



*J. Serb. Chem. Soc.* 75 (6) 855–872 (2010)  
JSCS–4013

## Decolorization of a textile vat dye by adsorption on waste ash

MIODRAG ŠMELCEROVIĆ, DRAGAN ĐORĐEVIĆ\*, MILE NOVAKOVIĆ  
and MIRJANA MIZDRAKOVIĆ

*University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia*

(Received 24 July 2009, revised 15 February 2010)

**Abstract:** An adsorption process using cheap adsorbents could be described as a simple, selective and low cost alternative for the treatment of colored waste water compared to conventional physical and chemical processes. In this study the use of a natural waste adsorbent–ash was investigated for the removal of a textile vat dye Ostanthren blue GCD remaining after the dyeing of cotton textile. The ash obtained as a waste material during the burning of brown coal in the heating station of Leskovac (Serbia) was used for the treatment of waste waters from the textile industry, *i.e.*, waste water after the dyeing process. The effect of ash quantity, initial dye concentration, pH and agitation time on adsorption was studied. The Langmuir model was used to describe the adsorption isotherm. Based on the analytical expression of the Langmuir model, the adsorption constants, such as adsorption capacity and adsorption energy, were found. Pseudo first and second order kinetic models were studied to evaluate the kinetic data.

**Keywords:** textile vat dye; adsorption; ash; Langmuir model; kinetics.

### INTRODUCTION

Many industries, such as the textile, leather, paper and plastics industries, are extensive dye users. Among them, the textile industry is the first by quantity and quality of dyes used for the dyeing of various fiber types. Wastewaters from the textile industry contain, in addition to dyes, a number of other polluting matters, such as toxic organic residuals, acids, bases and inorganic matter. Some dyes are carcinogenic and mutagenic being formerly produced from dangerous chemicals, such as benzidine, metals, *etc.* The effluence of colored liquid waste into receptor waters affects not only their esthetic nature but also the transmittance of sun light, thereby reducing photosynthesis and disturbing the natural balance of water life and the food chain.<sup>1–3</sup>

\* Corresponding author. E-mail: drdrag64@yahoo.com

doi: 10.2298/JSC090717051K

During the previous several decades, a number of physical, chemical and biological methods for purification–decolorization were published and some of them were accepted by the textile industry. Among many decolorization procedures, the adsorption technique gives good results because it can be used for the removal of various types of colored matter. Commercial systems use mostly activated carbon as the sorbent for decolorization of waste waters because of its excellent absorption ability. Although activated carbon has an advantage as a sorbent, its massive employment is restricted due to its high price. To reduce the treatment costs, cheap alternative adsorbents are being sought.

Various studies<sup>5,6</sup> have confirmed the existence of alternative materials as potential adsorbents for pollutants and colored compounds. The considered possibilities for the adsorptive removal of color<sup>7,8</sup> include synthetic<sup>9</sup> and natural materials<sup>6</sup> and the use of solid natural organic materials is increasing exponentially. Among the organic compounds, many materials have color removal potential but they are not economic. Natural materials and wastes<sup>10–15</sup> build a complete collection of cheap adsorbents and they are environmentally friendly. Many articles have been published about the use of corn cobs,<sup>16</sup> palm fruit parts,<sup>17–19</sup> eucalyptus bark,<sup>20</sup> cotton,<sup>21</sup> sunflower stalks<sup>22</sup> and wheat straw<sup>14</sup> as decolorizing adsorbents. The removal of textile dyes by new adsorbents is usually evaluated by comparing their efficiency with that of activated carbon. Activated carbon is neither economical nor effective due to its non-polar nature in the unactivated state and in the most cases due to the polar nature of dyes. Therefore activation is often performed to introduce polar groups intended for different applications of carbon adsorbents.

As with other substrates, the adsorption of dyes not only depends mainly on the characteristics of the dyes and their structures but also to the same degree on the surface chemistry of adsorbent.

#### EXPERIMENTAL

As the adsorbent, the ash from the “Heating Station Leskovac” (Serbia), obtained by burning brown coal, was used. After collecting and drying, the ash was sifted up to a particle size of 0.5 mm. To increase the functionality, the ash was demineralized by treatment with 7.5 % H<sub>2</sub>SO<sub>4</sub> for 60 min followed by copious rinsing with water, repeated treating with acid and finally adjustment of the pH of the water ash slurry to between 7 and 8.

As the adsorbate, vat dye Ostanthren Blue GCD (C.I. Vat Blue 14) from Synthesia, the Czech Republic was used.

The structure of the dye and its behavior in conventional textile dyeing processes are shown in Fig. 1. It should be noted that the dye samples used in the experimental part of this study were not obtained after the classical dyeing procedure but after heating the dye at 60 °C for 60 min without any additives and without textile material. The aim was to test the adsorption of the dye itself without any of the usual additives in the dyeing process, *i.e.*, reduction agents, hydrolysis agents, wetting agents, leveling agents, *etc.*, that would affect the adsorption process and complicate the interpretation of the results. It should be noted that the

dye is oxidized after dyeing and returns to its original insoluble form and as such exists in waste waters.

