



Organobentonites as multifunctional adsorbents of organic and inorganic water pollutants

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Abstract: The aim of this study was to find a low cost, easy to synthesize and efficient adsorbent for the simultaneous adsorption of both organic and inorganic pollutants (including textile dyes, toxic metals, *etc.*). The starting material, domestic bentonite clay from Bogovina, was modified with amounts of hexadecyltrimethylammonium cations corresponding to 0.5 and 1.0 times the value of the cation exchange capacity. The organobentonites were tested as adsorbents in a three-dye-containing solution, a three-component solution of Pb²⁺, Cd²⁺ and Ni²⁺ and a hexa-component solution containing all the investigated dyes and toxic metal cations. The used adsorbents showed the highest affinity toward acid yellow 99 and Ni²⁺. Dye adsorption was enhanced in the presence of toxic metal cations, while the adsorption of all toxic cations from the hexa-component solution was lower than from the three-component solution containing only toxic cations. The synthesized hexadecyltrimethylammonium bentonite could be regarded as an efficient multifunctional adsorbent for the investigated types of water pollutants.

Keywords: simultaneous adsorption; multi-component solutions; dyes; toxic metals; adsorption affinity.

INTRODUCTION

The treatment of soil and water contaminated with mixtures of organic and inorganic pollutants is a challenging task since inorganic and organic contaminants have different transport mechanisms and fate in the environment.¹

Naturally occurring bentonite clays are able to adsorb toxic metal cations from their aqueous solutions. In general, there are two mechanisms of adsorption:

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ion exchange in the interlamellar region and adsorption on the surface by complexation and precipitation. Ion exchange involves interlamellar cations in smectites.^{2,3} The second mechanism is pH dependent. Surface complexation and precipitation occur at surface sites (hydroxyl groups on the external layers and edges).^{4,5} By organomodification, bentonite clays obtain the ability to adsorb organic contaminants (non-polar organic compounds, toxic organic dyes, *etc.*).^{6,7} The adsorption of inorganic compounds on these materials was also studied.^{8,9} The earlier approach was to study independently metal uptake by bentonite¹⁰ and the uptake of organic contaminants by organobentonites.¹¹ However, the most current and potential uses of organoclays, *i.e.*, as landfill additives and reactive barriers, demand the simultaneous removal of organic and inorganic contaminants. The simultaneous adsorption of non-polar organic compounds and toxic metal cations on organoclays was studied^{8,12} but there is a lack of data on the simultaneous adsorption of polar organic compounds and toxic metals cations from their solutions.

In previous studies,^{13,14} organobentonites with partially substituted exchangeable cations were synthesized. The obtained materials exhibited simultaneously organophilicity and hydrophilicity. Therefore, these materials showed adsorption ability for the simultaneous adsorption of dye acid orange 10 and Pb^{2+} ,¹⁴ as well as reactive black 5 and Pb^{2+} .¹⁵ According to these results, two hexadecyltrimethylammonium bentonites (HDTMA-B) were chosen to be tested as multifunctional adsorbents for both organic and inorganic water pollutants. The 0.5 HDTMA-B and 1.0 HDTMA-B, obtained by ion exchange with amounts of hexadecyltrimethylammonium cation (HDTMA^+) corresponding to 0.5 and 1.0 times of the cation exchange capacity (*CEC*) value, respectively, were tested. The selected adsorbents differed in the composition of the interlamellar region and, therefore, expressed different affinities toward the adsorption of organic and inorganic pollutants.¹⁵

In this paper, adsorption from different solutions was investigated. The investigated solutions contained either the three selected organic dyes or the three selected toxic metals and finally all six chosen pollutants. The aim of this study was to show whether the investigated organobentonites are potential multifunctional adsorbents for the treatment of complex wastewaters.

