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MECHANISM OF TETRACYCLINE SORPTION ON CARBON-BENTONITE COMPOSITE

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Abstract. *Antibiotics increased industrial production is the reason of their occurrence in wastewater, soils, groundwater, and drinking water. In this regard, treating the environment for pharmaceuticals is one of the urgent environmental challenges. Synthesis of adsorbents using different types of raw materials by the methods of mechanochemical activation makes it possible to significantly increase their sorption capacity due to the accumulation of various kinds of defects in the crystal structure of the adsorbent. We obtained the bentonite-carbon composite using roller-ring vibratory mill with coal-bentonite ratio of 30 : 70 and 50 : 50. However, the nature of the interaction between carbon and bentonite correlates with changes of surface area and porosity. The porous structure parameters of the samples show the mechanochemical activation of the mixture involves their components interactions. The authors studied the structural and chemical changes during the modification of bentonite with activated carbon by analysing the vibrational spectra of carbon, initial, and modified aluminosilicate samples. According to infrared spectroscopy of adsorbents, absorption bands characteristic of Si-O-C bond vibrations occurred. The paper investigates the sorption capacity of mechanochemically modified natural clay mineral Dash-Salakhli bentonite towards tetracycline hydrochloride. Research investigates the kinetics of the process and rapid sorption of tetracycline. The paper provides possible mechanisms of chemisorption due to donor-acceptor interaction and ion-exchange processes.*

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Introduction

Bentonite is a flaked aluminosilicate – $Al_2[Si_4O_{10}](OH)_2 \cdot nH_2O$. It widely occurs in nature, contains at least 70% of the mineral montmorillonite [1, 2]. The most significant advantages of this sorbent include its wide distribution and availability, low cost, high temperature resistance, and the possibility of changing its technological parameters through mechanochemical modification.

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One of the methods for obtaining bentonite-based nanocomposites is modification of aluminosilicate. The introduction of external nanoparticles contributes to the destruction of the hierarchical structure. This structure is formed as a result of adhesion of individual crystallites of layered silicate. It can cause changes in textural and physicochemical properties of the obtained composite. Activated carbon is of interest among the modifiers used.

Therefore, the synthesis of adsorbents using mechanochemical activation (MCA) methods based on various raw materials is a challenging issue. This will significantly increase the sorption capacity of the material due to the accumulation of various kinds of defects in the crystal structure of the adsorbent. It also allows ones to increase the number of acid centres on their surface [3, 4].

The industrial production of antibiotics is accompanied by output of huge volume of wastewater. Antibacterial drugs rank first among all pharmaceutical products in terms of industrial production volume and economic indicators. Since 1948, tetracyclines have been used in medicine and veterinary medicine for the treatment of various diseases: pneumonia, chronic bronchitis, acne, brucellosis, whooping cough, etc. due to a wide spectrum of antibacterial action. The presence of antibiotics (in particular tetracycline) is being increasingly registered annually in wastewater, soil, groundwater, and drinking water. Therefore, environmental purification of pharmaceuticals is one of the urgent issues [6, 7].

The purpose of the present study is to obtain composites based on bentonite and activated carbon by mechanochemical method, as well as investigate their sorption properties in relation to tetracycline hydrochloride

Experimental part

We used a natural clay mineral Dash-Salakhli bentonite. Density is 2.18 g/cm^3. The ion exchange capacity of the clay is 75 to 120 mg-eq/100 clay. Activated carbon of BAU-A grade GOST 6217-74 was used as a modifying substance [8, 9].

Tetracycline hydrochloride, a pharmaceutical substance in the form of pills (manufacturer is AO Biohimik, Saransk, Russia) was used as a sorbable substance. Tetracycline is a condensed system consisting of four partially hydrogenated benzene rings.

The specific surface area of the clay adsorbents was determined by low-temperature adsorption and desorption of nitrogen vapour on a Sorbi-MS. The surface area was calculated according to the BET equation [10]. We calculated the total pore volume of aluminosilicates, pore size distribution using the Barrett-Joyner-Halenda (BJH) model.

We performed infrared spectroscopy of the investigated adsorbents by the diffuse reflectance method on a Tensor 27 FTIR spectrometer. This instrument allows ones to obtain spectra in the range 4000 cm^{-1} - 400 cm^{-1}.

According to available literature data [11], tetracycline is most stable in acidic medium; it decomposes in alkaline medium and undergoes hydrolysis in medium close to neutral. Therefore, we used acidic solutions of tetracycline. We studied tetracycline sorption by bentonite-carbon adsorbent in static mode at room temperature and pH=1.1.

We took 25 cm^3 of the initial solution of tetracycline into a chemical beaker, added 0.5 g of sorbent and kept it under stirring for certain time intervals; then the phases were separated. The initial concentration of antibiotic in the solution was C_o=0.0165-10^{-6} mol/l. We checked the

sorption process by the change in the optical density of the solution; it was determined by spectrophotometry at λ=262 nm (spectrophotometer U-2001, USA).

