Adsorption of Methylene Blue on the Composite Sorbent Based on Bentonite-Like Clay and Hydroxyapatite

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ABSTRACT

The adsorption of methylene blue from model aqueous solutions on bentonite-like clay, hydroxyapatite, and a composite sorbent has been investigated. The kinetic and thermodynamic parameters of adsorption in the temperature range 298–333 K have been calculated. The process is found to obey Langmuir isotherm equation. It is spontaneous but slightly endothermic. The maximal sorption capacity of the composite sorbent toward methylene blue is 175.4 mg/g at 25 °C that is 1.3 times higher than that for bentonite-like clay and 17.8 times hgiher than that for hydroxyapatite. Kinetics of the process is due to the combination of external and internal diffusion and can be described better by the model of pseudo-second order reaction.

Keywords: *adsorption; thermodynamics; methylene blue; composite sorbent*

ABSTRAK

Telah dilakukan penelitian mengenai adsorpsi metilen biru dari model larutan berair pada lempung bentonit, hidroksiapatit, dan komposit sorben. Parameter kinetik dan termodinamik dari adsorpsi pada rentang suhu 298-333 K telah dihitung. Dari perhitungan didapatkan bahwa proses adsorpsi mengikuti persamaan isoterm Langmuir yang bersifat spontan tetapi sedikit endotermik. Kapasitas penyerapan maksimum metilen biru menggunakan komposit sorben adalah 175,4 mg/g pada 25 °C. Kapasitas penyerapan maksimum ini 1,3 kali lebih tinggi dibanding adsorpsi dengan lempung bentonit dan 17,8 kali lebih tinggi dibanding menggunakan hidroksiapatit. Kinetika proses ini disebabkan oleh kombinasi difusi eksternal dan internal dan dapat digambarkan dengan lebih baik menggunakan model kinetika reaksi pseudo orde dua.

Kata Kunci: *adsorpsi, termodinamik; metilen biru; sorben komposit*

INTRODUCTION

Dyes have been known to be important raw materials in textile, polygraphic industry, and other related branches. The discharge of wastes containing organic dyes into natural water sources results in the decrease in dissolved oxygen concentration. It prevents light penetration and inhibits photosynthesis in plants. Many organic dyes are harmful to human beings and toxic to microorganisms. Besides, they can form coordination compounds with some poisonous metal ions.

Methylene blue (MB) is used as a disinfectant in medicine, in pharmaceutical formulations, in pesticides production, varnish and lacquer manufacturing, among others [1]. Cationic dyes such as MB are reported to be more toxic than anionic ones [2]. MB irritates human skin, eyes, and can even have a carcinogenic effect [3-4]. That is why the removal of MB and other dyes from wastewater is a serious ecological problem all over the world.

There are some ways to remove organic dyes, namely biodegradation [5], coagulation [6], oxidative catalytic degradation [7], membrane technologies [8], electrochemical degradation [9], adsorption [10]. However many organic dyes are resistant to sunlight, temperature effect, and many chemical reagents because of their complicated aromatic molecular structures, so they are difficult to remove from water by usual chemical methods [11-12]. On the contrary, the adsorption technique is one of the most popular methods of organic dyes removal because it is easy and highly efficient.

Nowadays search of inexpensive and readily available adsorbents brings scientists to find the more efficient use of natural, artificial, and synthetic materials as sorbents [13-14]. Clay minerals are the most widespread among natural minerals applied as adsorbents. Clay minerals of structural type 2:1 with changing basal spacing (montmorillonites) are known to

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Table 1. Some colloidal properties of the adsorbents

Parameters	Adsorbents		
	BT6	HA	C-HA
Zeta-potential of particles in water at pH = 7, mV	− 25	+ 2	− 22
Specific surface area, m^2/g	52.11	85.78	96.81
$pH_{pzc.}$ (zero point of charge)	5.7	6.9	6.8

be effective. Molecules of water and organic substances as well as positively or negatively charged ions can be included in the inter-package cavities of the minerals. Ion exchange with the ions from the surroundings can take place in them. The clay minerals concerned can swell because of increase of space between basal layers where absorbed ions or molecules are located [15].