EXPERIMENTAL

Adsorbates

Three commercial dyes, namely acid orange 10 (AO10), acid yellow 99 (AY99) and reactive black 5 (RB5) were selected as organic pollutants in this study (Fig. 1). These dyes are widely used in the dyeing of wool, leather, silk, paper and polyamide textiles. All dyes were purchased from Sigma–Aldrich. Toxic metal cations (Pb^{2+} , Cd^{2+} and Ni^{2+}) as nitrate salts were used as test models of inorganic pollutants. Lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) with the purity of 99.99 %, was supplied by the Aldrich Chemical Company, cadmium (II) nitrate

($\text{Cd}(\text{NO}_3)_2$) with the purity of >99 % was purchased from Carlo Erba and nickel (II) nitrate ($\text{Ni}(\text{NO}_3)_2$) with the purity of 99.8 % was purchased from Kemika, All compounds were used as received.

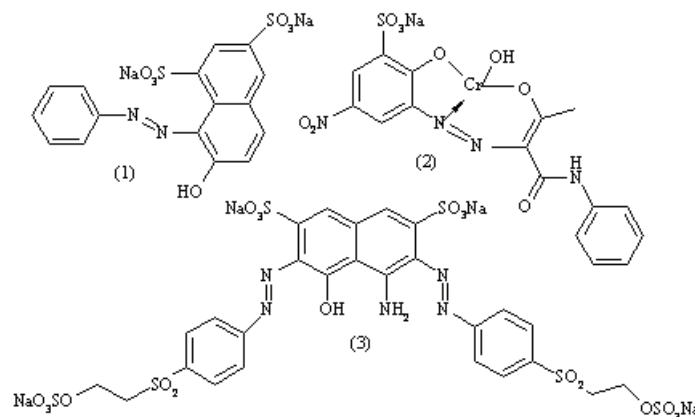


Fig. 1. The chemical structure of the investigated dyes: AO10 (1); AY99 (2); RB5 (3).

Adsorbents

Bentonite was obtained from the Bogovina Coal and Bentonite Mine in Serbia. It was crushed, ground and sieved through a 74- μm sieve. The chemical composition was reported previously.¹⁶

Na-enriched bentonite (Na-B) and partially exchanged organobentonites were synthesized using previously described procedures.^{11,13,14} The organobentonites (OBs) were obtained by the modification of Na-B with hexadecyltrimethylammonium (HDTMA) bromide (supplied by the Alfa-Aesar Chemical Company with purity of 98 %). For this study, the OBs with HDTMA/bentonite ratios of 0.317 and 0.633 corresponding to 0.5 and 1.0 times the value of *CEC* of the clay were chosen. The samples were denoted as 0.5 HDTMA-B and 1.0 HDTMA-B. Detailed characterization of these samples was reported previously.^{11,13,14}

Methods

The aqueous adsorbate solutions used in the adsorption study were: *i*) a three-component solution containing AO10, AY99 and RB5 dyes, *ii*) a three-component solution of Pb^{2+} , Cd^{2+} and Ni^{2+} toxic cations and *iii*) a hexa-component solution containing all the investigated dyes and toxic cations (AO10, AY99, RB5, Pb^{2+} , Cd^{2+} and Ni^{2+}). The initial concentration of each adsorbate in all solutions was 50 mg dm^{-3} . The initial pH value was unadjusted (5.5 ± 0.5).¹⁵

The adsorption was investigated with respect to the contact time (10, 20, 60, 90, 120, 180, 1440 and 2880 min). The experiments were realized at room temperature (25 °C) and using equal volumes of adsorbate solutions, $V = 50.0 \text{ cm}^3$. The mass of adsorbent (m_{ads}) in all the adsorption studies was 10.0 mg. The adsorption experiments were performed in a thermostated shaker (Mettmert WNE 14 and SV 1422). The samples were withdrawn from the shaker at predetermined times and the removed suspension was centrifuged (model Heittech Eva 21) at 17000 rpm for 10 min.

The amount of adsorbed pollutant after time t (q_t / mg g^{-1} or mmol g^{-1}), was calculated using the following mass balance relationship:

$$q_t = \frac{(c_0 - c_t)V}{m_{\text{ads}}} \quad (1)$$

where c_0 and c_t are concentrations of adsorbate at the initial and at time t , respectively. An equilibrium time of 24 h was taken for all the investigated processes, although for some experiments, equilibrium was reached after significantly shorter times. The equilibrium-adsorbed amount was denoted as q_e .