Common vat dyes are quinonic dyes and particularly common are the anthraquinones and indigoids. Moreover, vat dyes include the natural dyestuff, indigo, and the artificial dyes called by the trade names, indanthrene, and flavanthrene. These dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in the alkaline liquor produces the water soluble alkali metal salt of the dye (Fig. 1). In this leuco form, these dyes have an affinity for the textile fibers. Subsequent oxidation reforms the original insoluble dye. Most vat dyes are less suitable than fiber reactive dyes for domestic use as they are difficult to work with; they require a reducing agent to solubilize them.<sup>23</sup>

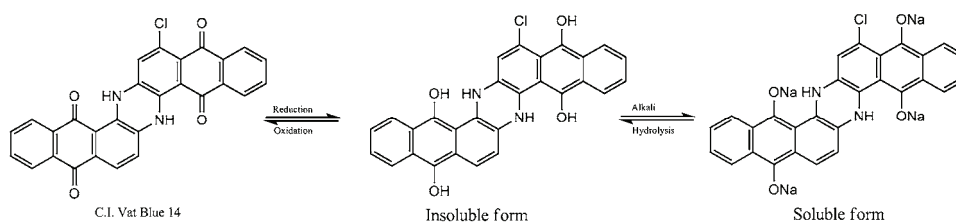


Fig. 1. Vat dye behavior in the process of textile dyeing.

The effect of pH on adsorption by the ash was tested by adjusting the pH of the solution to the required values with 1.0 M NaOH and H<sub>2</sub>SO<sub>4</sub> solutions. According to the obtained results, the most effective adsorption was obtained at pH 13 and all subsequent processes were performed at this pH value.

The adsorption experiments were performed at room temperature (20 °C) in glass Erlenmeyer flasks, closed with cork stoppers and placed on a shaker at 150 rpm. The quantity of ash was varied between 1 and 4 g, using a constant volume of solution (100 cm<sup>3</sup>) containing dye at concentrations of 50, 100, 150, 200 and 250 mg dm<sup>-3</sup>. The treatment times were 10, 20, 30, 45 and 60 min with continuous agitation.

The selected dye concentrations were chosen because they mostly correspond to the residual dye quantities in the solution after the dyeing of textile. In the experiments, pure dye was used without the additives usually present in the dyeing process. The equilibrium adsorption time for the adsorption of dye on ash was determined to be 60 min and extension of the treatment time did not change the quantity of adsorbed dye.

The degree of dye removal was determined by spectrophotometrically measuring the quantity of dye in the solution before and after adsorption using a Cary 100 Conc UV-Vis spectrometer (Varian) at a wavelength of 590 nm

The percent dye removal is given by:

$$\text{Dye removal} = 100(c_0 - c)/c_0$$

where  $c_0$  and  $c$  are the initial and final dye concentrations in the solution, respectively.

The adsorption of an adsorbate on a material can be described by the Langmuir isotherm, which in its linear form is given by:<sup>24</sup>

$$\frac{c_M}{a} = \frac{1}{a_{\max}} c_M + \frac{1}{a_{\max} b} \tag{1}$$

where:  $c_M$ ,  $\text{mg dm}^{-3}$ , is the equilibrium adsorbate concentration in the solution after adsorption;  $a$ ,  $\text{mg g}^{-1}$ , is the quantity of adsorbate adsorbed per mass unit of adsorbent;  $a_{\text{max}}$ ,  $\text{mg kg}^{-1}$ , is the maximum quantity of adsorbate that could be bound to the adsorbent;  $b$ ,  $\text{dm}^3 \text{kg}^{-1}$ , is the ratio of the adsorption rate constant and the desorption rate constant of the adsorbate.

The quantity of adsorbed dye (adsorbate) per mass unit of ash (adsorbent) was determined from the expression:

$$a = \frac{(c_M^0 - c_M)V}{w} \quad (2)$$

where:  $c_M^0$ ,  $\text{mg dm}^{-3}$ , is the initial adsorbate concentration in the solution;  $w$ ,  $\text{g}$ , is the mass of adsorbate and  $V$ ,  $\text{dm}^3$  is the volume of the solution used for the adsorption.

Equation (1) predicts that a plot of  $c_M/a$  vs.  $c_M$  should give a straight line, which is used for the determination of the values of the constants  $a_{\text{max}}$  and  $b$  as follows:

$$a_{\text{max}} = \frac{1}{\text{slope}} \quad \text{and} \quad b = \frac{1}{a_{\text{max}} (\text{ordinate intercept})_{c_M=0}}$$

In order to define the kinetics of the adsorption, pseudo first and pseudo second order models were considered. The linear form of the equation of pseudo first order kinetics is:

$$\log(a_{\text{max}} - a_t) = \log a - \frac{k_1}{2.303} t \quad (3)$$

and the equation of the linear form of pseudo second order kinetics is:

$$\frac{t}{a_t} = \frac{1}{k_2 a_{\text{max}}^2} + \frac{1}{a_{\text{max}}} t \quad (4)$$

where:  $a_{\text{max}}$ ,  $\text{mg g}^{-1}$ , is the maximum (equilibrium) adsorbed quantity of adsorbate per unit mass of adsorbent;  $a_t$ ,  $\text{mg g}^{-1}$ , is the adsorbed quantity of adsorbate per unit mass of adsorbent after time  $t$ ;  $t$ ,  $\text{min}$ , is the time of adsorption;  $k_1$ ,  $\text{min}^{-1}$ , is the equilibrium rate constant for pseudo first order kinetics and  $k_2$ ,  $\text{g min}^{-1} \text{mg}^{-1}$ , is the equilibrium rate constant for pseudo second order kinetics.