Results and Discussion

The bentonite-carbon composite was obtained using a *VM*-4 roller-ring vibromill with an oscillation frequency of 930 min^{-1} and an energy intensity of 5.4 kW/kg; the mass of the loaded material being 40.0 g; the activation time is 15 minutes. We obtained samples with carbon-bentonite ratios of 30 : 70 and 50 : 50.

We estimated the nature of the interaction between carbone and bentonite by changes of surface area and porosity. The specific surface area of carbon is 1070 m^2/g; of bentonite is 26 m^2/g (Table 1). We calculated the specific surface area of the composite taking into account the ratio of components and compared it with the measured one (Figs. 3, 4).

The specific surface area of adsorbents after mechanochemical activation increased compared to the calculated one for sample 3 by 11%; for sample 4 by 3%. Similar results were observed when comparing the value of total porosity. The increase in total porosity for the third sample was 19%; for the fourth sample – 17%.

It indicates the mechanochemical activation of the mixture is accompanied by interactions between the components.

Table 1. Parameters of the porous structure of the samples

Parameter	Sample			
	Activated carbon	Bentonite	Carbon : bentonite 30 : 70	Carbon : bentonite 50 : 50
Sample No.	1	2	3	4
Specific surface area, m^2/g	1070.0	26.1	373.8	562.7
Total pore volume, cm^3/g	0.519	0.048	0.225	0.331
Volume of micropores, cm^3/g	0.390	absent	0.091	0.176
Volume of meso- and macropores, cm^3/g	0.129	0.048	0.134	0.155

We obtained information on the nature of structural and chemical changes in the process of bentonite modification with activated carbon by analysing the vibrational spectra of carbon, initial, and modified aluminosilicate samples (Fig. 1).

The IR spectrum of activated carbon (Fig. 1, sample 1) shows a rather broad band in the wave number range of 3200-3600 cm^{-1}, which is characteristic of the O-H bond. Hydroxyl moieties are constituents of phenolic and carboxyl groups. In addition, the vibrations in adsorbed water molecules can be observed [12]. The bands corresponding to the valence vibrations of the C-H bond are located in the range of 2850-2950 cm^{-1}; the band at 1395 cm^{-1} corresponds to the strain vibrations of this bond. Several bands in the range 1600-1760 cm^{-1} characterise the valence vibrations of the C=O bond in carboxyl and ketone groups. The bands corresponding to vibrations of the C=C bond in the aromatic system are located in the same range. The 1090 cm^{-1} band corresponds to vibrations of the C-O bond in ether and alcohol groupings [13].

As in the case of activated carbon, the spectrum of the initial bentonite (Fig. 1, sample 2) shows a broad band in the range of 3400-3700 cm^{-1} with two extrema. The 3424 cm^{-1} band

reflects the vibrations of the O-H bond in water molecules; 3630 cm^{-1} indicates the vibrations of this bond in Si-O-H silanols [14]. The presence of structural water is confirmed by the 1630 cm^{-1} band [15]. The peak in the range of 1044 cm^{-1} corresponds to the vibrations of Si-O bond in aluminosilicate, and small bands at 794; 465 and 521 cm^{-1} characterize the vibrations of Si-O-Si and Al-O-Si bonds, respectively [16].

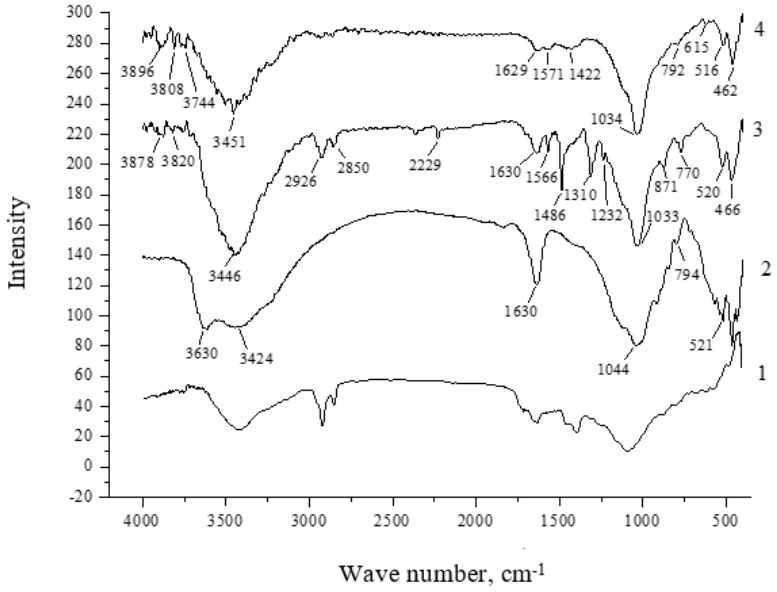

Fig. 1. IR spectra: 1. - Activated carbon; 2. - bentonite, 3 - carbon : bentonite = 30 : 70; 4 - carbon : bentonite = 50 : 50. The mechanoactivation time is 15 minutes.

