Structure, physicochemical properties, and adsorption performance of the ethyl cellulose/bentonite composite films

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Abstract Ethyl cellulose (EC) was filled with bentonite (Bent) particles by mechanical dispersion to produce composite film materials that were studied using various methods. According to X-ray diffraction (XRD) analysis, the inter-chain separation length was larger in EC/Bent composite then those in pure polymer. Infrared spectrometry indicated a formation of hydrogen bonds between the hydroxyl groups of EC and the silanol groups of clay. Tests showed an increase in tensile strength of the polymer material (by 35–40%) when doped with bentonite. It was found that modification of polymer with bentonite resulted in increasing of the adsorption efficiency of methylene blue (MB): the equilibrium concentration of MB ions in adsorbent phase increased 2.5 times. The MB adsorption kinetics obeyed the pseudo-first-order mechanism. Isotherms were in good agreement with Langmuir model. For the composite, the maximum monolayer adsorption capacity was 4 times higher than that for pure polymer.

Keywords Ethyl cellulose · Bentonite · Composite film · Structure and surface morphology · Tensile strength · Adsorption · Methylene blue

Introduction

A current trend in the field of chemistry of high-molecular compounds, related to the preparation and investigation of hybrid polymeric materials, has received intensive development. These composites can be used in medicine, biology, and different branches of industry as adsorbents, membranes, and media for targeted drug delivery (Alboofetileh et al. 2013; Alekseeva et al. 2018; Irfan et al. 2019; Lavorgna et al. 2014; Pawlicka et al. 2018; Rabbi et al. 2019).

The use of biodegradable natural polymers modified with inorganic fillers is relevant for this purpose. Among natural polymers, special attention is paid to polysaccharides as a renewable source of raw materials. One of these polymers is ethyl cellulose, a linear polysaccharide from the semi-synthetic cellulose derivative family. This is an inert, water-insoluble, hydrophobic polymer which has relatively low cost (Crabbe-Mann et al. 2018). Ethyl cellulose has excellent biocompatibility and biodegradability which makes it a suitable candidate for widespread application in the food, as adjunct in packaging materials for food storage also cosmetic, and biomedical and pharmaceutical technology (Do et al. 2010; Ni et al. 2009; Parida et al. 2016).

The introduction of inorganic particles into the polymer matrix leads to a significant increase in the mechanical properties of the composites, a change in
the barrier properties, and an increase in the biodegradability (Boesel 2015; Suvorova et al. 2013).

Bentonite type layered silicate clays, due to their high specific surface area and cation-exchange ability, low cost and non-toxicity are often used as fillers for cellulose ethers during the preparation of polymer composites. The literature provides information on the structure and properties of composites based on polysaccharides modified with silicates (Alekseeva et al. 2017a, b, 2019b; Delhom et al. 2010; Lavorgna et al. 2014). Special attention is paid in the publications to the practical application of such composites as biodegradable packaging materials, materials for tissue engineering. Such nanocomposite materials are of interest as membranes, catalysts and adsorbents for organic compounds operating in aqueous and organic liquid media (Anirudhan et al. 2019; Wang et al. 2019; Zhou et al. 2012).

An analysis of the literature indicates the widespread use of thiazine dyes, such as methylene blue, for dyeing cotton fabrics, wool, and paper (Khan et al. 2012). In addition, there is a surge of interest in MB as an antimalarial agent, in antimicrobial therapy, as a potential treatment for neurodegenerative diseases (e.g., Alzheimer’s disease) and Covid-19 (the latter is especially important) (Schirmer et al. 2011; Kayabaş and Erbaş 2020; Scigliano and Scigliano 2021; Fegenträger et al. 2013).

But synthetic organic dyes present certain hazards and environmental problems. The discharge of these dyes into water may be toxic to aquatic organisms. They cause health problems because they can be mutagenic and carcinogenic. Until now, various technologies were practiced for removal of dyes (including methylene blue) from water; however, adsorptive removal is promising in term of efficiency and low operation cost compared with others (Deng et al. 2012; Tong et al. 2018).