The application of apatite materials for adsorption and immobilization of various pollutants is a promising technique because of their high absorptivity, ease of use and environmental friendliness [16]. Hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$ has been known as the main inorganic constituent of bones and teeth of mammals and the component of phosphate mineral rocks [17]. HA has been used for the removal of toxic heavy metal ions, dyes, fluoride ions from aqueous solutions [18-22]. However, to separate suspended highly dispersed solid particles of HA from the aqueous solutions after adsorption is quite difficult [19-23]. Positive results of the application of composite materials based on HA for water purification are known.

The aim of the work is the investigation of methylene blue sorption on bentonite-like clay, hydroxyapatite, and the composite sorbent based on bentonite-like clay and hydroxyapatite (C-HA) prepared by the chemical precipitation.

EXPERIMENTAL SECTION

Materials

Three materials were used as sorbents, namely bentonite-like clay (BT6) from Tam Bo deposited (Lam Dong Province, Vietnam), hydroxyapatite (HA), and the composite sorbent (C-HA) prepared by the method described earlier [24].

Hydroxyapatite synthesis: HA was synthesized by adding a 10% (mass) solution of orthophosphoric acid to $Ca(OH)_2$ solution with the rate 1.5–2.2 mL/min per liter of the saturated solution of calcium hydroxide. The reaction mixture was stirred for 20–30 minutes with the stirring (1000 rpm) till the pH of the mixture achieved 10.5 ± 0.5, then the mixture was allowed to settle for 24 h. The product obtained was separated from the mother liquor by filtration, rinsed with distilled water and then dried in a baker at 105 ± 5 °C for 5 h. The samples were powdered in a porcelain mortar.

The preparation of the composite sorbent (C-HA): A 5 g sample of bentonite-like clay was added to a 5 L vessel containing 1880 mL of the saturated solution of $Ca(OH)_2$. The suspension was stirred with the stirring shaft mentioned above for 2 h. The required volume of a 10% solution of orthophosphoric acid was added with the rate of 1 mL/min at intensive stirring (1000 rpm) to provide the mole relation Ca:P equal to 1.67. Then the solution was stirred for 2 h. The precipitate formed was allowed to settle for 24 h at room temperature and then separated, filtered, dried and powdered as described above.

Some characteristics of the adsorbents are given in Table 1. Methylene blue, $C_{16}H_{18}ClN_3S \cdot 3H_2O$ supplied by Sigma-Aldrich was used as the adsorbate.

Instrumentation

To estimate if a surface is positively or negatively charged, zeta-potential of particles of the sorbents dispersed in distilled water was measured by electrophoresis method on Zetasizer Nano ZS (Malvern Instruments).

The ability of the investigated materials to adsorb methylene blue was studied at static conditions at 25 ± 2 °C using model aqueous solutions of the dye with initial concentrations from 5 to 350 mg/L. 50 mL of the model solutions were added to 100 mL cone flasks containing the samples of the sorbents 0.1 ± 0.001 g, the mixtures were shaken thoroughly. After the process had been completed the suspensions were centrifuged with the rate 6000 rpm for 10 min. The residual concentration of MB in the solutions was measured by spectrophotometry on SPECORD 120 PLUS (Germany) at λ = 663 nm in a 10 mm cuvette.

Adsorption was calculated according to the following eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (1)$$

where q_e is mass of MB adsorbed on adsorbents, mg/g; C_i, C_e are the initial and equilibrium concentrations of MB solutions respectively, mg/L; V is the volume of the solution, L; m is mass of absorbent, g.

pH of solutions varied from 4 to 12 by adding 0.1 M HCl and 0.1 M NaOH solutions. pH was measured with the pH meter Multitest IPL-101 (Russian Federation).

The effectiveness of adsorption of MB from model aqueous solutions was calculated as:

$$H = \frac{C_i - C_e}{C_i} \cdot 100 \ \% \qquad (2)$$

RESULT AND DISCUSSION

pH Effect on the Effectiveness of Adsorption of MB from Model Aqueous Solutions

pH value of dye solutions is essential to adsorption and influences substantially on its effectiveness because properties of the adsorbent surface depend on it. The dependence of the effectiveness of adsorption of MB from model aqueous solutions on pH is shown in Fig. 1.