The absorbance of supernatant solution was measured. The spectra of dyes were obtained using a Thermo Electron Nicolet Evolution 500 UV–Vis spectrophotometer.

In preliminary research, it was confirmed that the presence of the investigated toxic metal cations affected neither the position nor the intensity of the dye absorption band at the applied concentrations of the investigated pollutants.

The content of Pb^{2+} , Cd^{2+} and Ni^{2+} in the supernatant solutions was determined by inductively coupled plasma optical emission spectrometry (ICP–OES). The ICP–OES measurements were performed using a Thermo Scientific iCAP 6500 Duo ICP instrument (Thermo Fisher Scientific, Cambridge, UK). For each run, the ICP–OES measurements were performed in triplet. The emission lines Pb II at 220.353 nm, Cd I at 228.802 nm and Ni II at 231.604 nm were employed.

Calculation of the concentrations of the dyes. The determination of concentrations of each dye in the three- and hexa-component solutions was based on the Lambert–Beer Law, where the absorbance is considered as being proportional to the concentration in the lower concentration range, and the additive property of absorbance (Eqs. (2)–(4)). Prior to the concentration determination, calibration curves for each investigated wavelength and dye were plotted. In each case, a linear relationship between the absorbance and the dye concentration was obtained (correlation coefficients ≥ 0.999 within the concentration range 0–75 mg dm^{-3}).

The UV–Vis spectra of each investigated dye together with spectrum of three-component solution of all the investigated dyes are presented in Fig. 2.

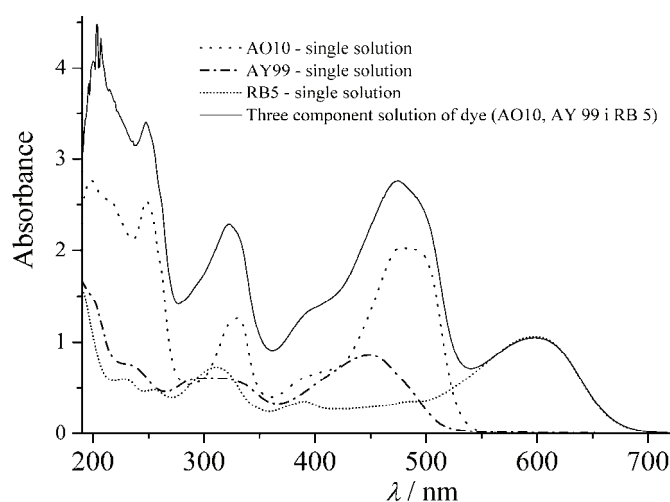


Fig. 2. UV–Vis spectra of the single component solutions of AO10, AY99, RB5 and their three-component solution.

In the solutions that contained the three dyes (AO10, AY99 and RB5), the calculations were performed using the absorbance at the wavelengths 478, 449 and 599 nm. Consequently, the measured absorbances were denoted A_{478} , A_{448} and A_{599} . These wavelengths were chosen since they represent the maximum absorption peaks for each of the investigated dyes. The concentration of each investigated dye was determined using the following equations:¹⁷

$$A_{478} = c_{AO10}0.0414^* + c_{AY99}0.0109 + c_{RB5}0.0076 \quad (2)$$

$$A_{449} = c_{AO10}0.0266 + c_{AY99}0.0163^* + c_{RB5}0.0065 \quad (3)$$

$$A_{599} = c_{RB5}0.0243^* \quad (4)$$

where c_{AO10} , c_{AY99} and c_{RB5} are the concentrations of AO10, AY99 and RB5, respectively. The symbol * indicates the calibration constants at the wavelength of maximum absorption peaks of each dye.

RESULTS AND DISCUSSION

Adsorption from the three-component solution of the selected dyes

The influences of the adsorption time on percent of the dyes removed are presented in Fig. 3a and b for the as adsorbents 0.5 HDTMA-B and 1.0 HDTMA-B.