## RESULTS AND DISCUSSION

Prior to commencing the presentation and analyses of the results of the present investigation of textile vat dye decolorization using waste fly ash, several facts regarding the justification of the use of this waste material from heating stations and power stations should be noted. Namely, it is known that one power station of 1000 MW produces about half a million tons of fly ash annually.<sup>25</sup>

Moreover, there are objectives to use this free material, available in huge amounts, for useful purposes or to dispose of it properly and hence prevent its dissemination because it contains potentially hazardous materials. Ash is an especially problematic residue as it contains high concentrations of heavy metals<sup>26</sup> and trace amounts of polychlorodibenzodioxins and furans.<sup>27,28</sup>

Heavy metals are nowadays among the most important pollutants in source and treated water, and are becoming a severe public health problem. They can be toxic to aquatic life and cause natural waters to be unsuitable as potable water

sources.<sup>29</sup> Heavy metal removal from aqueous solutions has commonly been realized by several processes: chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption.<sup>29,30</sup> Among these processes, adsorption using a suitable adsorbent can be an effective technique for the removal of heavy metals from wastewater.<sup>31–33</sup> As adsorbents activated carbon, alumina, silica and ferric oxide have been proposed. Although they generally have high metal adsorption capacities, they are expensive and difficult to separate from the wastewater after use. This has prompted over recent years growing research interest into the production of low cost alternatives to these adsorbents from a range of carbonaceous and mineral precursors. Ash, one of the most abundant waste materials from the combustion of powdered coal, and its major components make it a potential agent for the adsorption of heavy metal contaminants in water and wastewaters.<sup>30</sup>

Thus, fly ash is potentially a source of heavy metals that could be released into the environment, but it also can be used as an adsorbent for the removal of some heavy metals from their aqueous solutions.

Ash has potential application in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties, such as porosity, particle size distribution and surface area. Moreover, the alkaline nature of ash makes it a good neutralizing agent. Generally, in order to maximize metal adsorption by hydrous oxides, it is necessary to adjust the pH of the wastewater using lime and sodium hydroxide.<sup>32,33</sup>

Several new technologies, such as immobilization of the ash with cement,<sup>34</sup> acid neutralization,<sup>35</sup> wet chemical treatment<sup>36</sup> and thermal treatment, have been proposed for the removal of heavy metals. The goal is to decontaminate toxic residues and render them inert so that they can be reused or deposited without risk. The major components in the ash which includes cyclone ash and scrubber ash (referred to as fly ash herein) are silica, aluminum, and calcium.<sup>37</sup> One of the ways is the waste melting process, in which the most hazardous materials, such as heavy metals, are tightly fixed in a solid phase, and the slag generated by this process can be used as a construction material.<sup>38</sup> Glassy slag can be generated by melting waste at temperatures exceeding 1300 °C, after which the molten ash is water-quenched or air-cooled. The volume of the resulting slag can be reduced and the slag stabilized such that heavy metals become immobilized in a glassy Si–O matrix; thus, the leaching behavior is improved.<sup>39</sup> The most common processes include the use of the ash as a raw material in the manufacture of brick and as a pozzolan in concrete.<sup>29</sup>

Hence, waste fly ash used in dye adsorption and the heavy metals washed off the ash and solidified (by evaporation and filtration) can be disposed as described above.

Considering an adsorption process, it is known that adsorption from a solution towards a solid surface begins with the interaction of dipoles or charged species of adsorbent and adsorbate. In addition, anion and cation interchange also occurs when neutral molecules come sufficiently close to each other, when an interaction between dissolved organic components, dyes, solvent molecules, water, and the surface of the adsorbent, ash, begins.<sup>4-6</sup>

It could be stated that the adsorption of dissolved matter (adsorbate) from a solution or suspension onto solid matter (adsorbent) occurs according to one of the following mechanisms: interchange of molecules from the solution with those on the adsorbent, physical adsorption induced by van der Waals forces and chemisorption.<sup>7-10</sup>

Adsorption efficiency depends on a number of parameters, such as medium temperature, pH, mechanical agitation, dye diffusion rate, *etc.* As a rule, by increasing the solution temperature, the dyeing rate or rate of diffusion is increased, but likewise, increased temperature reduces the equilibrium dye exhaustion. On this basis, fast adsorbing dyes have an optimal dyeing temperature of, for instance, 40 °C, while with dyes that slowly bind to a fiber, the optimal dyeing temperature is 100 °C. The same analogy can be applied for “binding”, *i.e.*, adsorption of a dye onto the adsorbent (ash).<sup>4-6</sup>