The results demonstrate that the effectiveness of MB adsorption increases more significantly as pH raises from 8 to 12. It increases from 92 to 100% for BT6, from 7 to 38% for HA, and from 96 to 100% for C-HA in the pH range mentioned above. At lower pH, the effectiveness of MB adsorption decreases. This behavior can be explained by the reactions on the hydroxyapatite surface in aqueous media [25]. The scheme of the elementary fragment of HA surface is shown in Fig. 2. The dissociation of main groups on the surface according to the schemes $Ca - OH^+ \leftrightarrow Ca^{2+} + OH^-$ and $H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+$ is accompanied by the release of OH^- or H^+ ions to the outer side of the double-electric layer, which provides a positive or negative charge of HA particles.

pH values of zero point of charge ($pH_{pzc.}$) for HA and C-HA are 6.9 and 6.8 respectively. In basic media (pH > pH_{pzc}) protons split out and the surface of HA and C-HA gets a negative charge that promotes adsorption of MB cations. The surface of both of HA and C-HA is negatively charged at acidic pH (pH < pH_{pzc}) mainly due to the dissociation like as $Ca - OH^+ \leftrightarrow Ca^{2+} + OH^-$. As a result, the positively charged surface cannot absorb MB cations effectively because of electrostatic repulsion [14]. However, despite low pH, electrostatic repulsion, and competitive adsorption of H^+ ions, a substantial amount of amount of MB is absorbed.

The effectiveness of MB adsorption in pH range 4–8 is 80–92% for BT6, 6–7% for HA and 91–96% for C-HA. This result can be explained by other mechanisms of MB adsorption on both of HA and C-HA. As it is reported in Ref. [14], the group $\equiv$P-OH can bind with the group C=N of MB molecule by hydrogen bond. Besides, the nitrogen atom of MB can interact with Ca^{2+} in HA through Lewis acid-base interaction. The scheme of possible processes in MB adsorption on HA surface is shown in Fig. 3.

At pH < pH_{pzc} the adsorption is mainly due to the mechanisms (b) and (c), whereas at pH > pH_{pzc} it goes by (a) and (b).
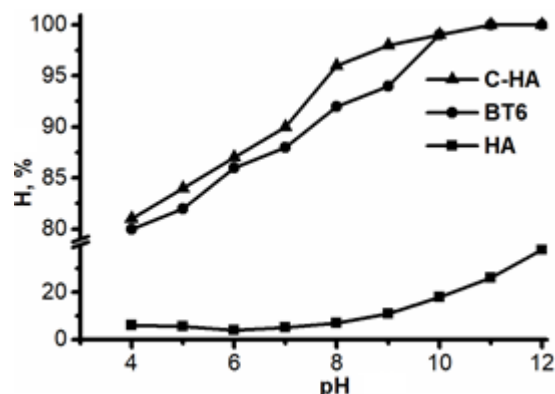

Fig 1. The dependence of the effectiveness of adsorption of MB from model aqueous solutions on pH for the adsorbents
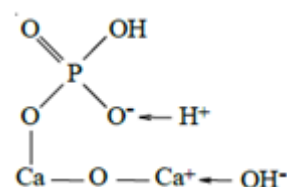

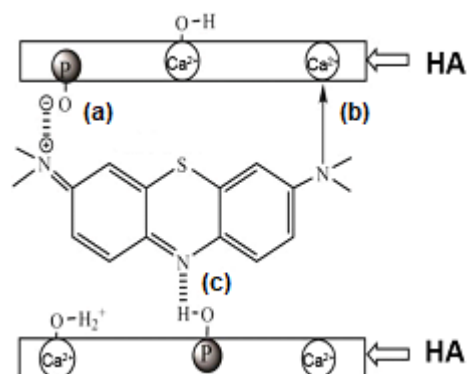**Fig 2.** The scheme of the elementary fragment of HA surface

Fig 3. The mechanism of MB sorption on HA surface: (a) – Electrostatic attraction; (b) – Lewis acid-base interaction; (c) – Hydrogen bonding

The analysis of these results showed that the removal efficiency MB on the BT6 sorbent increased with increasing pH values and reached than 92%. The removal efficiency for pH < 4 is lower due to the competition between the cations MB and protons H^+ from the acidic medium. These can be explained: For bentonite-like clay have finely divided layered silicate can be a source of both a constant (not dependent on pH) and variable surface charge (dependent on pH). The constant charge is characterized mainly by three-layered and four-layered clay silicate and is associated with the manifestation of heterovalent isomorphism in

the crystal lattice-isomorphous substitution of Si^{4+} to Al^{3+} in a tetrahedral grid and/or isomorphic substitution of Al^{3+} to Mg^{2+} in octahedral. The source of the variable charge, which is localized on the lateral cleavages of clay crystallites. Hydroxyl groups located on the lateral cleavages of clay crystallites are capable of protonation-deprotonation reactions depending on the pH of the surrounding solution [26].

