also developed for purifying sewage waters from dyes by using natural water
chemical conditioning sludge of hydraulic engineering installations. The findings have shown high
efficiency of using water-treatment sludge, containing ferrous chloride and alum, in purifying sewage
waters from coloring agents at textile plants [15].

The tea production waste as an adsorbent for ionic dyes was also studied. It was demonstrated that
the tea waste is a potentially cheap and effective adsorption material for textile industry sewage waters
purification [16].

Besides, agricultural waste products often cause the problem of their disposal. So, their usage as an
adsorption material is not only economically promising, but also environmentally sound [17, 18, 19].

In a number of works the crop farming waste is considered as an available and low-cost raw stuff
for obtaining carbonic or carbon-containing sorption materials [20,21], which are similar to activated
carbon in their physical-chemical properties [22], but can absorb large organic molecules [23].

The authors of this paper have chosen such crop farming waste as stalks of common sunflower
($\text{Helianthus ánnuus}$) for sorption purification of wastewaters from coloring agents. This plant is
cultivated all over the world. Sunflower seeds are used for producing sunflower oil, which is widely
used in cooking or in industrial processes. In spite of the seemingly wide application possibilities of all
parts of sunflower, in many regions of Russia the stalks of this plant find no usage after gathering
seeds.

The earlier research by the authors has demonstrated the possibility of using chopped sunflower
stalks as a sorption material for removing methylene blue (MB) coloring agent from water media [24].
The purification efficiency of test solutions with the initial concentration of methylene blue 50 mg/
dm$^2$ amounted to 92%.

The purpose of this work is to determine the sorption characteristics and thermodynamic
parameters of methylene blue adsorption process by using crop farming waste – the chopped
sunflower (Helianthus ánnuus) stalks – as a sorption material.

2. Materials and methods

As an adsorption material under research the chopped sunflower stalks (CSS) were used, photomicrographs of which are presented in Fig. 1.
The findings of the research, presented in Fig. 1, indicate the complicated structure of sunflower stalks – spongy with many cracks and cavities, having pores of various sizes, which allows assuming the possibility of using them as an adsorption material.

As test water media the methylene blue solutions were used with concentrations, g/dm$^2$: 2.5; 2.0; 1.5; 1.0; 0.5; 0.1; 0.05; 0.01.

Adsorption processes were studied in static conditions by alternating concentrations method.

The initial and final concentrations of MB coloring agent were determined by spectrophotometric method with spectrophotometer KFK–2 ($\lambda = 670$ nm) with reference to distilled water.

To determine the adsorption amount ($A$, mmol/g) the weighed quantity of adsorbent was added to a 250 ml flask with the test solution. The solid-liquid ratio was 1:100 by weight. The flasks with their content were periodically shaken within 24 hours till equilibration. Then the liquid was separated by centrifugation and the MB amount was evaluated.

The amount of substance, mmol/g, absorbed with the solid phase, was calculated by the formula:

$$A = \frac{(C_i - C_f)V}{m}$$  \hspace{1cm} (1)

where $C_i$ – initial concentration of MB, mmol/dm$^2$; $C_f$ – final concentration of MB after equilibration, mmol/dm$^2$; $V$ – volume of solution, dm$^2$; $m$ – the weighed quantity of adsorption material, g.

To determine the adsorption process mechanism, the obtained isotherm was processed by means of Langmuir, Freundlich, and Brunauer–Emmett–Teller (BET) adsorption models.

3. Results

According to the obtained values of static sorption capacity ($A$, mmol/g) of the material under study at various equilibrium concentrations of MB, an adsorption isotherm was built (Fig. 2).
The maximum sorption capacity of CSS biomass is 0.245 mmol/dm$^2$ for methylene blue coloring agent. The adsorption isotherm belongs to Type V isotherms according to classification by Brunauer-Deming-Deming-Teller (BDDT) or to the S-type, according to Giles’ classification.

As it is known, this type of isotherms is characteristic for porous sorbents with low adsorbent-adsorbate interaction energy. The S-type model indicates that if the interaction force between adsorbed molecules is higher than the interaction force between the dissolved matter and solid matter, the activation energy is increased.

To determine the adsorption process mechanism, the obtained isotherm was processed by means of Langmuir (Fig.2), Freundlich (Fig.3) and BET (Fig.4) adsorption models. In Tab. 1 regression equations and approximation coefficients’ values for various adsorption models are presented.

**Figure 2.** Adsorption isotherm (T=20 °C) of MB on the surface of CSS.

**Figure 3.** Langmuir sorption isotherm of MB on the surface of CSS.
Figure 4. Freundlich sorption isotherm of MB on the surface of CSS.

Fig 5. BET sorption isotherm of MB on the surface of CSS.
Table 1. Regression equations and correlation and approximation coefficients ($R^2$) of MB adsorption models with the CSS biomass.

| Model | Regression equation | Approximation coefficient $R^2$ | Correlation coefficient |
|-------|---------------------|-------------------------------|------------------------|
| Langmuir | $y = 4.6891x – 71.84$ | 0.7640 | 0.8740 |
| Freundlich | $y = 1.704x + 1.2427$ | 0.8479 | 0.9208 |
| BET | $y = 775.79x – 36.793$ | 0.9059 | 0.9517 |

The findings, presented in Tab. 1, have demonstrated that the adsorption of methylene blue with the CSS biomass is the most accurately described by the Brunauer–Emmett–Teller model (BET), based on the concept of multilayer adsorption.

4. Summary

So, the crop farming waste – chopped sunflower stalks – possess adsorption properties and are promising materials for purifying wastewaters from coloring agents.

The mechanism and nature of water media purification from MB coloring agent with the researched crop-farming waste have been determined. It was revealed that the adsorbent has low interaction energy with the adsorbate, and the interaction force between adsorbed molecules is higher than the interaction force between dissolved matter and solid matter.

The process of methylene blue adsorption with the CSS biomass is the most accurately described by the Brunauer–Emmett–Teller model (BET), based on the concept of multilayer adsorption.

5. References

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