According to You et al. (2021), the concentration of dye in wastewater is generally between 10 and 200 mg/L (that is, approximately 0.03–0.6 mmol/L). And, as the analysis of publications showed, most of the studies of MB adsorption were carried out for solutions with such initial concentrations of the dye (Hassanpour et al. 2019; Luo et al. 2011). However, in pharmacological and biomedical practice, MB solutions in the low μmol/L range are widely used, too (Schirmer et al. 2011; Chang et al. 2009). Therefore, studies of MB adsorption from solutions with a low dye concentration (for example, 2–7 μmol/L as in the current work) are topical.

It is known that cellulose and compounds based on it are capable of removing organic substances and dyes from various media (Pan et al. 2018). Note that usually, when studying the adsorption of dyes, the authors use 3D materials as adsorbents (powders, granules, gels, etc.). Such adsorbents exhibit high adsorption capacity. However, the reuse of spent adsorbent has become a complicated problem. The regeneration process of adsorbent is easier to carry out for adsorbents in the film form. Therefore, the study of dye adsorption using film adsorbents is important despite their slight adsorption performance. The aforementioned ethyl cellulose is a good film-forming polymer and can be used as a matrix for creating film composites in order to evaluate their adsorption performance. It is also necessary to mention recent publications (for example, Salahuddin et al. 2021), in which the authors reported that after adsorption, the resulting cellulose/MB composites may have antimicrobial activity and cytotoxicity. Therefore, cellulose and its derivatives can be considered as the carriers for MB, a model of biomedical drug.

In this regard, the goal of present study is to prepare the ethyl cellulose/bentonite composite films and to research their structure, morphology, mechanical properties, and adsorption action with respect to methylene blue. Special attention is paid to the mathematical processing of experimental data on MB adsorption using a number of kinetics and adsorption equilibrium models. In our study, we consider MB as a model compound for evaluating the adsorption performance of both EC and EC/Bent composite with respect to organic compounds, including drugs.

Materials and methods

Materials

Bentonite (Sigma Aldrich, US) and ethyl cellulose ([C₆H₇O₂(OH)₃-x(OC₂H₅)x]n, Hercules, US) with content of ethyl groups of 48%, substitution degree of 2.8, and viscosity of 7 cP were used to prepare polymer/clay composites. The main constituents of bentonite were as follows: SiO₂ (65.9%), Al₂O₃ (21.5%),
Fe$_2$O$_3$ (4.5%), Na$_2$O (2.7%), and CaO (1.6%). Toluene was purchased from Fisher Scientific (UK) and used as a solvent. Thiazine dye, methylene blue (Spain) was used to study adsorption activity of the EC films and composites.

Preparation of the EC/Bent composite films

The mechanical dispersion technique was used to produce the polymer/clay composites of ethyl cellulose and bentonite. Solutions of ethyl cellulose and bentonite in toluene were prepared at different weight ratios of polymer and clay. For this, the bentonite particles were dispersed in toluene, and 5% EC solution was added slowly to the bentonite dispersion. Then the prepared solution was agitated using a magnetic stirrer (180 rpm) until the state of homogeneous gel was reached. The films were produced by casting the prepared solutions onto a glass substrate followed by drying at room temperature for 3 days, and then at 40–50 °C in a vacuum oven until the solvent was completely removed. The change in the mass of the samples during the evaporation of the solvent was monitored by the gravimetric method (until a constant mass of the film was reached). Several samples of ethyl cellulose/bentonite film composites with filler concentration in range of 0–5 wt% were produced by this procedure (Fig. 1a). The film thickness was in range of 0.01–0.03 mm.

Characterization methods

Surface characterization of films was carried out based on data of optical microscopy and scanning electron microscopy (SEM). The composition of the film was determined using an energy-dispersive X-ray spectroscopy (EDS) detector with which the microscope was supplied. The test samples were placed on carbon tape. Then a layer of carbon 1 nm thick was applied to the samples.

The crystal structures of the pure EC and EC/Bent composite films were assessed with XRD measurements (CuK$_\alpha$ emission at a wavelength, $\lambda$, of 1.54 Å). The inter-chain separation length in polymer material ($R$) was calculated according to the equation (Verma and Riaz 2018):

$$R = \frac{5\lambda}{8 \sin \theta_0}$$

(1)

For samples of Bent, pure EC, and EC/Bent composite, the Fourier-transform infrared (FTIR) spectra were recorded in the region of 400–4000 cm$^{-1}$.