The broken bonds and M–OH bonds along the surfaces of the clay crystals result in hydrolysis [27].

At low pH (pH < pH_{pzc}), electrostatic repulsion occurred between the MB cations and the edge groups with a positive charge ($M-OH_2^+$) on the surface as follows:

$$MOH + H^+ \rightarrow MOH_2^+$$
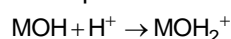
At high pH (pH > pH_{pzc}), the surface of clay becomes negatively charged and electrostatic repulsion decreases, the MB cations in solution will be attracted to the surface according to the following reactions:

$$MOH + OH^- \rightarrow MO^- + H_2O$$
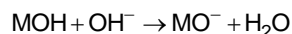
where M is the cation of Si^{2+}, Al^{3+} or Fe^{2+}

There might be another mode of adsorption (ion exchange) and the results are in harmony with the literature reports [27-28].

Kinetics of MB Adsorption on the Experimental Sorbents

Adsorption kinetics is one of the most important issues that are used to estimate the effectiveness of adsorbents. The obtained kinetic curves for MB adsorption on the sorbents involved are given in Fig. 4. As it can be seen the adsorption equilibrium is achieved in 20–40 min.

The pseudo-first and pseudo-second-order models are widely used to describe the kinetics of adsorption on a solution–solid boundary [11,29]. The corresponding linearized kinetic equations are as follows:
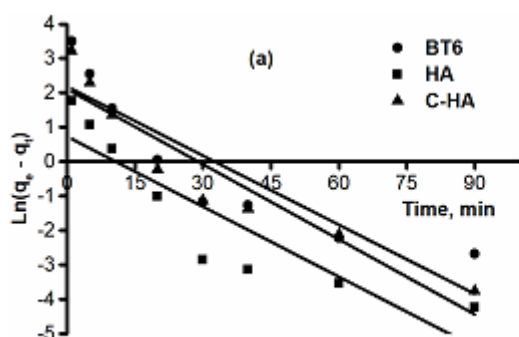
$$\ln(q_e - q_t) = \ln q_e - k_1 . t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{1}{q_e} . t \tag{4}$$

where k_1 is the rate constant in the pseudo-first-order model, min^{-1}; k_2 is the rate constant in the pseudo-second-order model, $g \cdot mg^{-1} \cdot min^{-1}$; q_t is mass of adsorbed MB on unit mass of an adsorbent at time moment t, $mg \cdot g^{-1}$.

The dependences $\ln(q_e - q_t) = f(t)$ and $t/q_t = f(t)$ for MB adsorption process on the sorbents are shown in Fig. 5.

The pseudo-first order kinetic equations are found to describe satisfactorily the experimental data just for initial stages of the process, whereas the pseudo-second-order model is acceptable in all time interval investigated. Values of k_1, k_2, and q_e calculated according to the eq. (3) and (4) are given in Table 2.

Correlation coefficients (R^2) are better when the pseudo-second-order model is applied. Values of equilibrium concentrations q_e calculated from the dependencies are in close agreement with experimental
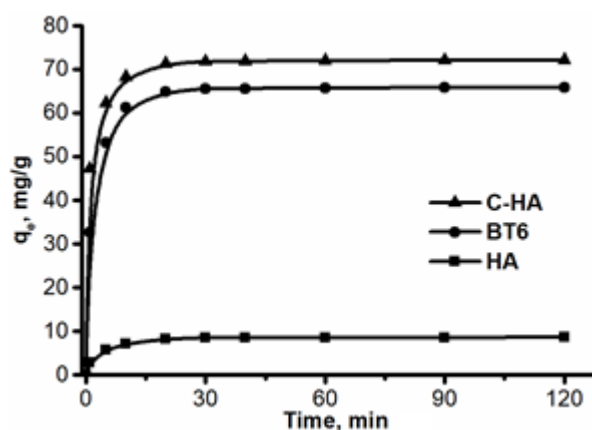
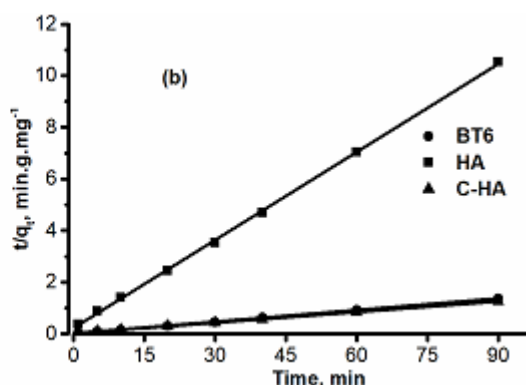**Fig 4.** The kinetic curves for MB adsorption on the experimental sorbents