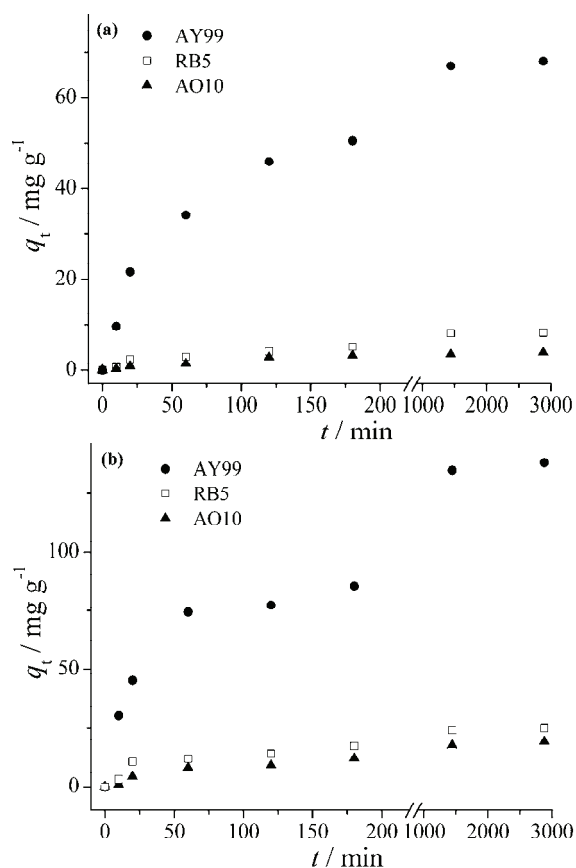


Fig. 3. Adsorption of AO10, AY99 and RB5 onto: a) 0.5 HDTMA-B and b) 1.0 HDTMA-B.

-B, respectively. The obtained values of the equilibrium-adsorbed amounts for each dye are given in Table I. For the sake of comparison, previously published q_e values obtained for adsorption from single dye solutions are also provided in Table I.

TABLE I. The q_e (mg g^{-1}) values for the dyes from the single-component and the three-component solutions

Adsorbent	Three-component solution			Single-component solution		
	Dye					
	AY99	AO10	RB5	AY99	AO10 ¹⁴	RB5 ¹⁵
0.5 HDTMA-B	68.12	8.26	3.97	103.53	9.16	11.9
1.0 HDTMA-B	138.26	19.12	25.00	142.25	22.83	54.67

The adsorption from three-component solution is slow and equilibrium was reached after 1440 min. Further extension of the adsorption time up to 2880 min did not lead to additional adsorption. Therefore, 1440 min was defined as equilibrium time. Both 0.5 HDTMA-B and 1.0 HDTMA-B had the highest affinity toward AY99. By analyzing the structure of the investigated dyes (Fig. 1), some possible explanations of the greater affinity of the adsorbents for AY99 in comparison to other two dyes can be given. Among the investigated dyes, AY99 has only one $-\text{SO}_3^-$, while the others have more than one. This somewhat reduced molecule polarity might be the reason for the enhanced affinity of AY99 toward the organic interlamellar layers. In addition, only AY99 has coordinatively bonded chromium, while AO10 and RB5 have no metallic cation in their structure. In order to explain the influence of presence of chromium in dye structure on the adsorption, additional investigations should be conducted. On the other hand, the adsorption efficiencies of AO10 and RB5 depend on the organophilicity of the adsorbents. The AO10 was better adsorbed on 0.5 HDTMA-B, while 1.0 HDTMA-B was more efficient in the adsorption of RB5. It is possible that the larger RB5 molecule is could be adsorbed more easily on the more organophilic 1.0 HDTMA-B due to the larger interlamellar spacing.¹⁵

Undoubtedly, it was shown that the adsorption of all dyes was more efficient on the more organophilic adsorbent, namely on 1.0 HDTMA-B. The q_e values for AY99 and AO10 adsorption onto 1.0 HDTMA-B were approximately doubled those on 0.5 HDTMA-B. This effect was even more pronounced for the adsorption of RB5, since the q_e was more than six times higher onto 1.0 HDTMA-B. Such trend was expected since it was already confirmed for different single component dye solutions.^{14,15,18} The adsorption of each dye is more pronounced from single component solutions than from three-component solution. These results were expected since competitive adsorption from the three-component solutions was expected to occur (each dye competing for the same organophilic sites).