It is known that the surface of ash acquires a positive charge by absorbing hydrogen ion (H<sup>+</sup>) after immersion in water. In the case of low pH and increased H<sup>+</sup> concentration in a system, the ash surface acquires a strong positive charge. The opposite is true in an alkaline medium.<sup>7,8</sup>

It was found that the highest percentage of vat dye removal occurred in a strong alkaline medium, meaning that under these conditions, a high physical interaction appeared, which was based on the attraction of opposite charges, (+) dye charge and (-) ash charge, Fig. 2. Therefore, an increasing or decreasing percentage dye removed depending on pH should be considered in the light of structural changes of the dye and the condition of the surface layer of the ash.

It was expected that in acidic medium, considering the positively charged dye form, the highest dye adsorption would occur if the ash were negatively charged. This was not the case with the maximum adsorption found when the pH of the solution was 12 and 13, *i.e.*, in a strong alkaline medium. However, it should be noted that the difference in adsorption in strong acid and in strong alkaline medium was very low, about 0.1 %.

The explanation should be looked for in the fact that the reaction in alkaline medium is more risky than in an acidic one because of possible deformations and structural changes of the dye molecule, which could be the for the somewhat higher adsorption observed under very strong alkaline conditions.<sup>40</sup>

On the other hand, it is well known that substances adsorb poorly when they are ionized. Usually, when the pH is such that an adsorbable compound exists in

an ionized form, adjacent molecules of the adsorbed species on the adsorbate surface will repel each other to a significant degree, because they carry the same electrical charge (forces of repulsion/attraction between the actual ions are strong, compared with weak forces, such as Van der Waals forces). Thus, the adsorbing species cannot pack together very densely on the surface, and the equilibrium amount of adsorbed solute is only modest.<sup>41</sup> In contrast, when the adsorbing species is in the non-ionized form, no electrical repulsion exists, and thus the packing density on the surface can be much higher, as in the present case.

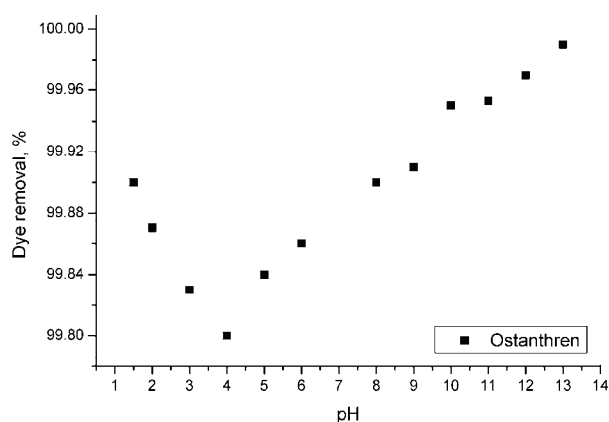


Fig. 2. Percentage of removed vat dye adsorbed on ash in acid and alkaline medium.

On reaction of a dye with an acid (*e.g.*,  $\text{H}_2\text{SO}_4$ ), a salt is obtained – hydrogen sulfate and/or sulfate. Hydrogen ions from the acid binds to one and/or both nitrogen atoms of the dye and the produced cations are balanced by hydrogen sulfate or sulfate anions, Fig. 3.

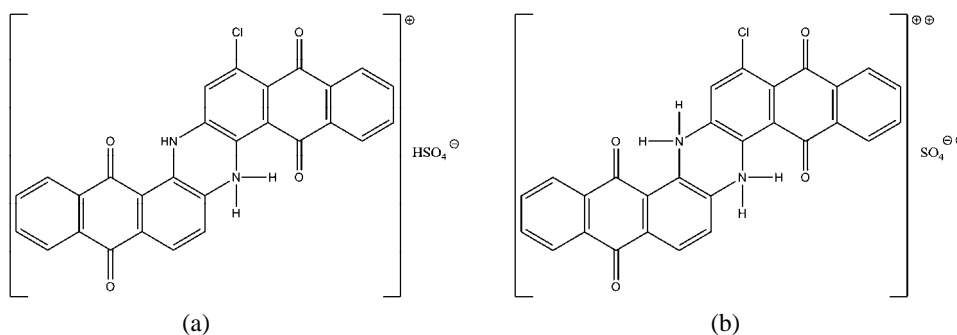


Fig. 3. Dye structure after reaction with sulfuric acid.  
a) hydrogen sulfate dye form; b) sulfate dye form.

In basic medium, reactions occur on the carbonyl groups and by reduction, two to four identical phenol  $-\text{OH}$  groups are obtained, with later replacement of the hydrogen atom by a sodium atom, Fig. 4.