Tensile strength of both pristine EC films and EC/Bent composite films were determined under the conditions of uniaxial extension. For measurements, the films were cut into strips (10×50 mm) and secured between two plates of the tensile tester. The strain rate was 2 mm/min. For each film sample, five tests were carried out.

Tensile strength ($\sigma$), percent elongation ($\epsilon$), and Young’s modulus ($E$) of each film were extrapolated from the stress–strain curves. The tensile strength is the force at which the film fractures. It was obtained using the following relationship:

$$\sigma = \frac{F_m}{wd}$$

(2)
where $F_m$ is the force at which the films breaks, $w$ is the film width, and $d$ is the film thickness which was in range of 0.01–0.03 mm.

The percent elongation was estimated from the film’s strain at break as follows:

$$\varepsilon = \frac{l_f - l_0}{l_0} \times 100\%,$$

(3)

where $l_f$ is the final length of the film at failure and $l_0$ is the initial length of the film between grips.

Young’s modulus was obtained from the slope of the initial linear section of the stress–strain curve where the film withstands elastic deformation.

Adsorption experiments

Adsorption activity of pristine EC and EC/Bent composite was evaluated in studies of the removal process of the thiazine dye methylene blue (Fig. 1b) from aqueous solutions with the initial concentration ($C_0$) in range of $2–7 \times 10^{-3}$ mmol/L. Kinetic experiments were performed at the room temperature and adsorption conditions: pH = 6.5; adsorbent dosage = 10 g/L. For this, a weighed sample portion of the adsorbent (0.05 g) was placed into tubes, mixed with aqueous MB (0.005 L), held under stirring during certain time interval, and then the phases were separated.

The dye concentrations in solution after adsorption ($C_t$, mmol/L) were determined spectrophotometrically at 665 nm. Then amount of MB in solid phase ($A_t$, mmol/g) was calculated using relation:

$$A_t = \frac{C_0 - C_t}{10},$$

(4)

The $A_t$ values were plotted against time ($t$) and the found dependencies of $A_t$ on $t$ were described using different mathematical models. The dye removal level ($\alpha$) was determined as the ratio of the dye amount removed at equilibrium ($N_0 - N_{eq}$) and the initial concentration ($C_0$).

To recorded the MB adsorption isotherms, we plotted the dependencies of the equilibrium dye amount in adsorbent ($A_{eq}$, mmol/g) on the equilibrium dye concentration in solution ($C_{eq}$, mmol/L) and fitted using various mathematical models.

Results and discussion

Characterization of bentonite

Grading and porosity of bentonite were studied by us previously using $N_2$ adsorption–desorption and laser diffraction techniques (Alekseeva et al. 2019a). It was found that the particle diameter of bentonite did not exceed 14 μm; the particle-size distribution was mono-modal with peak near 5.6 μm. The specific surface area and the average pore diameter of bentonite were found equal to 58 m$^2$/g and 7 nm, respectively.

Surface morphology of the EC/Bent composite films

To study surface morphology and composition of the EC/Bent films, we used optical microscopy and SEM–EDS analysis. The optical micrographs of pure EC and EC/Bent composite with 5 wt% of filler are represented in Fig. 2(a, b). It can be seen in Fig. 2a, the pristine polymer film is homogeneous, since its surface is even, without any distinctive flaws. In the EC/Bent composite film, the filler particles of different sizes and shapes are distributed quite uniformly (Fig. 2b).

Microscopic investigation of films surfaces by SEM confirmed the homogeneity of EC films. The surface of the pure polymer has a uniform structure (Fig. 3a). In contrast, the agglomerates of filler particles with different sizes and shapes are visible in the films containing 3 and 5 wt% of Bent (Fig. 3b, c).

The EDS analysis was carried out in order to evaluate composition of the EC and EC/Bent composites (Fig. 4a–c). Elemental analysis for carbon and oxygen estimated their contents in pure polymer to be near 64 and 36%, respectively (Table 1). In addition, small amounts of silicon and aluminum were detected on the tested sites of the composite films surface.