Fig 5. The kinetic dependences for MB adsorption on the experimental sorbents as a pseudo-first (a) and pseudo-second (b) order process

Table 2. Kinetic parameters of MB adsorption on the experimental sorbents

Adsorbent	q_e experimental, mg·g⁻¹	pseudo-first model			pseudo-second order model		
		k_1 min⁻¹	q_e mg·g⁻¹	R^2	k_2 g·mg⁻¹·min⁻¹	q_e mg·g⁻¹	R^2
BT6	65.85	0.0955	14.73	0.885	0.0176	66.67	0.999
HA	8.57	0.0678	2.07	0.812	0.0583	8.81	0.999
C-HA	72.08	0.0726	8.16	0.886	0.0251	72.46	0.999

data in this case. On the contrary, calculated and experimental values q_e are quite different if the pseudo-first-order equation is used.

The most part of sorption processes occurs by a series of steps. These multi-step mechanisms include (i) diffusion of a sorptive through a liquid film surrounding solid particles (the process of external mass transport), (ii) diffusion inside the particles (intraparticle diffusion), and (iii) a physical or chemical adsorption [30].

First, to describe the mechanism of MB adsorption on the investigated sorbents and to determine its limiting stage we used Weber and Morris model [31], which is applicable to intraparticle diffusion. According to the model, q_t depends on time as

$$q_t = k_i(t^{1/2}) \tag{5}$$

where k_i – the rate constant for intraparticle diffusion, (mg/g min^{1/2}).

The dependences of adsorption q_t on $t^{1/2}$ calculated from experimental data are given in Fig. 6. A linear approximation of the experimental data for all three sorbents gives two straight-lined segments which point to two stages of MB diffusion to the sorbents. Here the kinetic parameters corresponding to intraparticle diffusion are characterized by the slope of the second segment. The Y-intercept is proportional to the thickness of the film surrounding the particles of the sorbents [30-31].

To determine the limiting stage of the sorption process the equation given by Boyd [29,31] was used

$$F = 1 - (6/\pi^2)\exp(-Bt) \tag{6}$$

where F is the fraction of solute adsorbed at different times t, and Bt is a mathematical function of F, which are given by the following relationships

$$F = q_t / q_e \tag{7}$$

$$Bt = -0.4977 - \ln(1 - q_t / q_e) \tag{8}$$

Using experimental data for q_t and q_e we calculated Bt. The linear dependence of Bt on t (Fig. 7) is considered to argue for interdiffusion limiting [31].

Our dependences are linear for all investigated sorbents but they do not pass through the origin. This means that the external mass transfer seems to control the process of sorption [29,31].
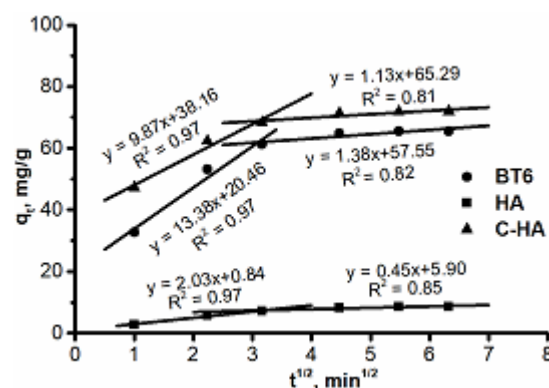
Fig 6. The experimental dependences of q_t on $t^{1/2}$ for the experimental sorbents
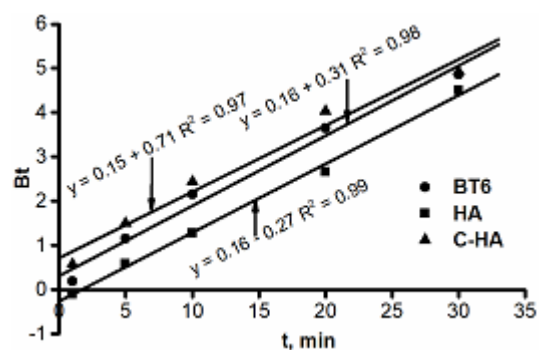
Fig 7. The dependence of Bt on t