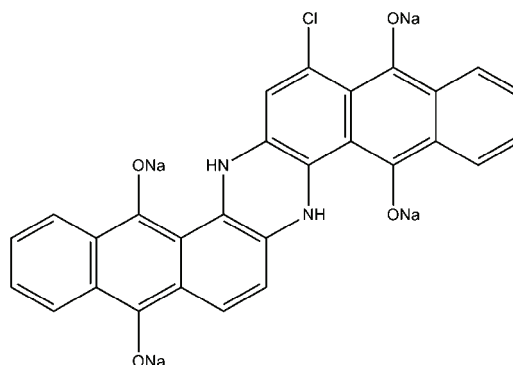


Fig. 4. Dye structure after reaction with sodium hydroxide.

The removal yields of vat dye as a function of the initial and equilibrium dye concentration for the minimum quantity of ash (1 g) are shown in Fig. 5. At lower concentrations, it is obvious that a higher percentage of dye was removed dye is obvious, irrespective of whether the initial or equilibrium dye concentration was considered. On the other hand, generally, the maximum dye concentration ( $250 \text{ mg dm}^{-3}$ ) was considerably higher than the previously used concentrations ( $200, 150, 100$  and  $50 \text{ mg dm}^{-3}$ ) but the percentage dye removed was only slightly lower than the values obtained with the other initial concentrations. This means, effectively, that a higher amount of dye was adsorbed with the highest initial concentration. Therefore, the percentage removed dye and the adsorption percentage decreased with increasing dye concentration in solution but the actual quantity of dye adsorbed increased with increasing dye concentration.

Based on this behavior of the dye in a solution containing ash, it could be concluded that the faster removal indicates that the sorption process could be ionic in nature when the dye molecules bind to oppositely charged groups on the adsorbent surface.

Moreover, from the plot in Fig. 5, it is obvious that the adsorption time plays a key role, *i.e.*, with increasing time, the quantity of dye removed from solution by the ash increased. The same effect was found with all the employed quantities of ash.

Plots of % removed dye at equilibrium time *vs.* the quantity of ash for different concentrations of vat dye are shown in Fig. 6, from which a constant increase in the % removed dye with increasing adsorbent mass is obvious and that the lowest dye concentration showed the highest % removed dye, whereas the highest dye concentration gives the lowest % removed dye. Nevertheless, the actual quantity of adsorbed dye increased with increasing dye concentration.

The results of the amount of dye adsorbed on the ash adsorbent with time for different initial concentrations of vat dye and different ash quantities are shown in Fig. 7.



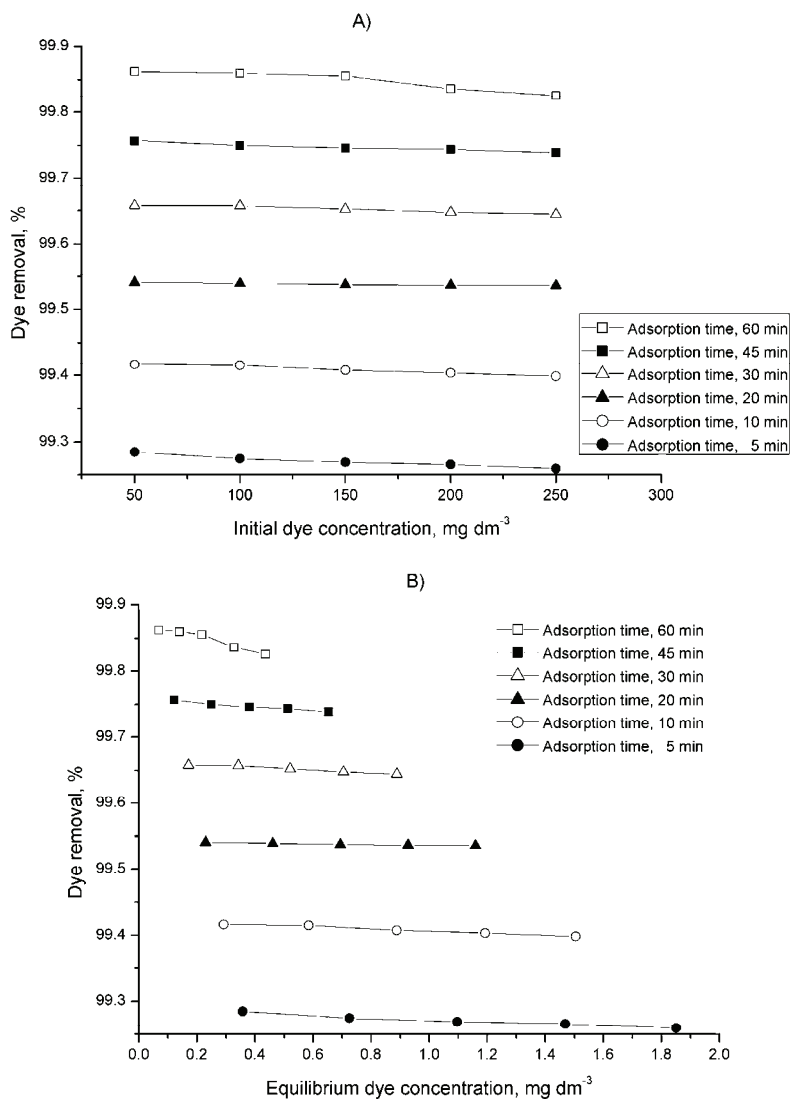


Fig. 5. Percentage of removed vat dye adsorbed on ash as a function of A) the initial and B) the equilibrium dye concentration (adsorption on 1.0 g of ash).