Crystal structure of EC/Bent composites

To research crystal structure of studied materials, we used X-ray diffraction method. Figure 5 shows the XRD patterns for bentonite powder, pure EC and EC/Bent composites. In the diffractogram of bentonite, a pronounced reflection near 7° (2θ) is observed (Fig. 5, insertion). This characteristic peak conforming to the basal distance of 1.26 nm can be indexed to the crystal plane (001).
Pure EC film (Fig. 5, pattern 1) and EC/Bent composites (Fig. 5, patterns 2 and 3) demonstrate the presence of two amorphous halo centered at \(2\theta = 10^\circ\) and \(20^\circ\), that indicates the amorphous nature of these systems. According to Bala et al. (2004), in polymer material, the strong innermost peak is arisen from the interatomic vectors between adjacent chains. On the basis of this assumption, the inter-chain separation length can be calculated from the position of the first diffraction maximum by using Eq. (1) above mentioned.

The inter-chain separation length for pure EC and EC/Bent composites is given in Table 2. Note that the \(R\) value found for EC (1.123 nm) agrees well with the data reported by Lomakin et al. (2011) (1.130 nm). The \(R\) value for pure EC is less than for composites (Table 2), that is, the polymer chains in the EC are closer and more compact. However, the dependence of the inter-chain distance on the concentration of bentonite in composite is nonmonotonic, which may be due to the complex nature of interactions between clay and polymer chains. This is consistent with the FTIR data. Interestingly, a similar non-monotonic relationship was observed for natural rubber/organoclay composites (Bala et al. 2004).

**FTIR analysis**

By analyzing IR spectra of clay, pure EC, and EC/Bent composite, one can obtain information on the nature of the interaction between ethyl cellulose and bentonite.

In the IR spectrum of bentonite (Fig. 6, spectrum 1), the bands in the interval of 3700–3000 cm\(^{-1}\) are O–H stretching and H–O–H hydrogen-binding water. The band at 1631 cm\(^{-1}\) corresponds to deformation vibrations of adsorbed H\(_2\)O molecules. The band with a peak at 1048 cm\(^{-1}\) conforms to the Si–O–Si valence vibrations of the SiO\(_4\) tetrahedra in the clay (Khashirova et al. 2009; Lou et al. 2015). The bands at 528 and 469 cm\(^{-1}\) assign to the bending oscillations of the Si–O–Si groups (Ramya et al. 2017).

The IR spectrum of the pure EC film (Fig. 6, spectrum 2) shows the broad band in the interval of 3700–3050 cm\(^{-1}\) (maximum at 3459 cm\(^{-1}\)) which can be assign to OH stretching mode, involved in the formation of intermolecular H-bonds in the polymer. The band in the absorption range of 3000–2800 cm\(^{-1}\) corresponds to the vibrations of the C–H bond in the –C\(_2\)H\(_5\)O radicals. The absorption band at 1631 cm\(^{-1}\) associates with adsorbed water. A weak band at 1735 cm\(^{-1}\) indicates the presence of a small amount of the –C=O carbonyl groups in the polymer. A wide band of 1550–1250 cm\(^{-1}\) (maximum at 1379 cm\(^{-1}\)) can be attributed to deformation plane vibrations of the C–H bond. A wide band of 1200–1000 cm\(^{-1}\) with a maximum at 1057 cm\(^{-1}\) can be assign to the stretching vibrations of the –C–O–C and –C–OH groups (Suvorova et al. 2013).