The IR spectra of samples obtained by co-machining of activated carbon and bentonite (Fig. 1, samples 3 and 4 show bands characteristic of both these materials. Primarily, the disappearance of the 3630 cm^{-1} band can be explained by the interaction between carbon and aluminosilicate via silanol groupings. As a result, Si-O-C bonds can be formed (1232 cm^{-1}) [17]. The condensation of several silanol fragments to give Si-O-Si siloxanes is also probable. The appearance of several bands in the range 3700-3900 cm^{-1}, reflecting vibrations of the Al-O-H bond, is also noted. Apparently, displacement and rearrangement of vacancies for OH-groups occurs during mechanical activation. This is consistent with the decrease in the intensity of the 1630 cm^{-1} band. The formation of additional functional groups acting as active centres has a positive effect on the adsorption properties. The spectrum of sample 4 almost completely lacks bands in the range of 2850-2950 cm^{-1}, and their intensity in the spectrum of sample 3 is reduced. This may indicate oxidation of the activated carbon. It may result in the formation of additional oxygen-containing groups. Therefore, the appearance of new bands at 1570 and 1310 cm^{-1} is noted; the most significant one is in sample 3.

We estimated the sorption capacity (SC, mol/g) of bentonite-carbon adsorbent towards tetracycline according to the formula:

$$SC = \frac{(C_{initial} - C_{residual}) \times V}{m},$$

where $C_{initial}$ is the concentration of tetracycline before sorption; $C_{residual}$ is the concentration of tetracycline after sorption, mol/cm^3; V is the volume of solution used for sorption (25 cm^3); m is the mass of sorbent (0.5 g).

We plotted the sorption isotherms of tetracycline for different time intervals using the calculated values of SC and C_{equiv}. Fig. 2 shows the obtained kinetic curves of the dependence of sorption capacity (SC) on sorption time.

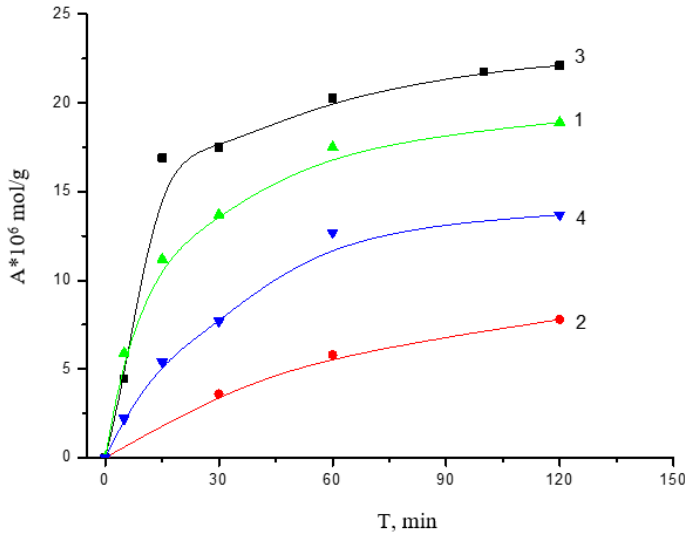

Fig. 2. Sorption curves of tetracycline: 1. - Activated carbon; 2. - bentonite, 3 - carbon : bentonite = 30 : 70; 4 - carbon : bentonite = 50 : 50.

According the study, the process of tetracycline sorption on the sorbent is quite rapid, mainly within the first minute. Further, the process of sorbent saturation slows down and by 30 minutes is practically unchanged, i.e. sorbent saturation occurs.

The mechanism of tetracycline adsorption by the composite in acidic medium can be described as follows: the protonated dimethylamino group of tetracycline, having a vacant orbital, is able to coordinate with the n-electrons of the silanol and siloxane groups in the bentonite-carbon adsorbent. Therefore, a donor-acceptor interaction is possible between the electron pair acceptor - positively charged nitrogen atom of tetracycline and the electron pair donor-oxygen of silanol and siloxane groups of the sorbent. A similar mechanism was described in [18]. The natural silica clay, was used as composite, silanol and siloxane groups – as a sorbent, and tetracycline – as a sorbate. However, considering tetracycline sorption is performed from acidic medium (pH=1.1), we cannot exclude the ion exchange mechanism associated with the substitution of protons sorbed on the adsorbent surface for tetracycline ions [19].

Conclusions

We performed mechanochemical modification of bentonite with activated carbon and obtained carbon-bentonite composite. The increase in specific surface area and porosity after mechanochemical activation compared to the calculated one. It indicates the interaction between the components. IR spectroscopy revealed the formation of additional functional groups. They can act as active centres and positively affect the adsorption properties. Hence, the carbon-bentonite composite has high sorption activity towards the drug tetracycline hydrochloride. The data obtained can serve to the development of effective sorbents for wastewater treatment of pharmaceutical enterprises.

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