Adsorption Isotherms

To interpret experimental data the linearized Langmuir and Freundlich equations were used

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \cdot K_L} \tag{9}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{10}$$

where q_m is the maximal adsorption (adsorption capacity) mg/g; K_L Langmuir constant, L/mg; K_F, n are constants in Freundlich sorption isotherm.

The experimental adsorption isotherms at 298 K, pH = 8–9, and the dependences linearized according to both of Langmuir and Freundlich equations are shown in Fig. 8.
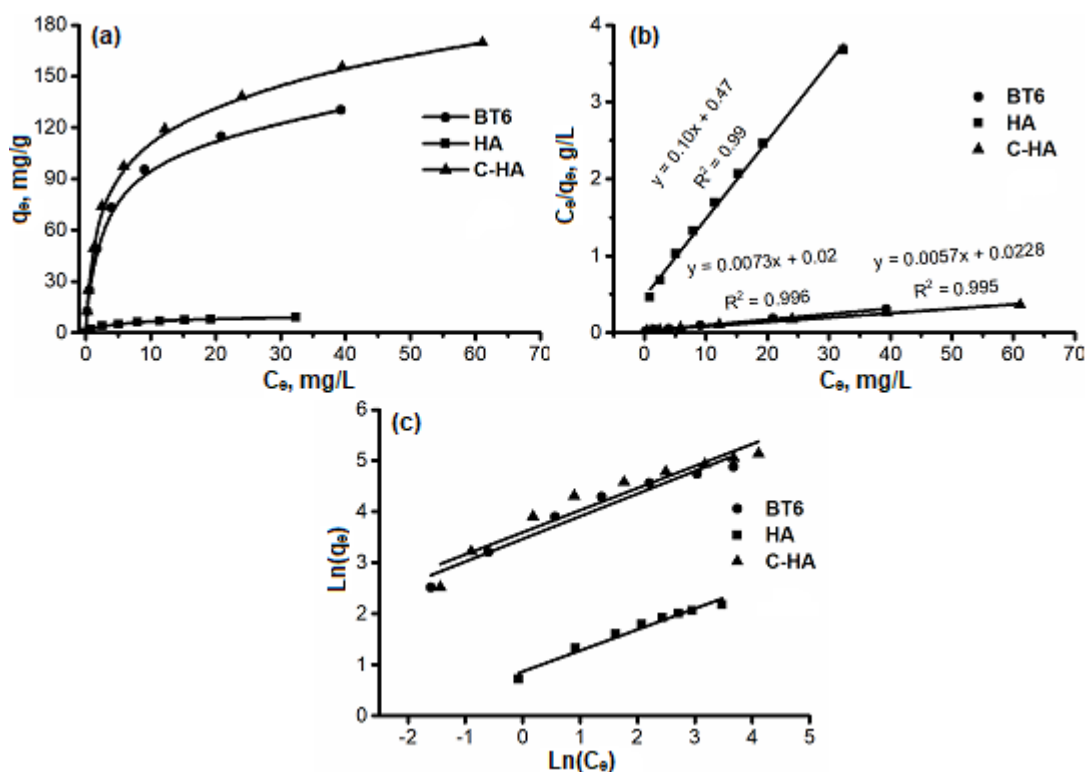
Alexandr Ivanovich Vezentsev et al.