In the composite spectra (Fig. 6, spectra 3 and 4), in comparison with the EC spectrum, the broadening of band in the interval of 1200–1000 cm\(^{-1}\) and a small shift of its maximum at 1057 cm\(^{-1}\) by 2 cm\(^{-1}\) to the low frequency region are observed. This may be due to the overlapping of characteristic bands corresponding to the –OH groups in polymer and –Si–O–Si groups in bentonite. The band at 1631 cm\(^{-1}\) is shifted...
to the high-frequency region by 6 cm\(^{-1}\). Splitting and a significant narrowing of the wide band in the region of 800–400 cm\(^{-1}\) are observed. Note that bands with peaks of 528 and 469 cm\(^{-1}\) attributed to the deformation vibrations of the Si–O–Si groups are observed only in the spectrum of the composite with 5 wt% of bentonite (Fig. 6, spectrum 4). In the high-frequency region of 3700–3050 cm\(^{-1}\), there is a broadening of the band attributed to the OH groups of polymer connected by an intermolecular hydrogen bond, and a hypsochromic shift of its maximum by 15 cm\(^{-1}\) (Fig. 6, spectrum 4). These changes in the spectrum of the composite indicate the formation of hydrogen bonds between the unsubstituted hydroxyl groups of the glucoside rings of EC and the silanol groups of bentonite.

Mechanical properties

The breaking elongation, tensile strength, and Young’s modulus of the produced EC/Bent composite films were measured for comparison with those of pure ethyl cellulose. These results are important for assessing the prospects for application in packaging and coating materials.

Figure 7 displays the typical stress–strain dependences that are characteristic for the deformation of forced elastic polymer materials. It should be noted that pure EC films and EC/Bent composite films have approximately the same general shape. The pure EC specimen demonstrates a smooth curve until the ultimate stress is reached at 144 MPa with no yield point before breaking. The EC/Bent (0.5 wt% of filler) composite film has a higher limiting stress (207.5 MPa) and a lower elongation at break.

The initial linear section of the stress–strain curve relates to elastic deformation and the reorientation of macromolecules at constant stress up to the destruction of matter. The Young’s modulus (which is determined from the slope of this linear section) corresponds to the resistance of the film to elastic deformation. Table 3 shows that the \(E\) value increases with the filler content, i.e., polymer becomes less flexible when clay is added. Similar trend was observed for regenerated cellulose/halloysite nanotube nanocomposite films (Soheilmoghaddam et al. 2013).
A tensile test showed a partial positive result of the introduction of bentonite into the ethyl cellulose matrix. With a filler content (up to 0.5 wt%), the tensile strength increases by 35–40%. The increase in tensile strength of polymer composites is may be associated with good adhesion between bentonite particles and EC molecules. Moreover, FTIR studies show that there are the strong polar interactions, especially hydrogen bonds between the unsubstituted hydroxyl groups of polymer and the silanol groups of clay (para “FTIR analysis”). Hydrogen bonds cause the stretching resistance of the oriented backbone of the polymer chain. This restricts the mobility of polymer chains and improves the tensile strength.
However, further increase in the filler content (higher than 0.5%) reduces the tensile strength possibly due to the incomplete dispersion and aggregation of the aluminosilicate particles (Alexandre and Dubois 2000). Apparently, aggregation destroys the adhesion between the polymer matrix and clay particles. In addition, agglomerates act as defect points in the polymer matrix when the composite is loaded, which reduces the reinforcing effect of bentonite. For the EC/Bent composites studied in this work, the maximum improvement in the tensile strength was observed when 0.5% of bentonite was used. It should be noted that Alboofetileh et al. (2013) found a non-monotonic dependence of the tensile strength on the filler concentration too.

The mechanical strength values of the EC/Bent composite films were compared with those for other cellulosic materials modified with inorganic fillers (Table 4). Analyzing the data presented, it can be seen that the tensile strength of the EC/Bent films is higher or approximately the same in comparison with the given cellulose composites, even at low concentrations of filler.

Value of elongation at break for the EC materials under study slightly decreases with the bentonite content. This means that bentonite is not a plasticizer for ethyl cellulose. Moreover, the layered silicates might provide nucleation sites and thus contribute to the growth of crystallites. The crystallization process causes brittleness of composites and this reduces their strain at break.

Overall, the obtained data advocate the promising role of bentonite for modification of EC, despite a partial reduction in elasticity of material. Such an environmentally safe bio-composite can potentially be applied for food packaging.

### MB adsorption kinetics by EC and EC/Bent composite

To assess the value of EC/Bent composites in environmental protection, its performance in the removal of methylene blue was studied.

Figure 8a shows the change in the amount of dye in the unmodified polymer phase: the $A_t$ value increases with time and reaches an equilibrium value ($A_{eq}$). It can be seen that the adsorption equilibrium in the system is established very slowly—for 3000 min.
The MB removal level is 36%, which indicates a low sorption activity of the pure EC.