Adsorption from the three-component solution of the selected toxic metal cations

The adsorption of selected toxic cations: Pb^{2+} , Cd^{2+} and Ni^{2+} from their three-component solution onto 0.5 HDTMA-B and 1.0 HDTMA-B was investigated (Fig. 4a and b, respectively). The obtained q_e values for these adsorption processes are given in Table II.

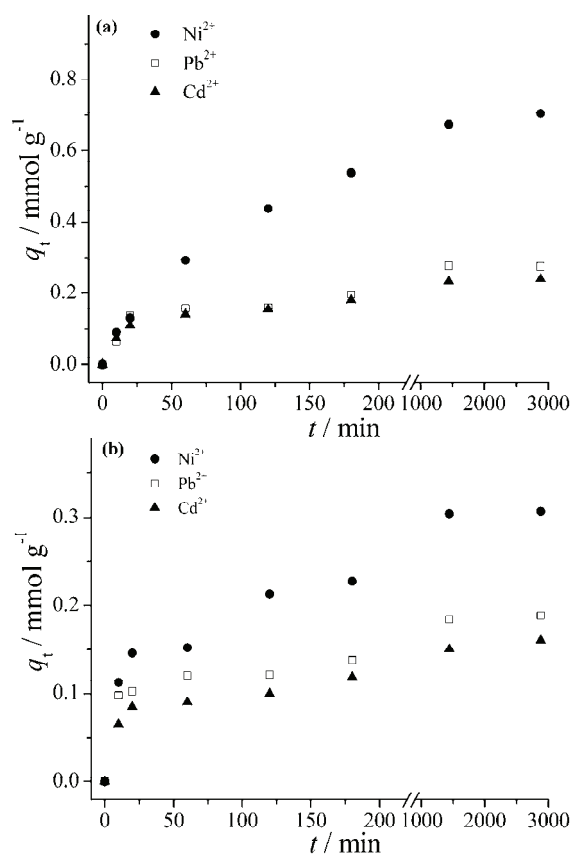


Fig. 4. Adsorption of Pb^{2+} , Ni^{2+} and Cd^{2+} onto: a) 0.5 HDTMA-B and b) 1.0 HDTMA-B.

TABLE II. The q_e (mmol g^{-1}) values for the toxic metals from the single component and the three-component solutions

Adsorbent	Three-component solution			Single-component solution ¹⁴
	Metal			Pb^{2+}
	Ni^{2+}	Cd^{2+}	Pb^{2+}	
0.5 HDTMA-B	0.70	0.24	0.27	0.13
1.0 HDTMA-B	0.31	0.16	0.19	0.09

The adsorption of inorganic cations was the most efficient on unmodified clay (sodium-bentonite) and further decreased with the increase of organophilicity of adsorbents.¹⁴ Thus, the amount of adsorbed toxic cations was higher onto

0.5 HDTMA-B than onto 1.0 HDTMA-B. Corresponding q_e values for the adsorption on 1.0 HDTMA-B were approx. 30 % lower for Cd^{2+} and Pb^{2+} (Table II). The adsorption of Ni^{2+} on 1.0 HDTMA-B although still higher than adsorption of Cd^{2+} and Pb^{2+} was more than two time lower than on 0.5 HDTMA-B.