Fig 8. The isotherms of MB adsorption on the experimental sorbents (a). The linearized isotherms according to Langmuir (b) and Freundlich (c) equations

Table 3. Parameters of Langmuir and Freundlich equations for MB adsorption isotherms on the investigated sorbents

Sorbent	T, (K)	Parameters					
		Langmuir			Freundlich		
		q_m, mg/g	K_L, L/mg	R^2	K_F	n	R^2
BT6	298	136.98	0.323	0.996	31.928	2.255	0.955
	313	138.89	0.391	0.994	35.769	2.377	0.961
	333	140.85	0.483	0.992	39.721	2.395	0.956
HA	298	9.88	0.216	0.996	2.380	2.433	0.970
	313	10.67	0.213	0.992	2.559	2.427	0.979
	333	11.21	0.229	0.989	2.808	2.480	0.985
C-HA	298	175.44	0.252	0.995	36.98	2.322	0.946
	313	181.82	0.314	0.992	41.89	2.321	0.950
	333	185.19	0.422	0.991	49.01	2.392	0.954

Adsorption ability of the sorbents can be seen to increase in the same consequence like as the rate of MB adsorption HA < BT6 < C-HA. The maximal adsorption (adsorption capacity) for the composite sorbent C-HA is 175.4 mg/g at 298 K which is 1.28 times more than that for bentonite-like clay, and 17.8 times more than that for HA. This behavior can be explained: The adsorption of MB is primarily influenced by the surface charge on the adsorbent [32] (Zeta-potential of BT6 = – 25 mV; HA = + 2 mV; C-HA = – 22 mV). In addition, methylene blue can be adsorbed both on the surface of montmorillonite and in the interlayer space (ion exchange). The large specific surface area of C-HA promotes an increase in the adsorption of the dye (Specific surface area of BT6 =

52.11; HA = 85.78; C-HA = 96.81 m^2/g). Parameters of both Langmuir and Freundlich equations calculated from the linearized isotherms are given in Table 3.

Data from Table 3 and Fig. 8 (b, c) demonstrate that Langmuir equation seems to be a bit more preferable to describe adsorption of MB on bentonite-like clay BT6, hydroxyapatite HA, and composite sorbent C-HA (R^2 > 0.99).

Thermodynamics of MB Adsorption on the Sorbents

To describe thermodynamics of MB adsorption the isotherms at three values of temperature, namely 298, 313, and 333 K, were obtained (pH = 10.0). The constant
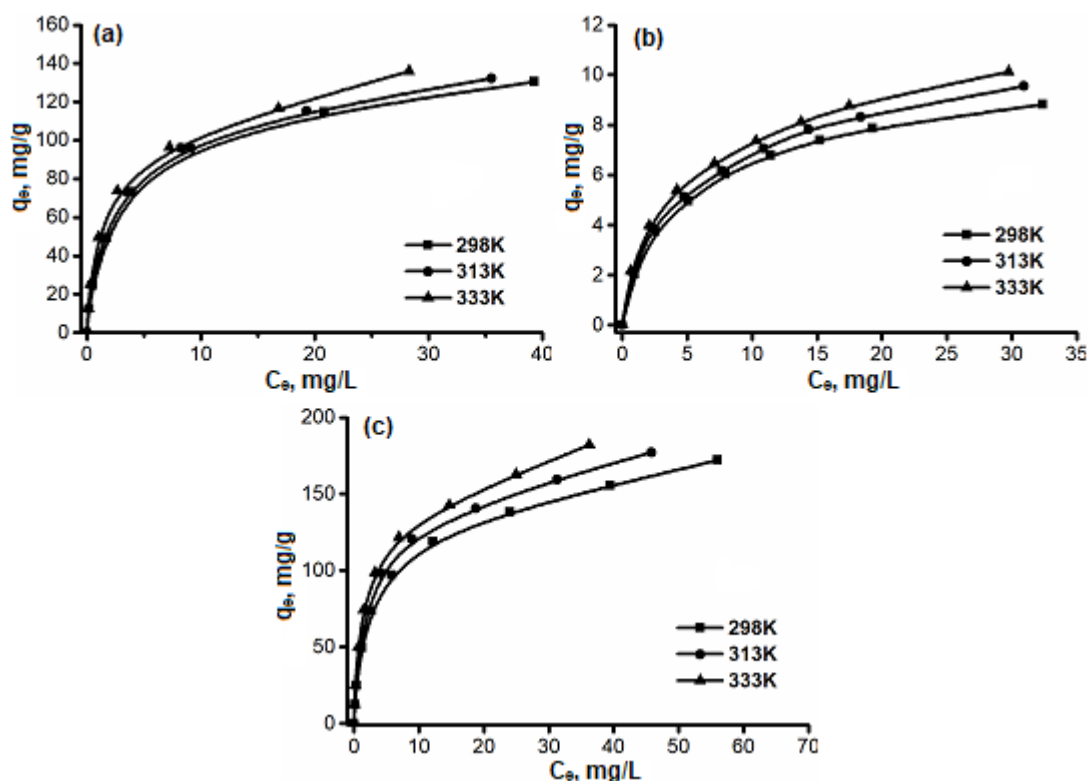
Fig 9. MB adsorption isotherms at three temperatures on the experimental sorbents: (a) BT6, (b) HA, (c) C-HA