When MB adsorption on the EC/(5 wt% of Bent) composite, the equilibrium in the system is established for 600 min (Fig. 8b), that is 5 times faster than for the EC film. Adsorption activity of polymer composite (the $A_{eq}$ value) increases 2.5 times and the dye removal level reaches 83% (Table 5). Reducing in the equilibrium time is due to a higher rate of the dye adsorption on hydrophilic bentonite compared to the hydrophobic ethyl cellulose.

The kinetic curve characterizing the MB removal by bentonite powder is shown in Fig. 8c, which demonstrates higher adsorption characteristics compared to pure EC and EC/Bent composite. This effect is associated with a large specific area of the bentonite surface and a significant number of adsorption-active centers.

The effect of the adsorbent composition on adsorption performance of it is shown in Fig. 9. As can be seen, the higher the bentonite concentration in the composite, the higher the equilibrium concentration of MB ions adsorbed.

Table 4 Literature data on the tensile strength of polymer composites

| Composite                                  | Tensile strength (MPa) | References |
|-------------------------------------------|------------------------|------------|
| Regenerated cellulose/nano-SiO$_2$ (2%)   | 95.1                   | Reddy et al. [https://doi.org/10.1007/s10570-018-2059-x] |
| Regenerated cellulose/halloysite (6%)     | 49.1                   | Moghaddam et al. [https://doi.org/10.1016/j.matchemphys.2013.06.029] |
| Hydroxyethyl cellulose/bentonite (3%)     | 150                    | Alekseeva et al. [https://doi.org/10.1016/j.arabjc.2015.07.011] |
| Microcrystalline cellulose/montmorillonite (6%) | 67                    | Mahmoudian et al. [https://doi.org/10.1016/j.carbpol.2012.01.088] |
| Cellulose acetate/carbon nanotube (0.5%)  | 140                    | Salama et al. [https://doi.org/10.1002/adv.21919] |
| Ethyl cellulose/bentonite (0.5%)          | 207                    | Present work |

The values of the listed parameters were found from the experimental data using non-linear curve fitting procedure. The value of the determination coefficient ($R^2$) was used to assess the adequacy of the model.

The kinetic data were fitted using the pseudo-first-order kinetic model, the pseudo-second-order kinetic model, as well the intraparticle diffusion model (Cazetta et al. 2011; Ho 2004; Mohammed et al. 2015). The following equations correspond to the listed models:

\[
A_t = A_{eq} \left[ 1 - e^{-k_1 t} \right]
\]  
(5)

\[
A_t = A_{eq} \frac{k_2 A_{eq} t}{1 + k_2 A_{eq} t}
\]  
(6)

\[
A_t = k_d \sqrt{t} + c
\]  
(7)

In Eqs. (5) and (6), $k_{1,2}$ are the kinetic constants; $A_{eq}$ is the equilibrium MB concentration in solid phase. In Eq. (7), parameters of $k_d$ and $c$ associate with the diffusion rapidity and the thickness of boundary layer.

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The values of the listed parameters were found from the experimental data using non-linear curve fitting procedure. The value of the determination coefficient ($R^2$) was used to assess the adequacy of the model.

Figures 11 and 12 show experimental points along with fitting curves for the dye removal by pure EC and EC/Bent composite, respectively. It can be seen that Eq. (5) is preferred for the mathematical description of MB adsorption on the original and modified polymer, since the determination coefficients are higher for this model ($R^2 = 0.974$) in comparison with other models used.
The results of calculations using Eq. (5) are presented in Table 5 that shows the increasing in the $A_{eq}$ and $k$ parameters when modifying ethyl cellulose with bentonite. It can be assumed that the increasing in the MB adsorption efficiency by

![Kinetic curves for MB adsorption by pure EC (a), EC/Bent (5 wt% of filler) composite (b), and Bent (c)](image)