In the main diagrams, Figs. 7A and 7B, are only shown the dependencies for dye concentrations of 50 and 250 mg dm<sup>-3</sup> and for adsorbent quantities of 1.0 and 4.0 g, respectively. The changes for other dye concentrations were similar but for sake of clarity, they were not given in the main diagrams. In the lower right hand side of the main diagrams, auxiliary diagrams showing the dependencies for all dye concentrations are inserted. Practically, one curve each was chosen from the auxiliary diagrams to give the main diagrams marked as A and

B. Such a presentation gives a more prominent picture of the dependency of the change of amount of dye adsorbed on the adsorbent with time compared to the same presentation in the auxiliary diagrams.

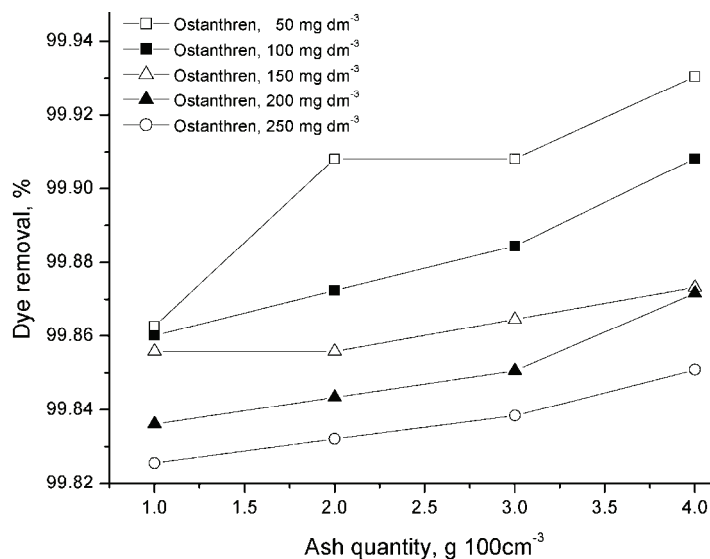


Fig. 6. The percentage of vat dye removed by adsorption as a function of ash quantity for different initial dye concentrations.

The continuity of changes with time are obvious, *i.e.*, the amounts of dye adsorbed per unit mass of adsorbent increased with increasing time. Moreover, the highest adsorption occurred with the highest dye concentration, which was expected.

The Langmuir adsorption isotherm in two forms is shown in Fig. 8, *i.e.*, Fig. 8A represents the relation between adsorbed dye per unit of the minimal used ash mass and equilibrium dye concentration and Fig. 8B shows the relation of  $c_m/a$  to the equilibrium concentration of the dye.

It is obvious that adsorption curves are smooth and continuous, indicating that the process proceeds to saturation with different concentrations of dye on the outer interface of the adsorbent. This implies the possibility of the formation of a mono-layer coverage of the adsorbent, which is described by the Langmuir Equation. From the slope and intercept of the right hand plot in Fig. 8, according to Eq. (1), the Langmuir constants  $a_{\max}$  and  $b$ , representing the maximum quantity of adsorbate bound to the adsorbent and the adsorption energy, respectively, were determined.

Under ideal conditions of medium pH and maximum interactions of the dye molecules with the adsorbent, the plots in Fig. 8 represent the essential functionality of the variables, *i.e.*, a high correlation was achieved. The essence of the

adsorption process in this case, covered by the Langmuir isotherm, is based firstly on the initial dye concentration, being an important driving force to overcome all the resistance to mass transfer between the aqueous and solid phase. Generally, a higher initial concentration of vat dye enhances the adsorption process. The case was similar for adsorption onto the maximum amount of ash employed, Fig. 9.