It was observed that 0.5 HDTMA-B and 1.0 HDTMA-B showed the same selectivity for the investigated toxic metals: $\text{Ni}^{2+} > \text{Pb}^{2+} \geq \text{Cd}^{2+}$. The higher adsorption of Ni^{2+} in comparison to Cd^{2+} and Pb^{2+} onto both investigated adsorbents could be explained by the strong tendency of Ni^{2+} cations to form mixed hydroxo-Ni precipitates at the edges of phyllosilicate particles.¹⁹ Moreover, the observed slightly more pronounced adsorption of Pb^{2+} in comparison to Cd^{2+} is in accordance with literature data.^{20–22} Despite the organophilicity of the 0.5 HDTMA-B and 1.0 HDTMA-B adsorbents, the obtained q_e values for all the investigated toxic metal cations were higher than for some hydrophilic adsorbents reported in the literature.²³

After 180 min (Fig. 4a and b), an increase in the q_t values for all investigated cations was observed. It is assumed that for shorter adsorption times (up to 180 min), the main adsorption mechanism was cation exchange, while the mechanisms of surface complexation and precipitation were more pronounced for longer adsorption times.

Adsorption from the hexa-component solution

The above-obtained results showed that both adsorbents (0.5 HDTMA-B and 1.0 HDTMA-B) were able to adsorb textile dyes and toxic metal cations, and that they could be used as multifunctional adsorbents. However, since the 1.0 HDTMA-B possessed a more organophilic surface, it is more appropriate for effluents with a higher content of organic pollutants and a lower concentration of toxic cations, such as textile wastewaters.^{24,25} Therefore, in this study, only 1.0 HDTMA-B was used as adsorbent for the purification of the hexa-component solution from all the investigated dyes (AO10, AY 99 and RB5) and toxic metals (Pb^{2+} , Ni^{2+} and Cd^{2+}). The obtained results are presented in Fig. 5a and b and Table III.

The affinity of 1.0 HDTMA-B toward each of the investigated textile dyes from their three- component solution (Table I) and from the hexa-component solution (Table III) followed the same trend $\text{AY99} > \text{RB5} > \text{AO10}$. Comparing the q_e values for the adsorption of the dyes from the hexa-component solution with those from the three-component solution of the dyes, it was observed that the q_e values were higher for the hexa-component solution. Therefore, the adsorption of the dyes was more efficient from the hexa-component solution. This almost unexpected result could be explained through the adsorption mechanism in the presence of cations. The adsorption textile dyes occurs on organophilic sites,¹⁸ while the adsorption of toxic metal cation occurs on hydrophilic

sites.^{5,20,26} The toxic cations adsorbed by the surface complexation mechanism^{4,20} could be considered as new adsorption sites for the adsorption of textile dyes *via* electrostatic interaction of the toxic cations with the $-\text{SO}_3^-$ groups of the dyes (Fig. 1).

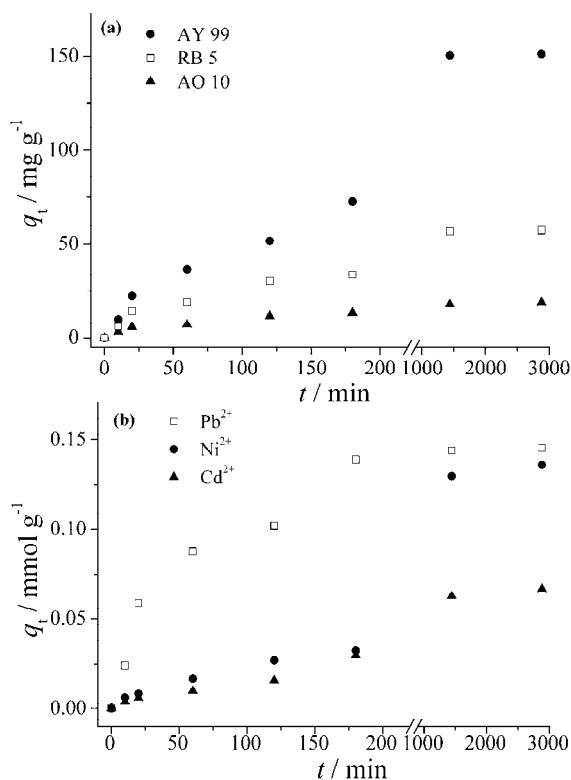


Fig. 5. Adsorption from the hexa-component solution by 1.0 HDTMA-B of: a) AO10, AY99 and RB5, and b) Pb^{2+} , Ni^{2+} and Cd^{2+} .