**Table 5** Summary of the MB adsorption kinetics on pure EC and EC/Bent (5 wt% of filler) composite calculated according to the pseudo-first-order reaction model. Adsorption conditions: pH = 6.5; adsorbent dosage = 10 g/L; $C_0 = 6.93 \times 10^{-3}$ mmol/L

| Adsorbent  | $t_{eq}$ (min) | $\alpha$ (%) | $A_{eq} \times 10^4$ (mmol/g) | $k_1$ (min$^{-1}$) | $R^2$ |
|------------|----------------|--------------|-----------------------------|------------------|-------|
| EC         | 3000           | 36           | 2.44                        | 0.001            | 0.974 |
| Composite  | 600            | 83           | 6.16                        | 0.005            | 0.974 |

![Effect of the bentonite concentration in the composite on the equilibrium concentration of MB ions adsorbed](image)

![Effect of the initial MB concentration on the dye amount adsorbed by the EC/Bent (5 wt% of filler) composite](image)

**Fig. 8** Kinetic curves for MB adsorption by pure EC (a), EC/Bent (5 wt% of filler) composite (b), and Bent (c). Adsorption conditions: pH = 6.5; adsorbent dosage = 10 g/L; $C_0 = 6.93 \times 10^{-3}$ mmol/L

**Fig. 9** Effect of the bentonite concentration in the composite on the equilibrium concentration of MB ions adsorbed. Adsorption conditions: pH = 6.5; adsorbent dosage = 10 g/L; $C_0 = 6.93 \times 10^{-3}$ mmol/L

**Fig. 10** Effect of the initial MB concentration on the dye amount adsorbed by the EC/Bent (5 wt% of filler) composite. Curve numbers are assigned to the $C_0$ values: 2.22 $\times 10^{-3}$, 3.47 $\times 10^{-3}$, and 4.58 $\times 10^{-3}$ mmol/L. Adsorption conditions: pH = 6.5; adsorbent dosage = 10 g/L
composites in comparison with pure polymer is due to appearance of the new adsorption-active centers (Si–OH and Si–O–Si) that are in bentonite. This is consistent with the presence of bands with peaks of 469 and 528 cm\(^{-1}\) attributed to bentonite in the composite spectrum (Fig. 6, spectrum 4).

**MB adsorption equilibrium by EC and EC/Bent composite**

The study of the adsorption isotherm is the basis for determine the type of adsorption process on the surface of the adsorbent. In current research, the MB adsorption isotherms on the pure EC film and the EC/Bent composite film with 5 wt% of filler were plotted and presented in Figs. 13 and 14. Comparing these figures, we can conclude that the composite has greater adsorption efficiency than pure polymer.

Freundlich, Langmuir and Temkin isotherms models (Ayawei et al. 2017) were used to fit the MB adsorption equilibrium data.

Langmuir model describes is applicable to adsorption processes on homogeneous adsorbent surface with identical adsorption sites. It can be represented as:

\[
A_{eq} = A_m \frac{K_L C_{eq}}{1 + K_L C_{eq}}
\]

(8)

where \(A_m\) is the maximum adsorption capacity of monolayer; \(K_L\) is the Langmuir constant; \(C_{eq}\) is the equilibrium concentration of adsorbate in solution.

Freundlich model describes adsorption processes on the heterogenous surfaces with a non-uniform distribution of heat of adsorption. It is given as:

\[
A_{eq} = A_m \frac{K_L C_{eq}^{1/n}}{1 + K_L C_{eq}^{1/n}}
\]

(9)

where \(A_m\) is the maximum adsorption capacity of monolayer; \(K_L\) is the Langmuir constant; \(C_{eq}\) is the equilibrium concentration of adsorbate in solution.
where $K_F$ is related to the adsorption capacity and $1/n$ is heterogeneity factor which ranges from 0 to 1.

Temkin isotherm model is used for a linear energy distribution of adsorption centers and it is expressed by the following equation:

$$A_{eq} = B_T \ln \left( K_T C_{eq} \right)$$

where $B_T$ and $K_T$ are the Temkin isotherm constants.

The legends in Figs. 13 and 14 exhibit the values of $R^2$ determined by non-linear fitting of listed models. Comparing the data given, one can conclude that the Langmuir isotherm model is applicable for description of the MB adsorption equilibrium on the pure EC and EC/Bent composite film.