Table 4. Thermodynamic functions for MB adsorption on the investigated sorbents

Sorbent	T (K)	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/mol·K
BT6	298	− 38.56		
	313	− 40.98	9.47	161.2
	333	− 44.21		
HA	298	− 37.52		
	313	− 39.48	1.43	130.7
	333	− 42.09		
C-HA	298	− 37.93		
	313	− 40.45	12.17	168.1
	333	− 43.81		

of adsorption equilibrium and its dependence on temperature make it possible to estimate Gibbs free energy change, enthalpy, and entropy for the process.

The standard Gibbs free energy change was calculated as follows:

$$\Delta G^0 = -RT \ln K^0 \tag{11}$$

where R is gas constant, T is absolute temperature, K^0 is the constant of adsorption equilibrium (dimensionless). Values K^0 can be found using Langmuir constants K_L according to the relationship [33]:

$$K^0 = K_L \left(L / mg \right) \times 1000 \times M_{MB} (g / mol) \times 55.5 \tag{12}$$

$M_{MB} = 319.85$ (g/mol) is the molar mass of MB.

Temperature dependence of the equilibrium constant can be written as

$$\ln K^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{13}$$

The experimental isotherms of MB adsorption at different temperatures are shown in Fig. 9. Values of enthalpy ΔH^0 and entropy ΔS^0 were found from the slope and intercept of linear dependence of $\ln K^0$ on reciprocal temperature (Fig. 10). The results are given in Table 4. As it can be seen the enthalpy changes ΔH^0 are slightly positive in the temperature range investigated that argues for the endothermic character of the process. Values of standard Gibbs free energy change ΔG^0 are negative and they decrease in the range of temperature 298–333 K. They point out the spontaneity of MB adsorption on the adsorbent involved and the values are
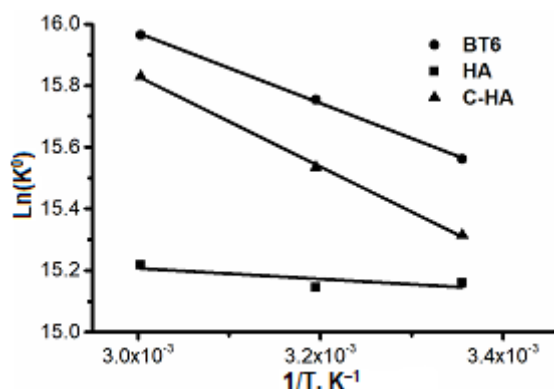
Fig 10. The dependences of ln K^0 on reciprocal temperature for MB adsorption on the experimental sorbents

consistent with other results [34]. The process becomes a bit more preferable as the temperature rises. Positive entropy changes ΔS^0 correspond to the increase of freedom in the system because of MB adsorption. Entropy increase can be explained by the release of hydrated inorganic cations from adsorbents and structural changes as a result of MB molecules interaction with an active group on the surfaces of adsorbents [35].

CONCLUSION

The results of the investigation have shown that adsorption of methylene blue on the adsorbents involved obeys Langmuir isotherm equation. It is spontaneous but slightly endothermic. The maximal sorption capacity of the composite sorbent is found to be equal 175.4 mg/g at 25 °C that is 1.3 times higher than that for bentonite-like clay and 17.8 times higher than that for hydroxyapatite. Kinetics of the process is due to the combination of external and internal diffusion and can be described better by the model of pseudo-second order reaction. The results can be useful in the development of adsorption technology of natural and wastewater purification from methylene blue and other organic cationic dyes using the composite sorbent based on bentonite-like clay and hydroxyapatite.

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