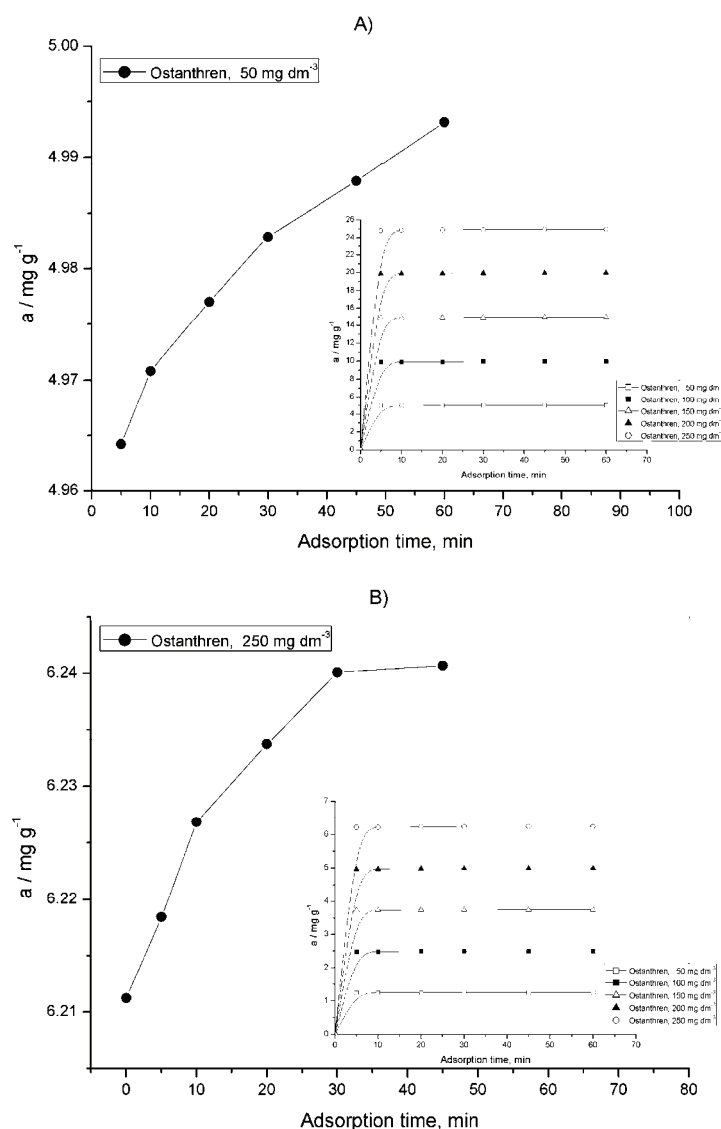
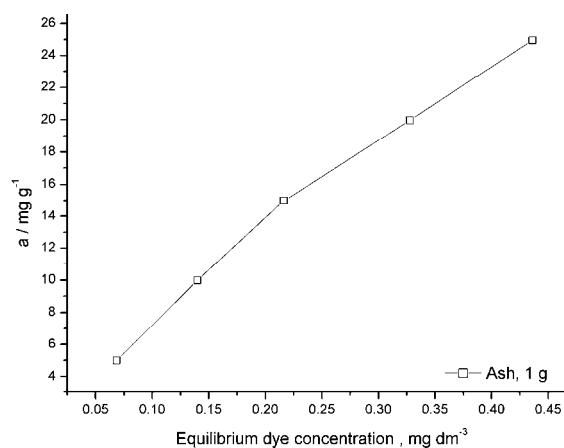
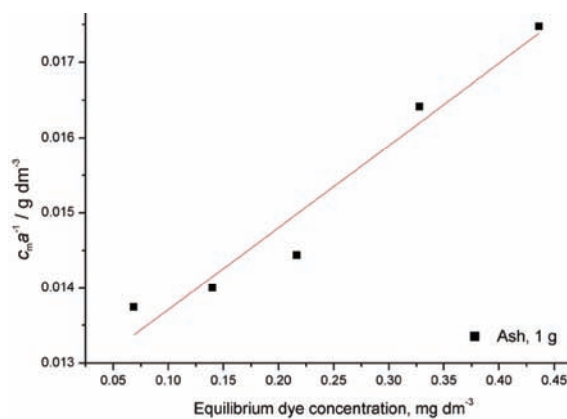


Fig. 7. Adsorbed quantity of adsorbate on adsorbent in time for different dye concentrations. A) 1g of ash; B) 4 g of ash.



(A)



(B)

Fig. 8. Langmuir adsorption isotherms for the minimum studied amount of adsorbate.

The various methods of dye adsorption on ash, as well as the analytical expressions of Langmuir isotherm and Langmuir parameters  $a_{\max}$  and  $b$ , together with the values for the coefficient of determination  $R^2$  for the Langmuir plot  $c_M/a$  vs.  $c_M$  are listed in Table I. The coefficient of determination is a relative measure of the typicality of the regression line or, in this case, a measure of the usefulness of the Langmuir model. The fact that all  $R^2$  values were greater than 0.9 showed that the Langmuir Equation fitted the experimental data very well. The maximum quantity of adsorbate that can be bound to the adsorbent,  $a_{\max}$ , or the monolayer adsorption capacity, decreased with increasing quantity of the adsorbent, while the ratio of the adsorption and desorption rate constants of the adsorbate,  $b$ , which is a constant related to the adsorption free energy, increased.

The results for the kinetics of dye sorption on ash with the minimum and maximum amounts of adsorbent and different initial dye concentrations are shown in Figs. 10 and 11. According to the linear forms of pseudo-first and pseu-

do-second order models and the obtained results, it can be concluded that adsorption rate, under the given experimental conditions, was completely described by the second order model. This was also the case with other used ash quantities (2 and 3 g).