Table 6 shows the values of $A_m$ and $K_L$ determined using the Langmuir isotherm model. It can be seen that the modification of ethyl cellulose with clay particles results in an increase in the maximum adsorption capacity of monolayer (value of $A_m$) by 4 times. As noted above, this increase is due to the appearance of new adsorption-active centers that are in bentonite.

In addition, the adsorption mechanism seems to change. During adsorption on a pure polymer, functional groups of MB are attracted to unsubstituted hydroxyl groups of glucoside rings in EC due to the formation of hydrogen bonds. Upon adsorption on the EC/Bent composite, electrostatic interactions can develop between a negatively charged adsorbent and a positively charged MB. This can explain the higher adsorption capacity of the composite in comparison with the pure EC.

Comparison of results with others adsorbents

In current paper, we have researched the adsorption properties of the EC/Bent composite materials concerning methylene blue. These composites were in film form. We found that the EC/Bent (5 wt% of filler) composite exhibited fairly high (83%) removal efficiency of dye (Table 5). This magnitude is close to that for a number of three-dimensional cellulose-based adsorbents (powders, beads, gels, etc.) (Table 7). It can be seen that the removal percentage, $\alpha$, depends on the nature of the adsorbent, as well as on the adsorbent dose and the initial concentration of MB.

The big advantage of the EC/Bent composite film in comparison with 3D adsorbents is the ease of its removal from aqueous media after the completion of the adsorption process and the possibility of regeneration. Therefore, such film materials can be considered promising adsorbents, at least for solutions with a low concentration of MB, which is inherent in pharmaceutical and biomedical technologies.

Conclusions

In this research, the ethyl cellulose/bentonite composite films were prepared via solution intercalation technique. It was found that in the Bent-modified polymer film, filler particles of various sizes and shapes were distributed fairly evenly. In composites, the inter-chain separation length was larger...
then those in pristine polymer. IR spectroscopy data indicated the formation of hydrogen bonds between the hydroxyl groups of the glucoside rings of EC and the silanol groups of bentonite. Mechanical tests demonstrated a growth in tensile strength of polymer material when modifying with bentonite. In addition, increase in the MB adsorption efficiency by composites in comparison with pristine polymer was revealed. Revealed data are important for assessing the promising use of EC/Bent composites as the packaging and coating materials as well adsorbents for the removal of organic substances.

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Data availability The raw data and the processed data required to reproduce these findings are available immediately if needed and can be obtained by sending an email to the corresponding author at avn@isc-ras.ru.

Declarations

Conflict of interest The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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### Table 7 The comparison of adsorption efficiency of the EC/Bent composite film reported in this work with similar adsorbent from the literature

| Adsorbent                                      | Adsorbent form | C0 (mg/L) | Adsorbent dose (g/L) | α (%) | References                                      |
|------------------------------------------------|----------------|-----------|----------------------|-------|------------------------------------------------|
| α-cellulose obtained from teakwood sawdust    | Powder         | 15        | 1                    | 97.2  | Olivera et al. (2018) https://doi.org/10.1166/ mat.2018.1490 |
|                                                |                | 30        | 1                    | 88.6  |                                                 |
| Modified cotton fibers                         | Fiber          | 500       | 4                    | 40    | Yue et al. (2019) https://doi.org/10.1177/1558925019828194 |
| Sodium periodate-modified nanocellulose        | Paste          | 10        | 10                   | 39.3  | Kara et al. (2021) https://doi.org/10.1155/2021/9965452 |
|                                                |                | 30        | 10                   | 78.1  |                                                 |
| Microcrystalline cellulose extracted from oil palm fronds | Powder       | 10        | 400                  | 81.4  | Tan et al. (2018) https://doi.org/10.1016/j.ajra.2018.08.001 |
| Carboxymethyl cellulose prepared from sugarcane bagasse | Powder     | 100       | 0.75                 | 80    | Begum and Mahbub (2013) Dhaka Univ. J. Sci. 61(2): 193–198, 2013 (July) |
| Ethyl cellulose/bentonite composite            | Film           | 2.6*      | 10                   | 83    | Present work                                     |

*This value is calculated taking into account the molecular weight of MB
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