TABLE III. The q_e values for the dyes and toxic metals from the hexa-component solution

Adsorbent	$q_e / \text{mg g}^{-1}$			$q_e / \text{mmol g}^{-1}$		
	AY99	AO10	RB5	Ni^{2+}	Cd^{2+}	Pb^{2+}
1.0 HDTMA-B	151.18	18.96	57.16	0.13	0.07	0.15

Generally, the adsorption of all toxic cations from the hexa-component solution (Table III) was lower than from the three-component solution containing only toxic cations (Table II). This effect was very pronounced in the case of Ni^{2+} and Cd^{2+} , while it was less expressed in the case of Pb^{2+} . It appears that the presence of adsorbed dyes acts as an obstacle for toxic metal cations, perhaps due to the large dimensions of the dye molecules.

CONCLUSIONS

Two organobentonites were obtained by modification of sodium bentonite with the hexadecyltrimethylammonium (HDTMA) cation. The bentonite/HDTMA ratio used for modification corresponded to 0.5 and 1.0 times of the value of the cation exchange capacity. The obtained adsorbents were denoted as 0.5 HDTMA-B and 1.0 HDTMA-B. Three different solutions were used for the adsorption studies at room temperature: a) a three-component solutions of the dyes (AO10, AY99 and RB5), b) a three-component solution of the toxic metal cations (Pb^{2+} , Ni^{2+} and Cd^{2+}) and c) a hexa-component solution of all the selected organic and inorganic pollutants. Both 0.5 HDTMA-B and 1.0 HDTMA-B showed the highest affinity toward AY99 and Ni^{2+} . The amount of adsorbed dyes was higher on the more organophilic adsorbent (1.0 HDTMA-B). The adsorption of the toxic cations was the reverse. The adsorption from the hexa-component solution (AO10, AY99, RB5, Pb^{2+} , Ni^{2+} and Cd^{2+}) was performed only on the multifunctional adsorbent with a higher affinity toward organic dyes (1.0 HDTMA-B), which are the main type of contaminant in textile industry wastewaters. A synergistic effect of the simultaneous adsorption of dyes from hexa-component solution was observed. Dye adsorption was enhanced in the presence of the toxic metal cations. It was assumed that the previously adsorbed metal cations acted as new adsorption sites for dye adsorption. On the other hand, the adsorption of all toxic cations from the hexa-component solution was lower than from the three-component solution containing only toxic cations.

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ИЗВОД

ОРГАНОБЕНТОНИТИ КАО ВИШЕФУНКЦИОНАЛНИ АДОРБЕНТИ ОРГАНСКИХ И НЕОРГАНСКИХ ЗАГАЂИВАЧА ВОДЕ

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Циљ овог рада је био добијање јефтиног и ефикасног адсорбенса који може да се користи за симултану адсорпцију органских и неорганских загађивача (укључујући текстилне боје, токсичне метале и др.). Полазни материјал је домаћа бентонитна глина из рудника Боговина, која је модификована хексадецилтриметилмонијум катјонима (HDTMA^+). Количина HDTMA^+ коришћена за модификацију одговарала је половини и целој вредности капацитета катјонске измене полазне глине. Овако добијени органобентонити су тестирани као адсорбенси трокомпонентне смеше текстилних боја, трокомпонентне смеше метала (Pb^{2+} , Cd^{2+} и Ni^{2+}) и шестокомпонентне смеше која је садржавала све испитиване боје и катјоне токсичних метала. Коришћени адсорбенси пока-

зују највећи афинитет према боји acid yellow 99 и јонима Ni²⁺. Адсорпција боја је била поспешена присуством катјона токсичних метала, док је адсорпција свих токсичних катјона била нижа из шест-компонентног него из три-компонентног раствора токсичних катјона. Синтетисани хексадецилтриметиламонијум-бентонити могу бити ефикасни мултифункционални адсорбенти за испитане типове загађивача вода.

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