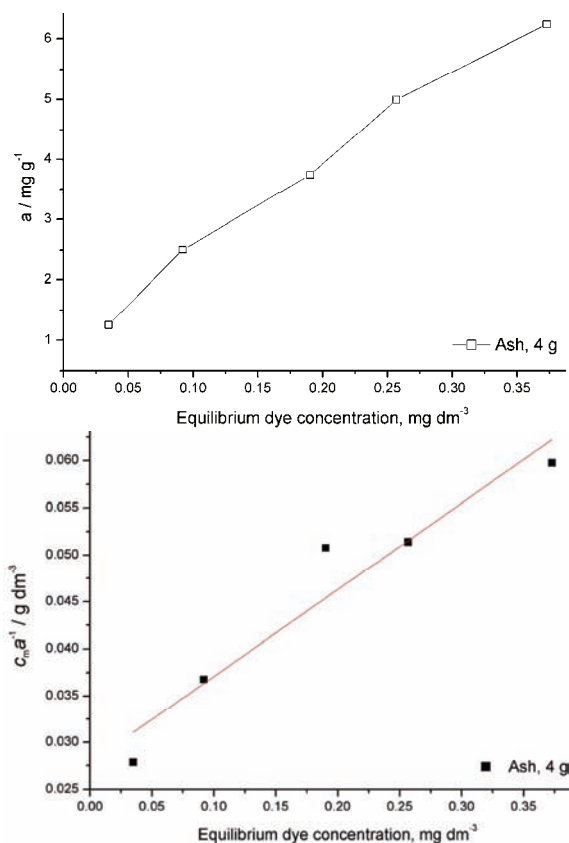


Fig. 9. Langmuir adsorption isotherms for the maximum studied amount of adsorbent.

TABLE I. Analytical expression of the Langmuir isotherm with coefficients

Mass of adsorbant, g	Analytical expression of curve (Langmuir expression)	Langmuir parameters		$R^2$
		$a_{max} / \text{mg g}^{-1}$	$b / \text{dm}^3 \text{mg}^{-1}$	
1	$c_M/a = 0.0126 + 0.0109c_M$	91.6	0.865	0.952
2	$c_M/a = 0.0190 + 0.0383c_M$	26.1	2.02	0.907
3	$c_M/a = 0.0271 + 0.0570c_M$	17.5	2.10	0.954
4	$c_M/a = 0.0279 + 0.0921c_M$	10.8	3.31	0.930

The results of the determination of the kinetic parameters for the adsorption process of vat dye on ash (equilibrium rate constant of pseudo-first and pseudo-second order kinetics) for all the studied adsorbent quantities and all the initial dye concentrations together with values of the parameter  $a_{max}$  (calculated,  $a_{max,cal}$ , and experimental,  $a_{max,exp}$ ) are listed in Table II.

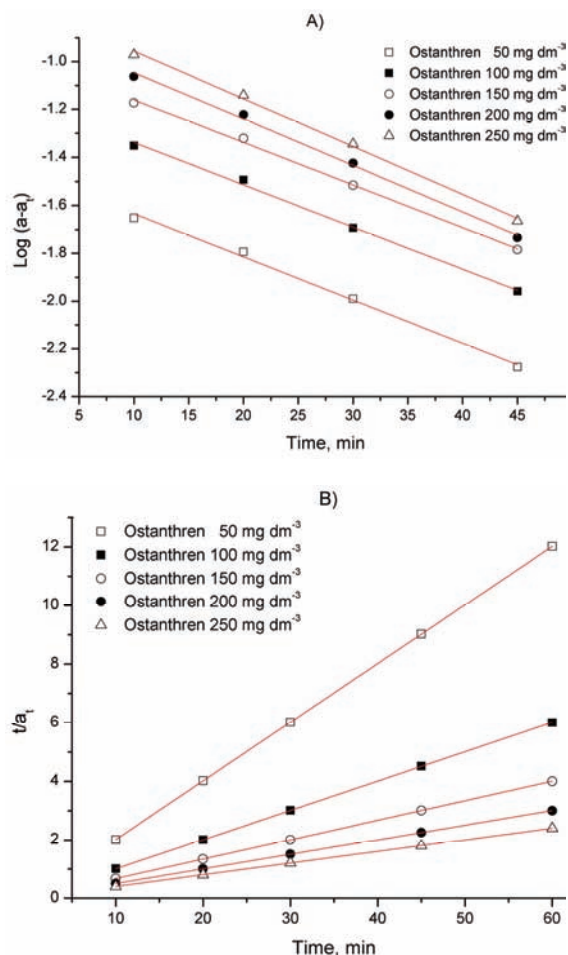


Fig. 10. Sorption kinetics of vat dye with the minimum studied adsorbent quantity; A) pseudo-first order; B) pseudo-second order.

The pseudo first and pseudo second order models were used to check the experimental data, whereby an attempt was made to explain the kinetics of the adsorption process under the given experimental condition.

Although coefficients of determination for the pseudo first order kinetics model were generally higher than 0.9 for all amounts of adsorbent and all the initial dye concentrations, much lower values of the calculated parameter  $a_{\text{max}}$  ( $a_{\text{max,cal}}$ ) were obtained compared to those of the experimental parameter  $a$  ( $a_{\text{max,exp}}$ ). Therefore, the adsorption cannot be best described by the pseudo first order kinetics model because in most cases first order equation does not cover adequately the whole range of contact times.

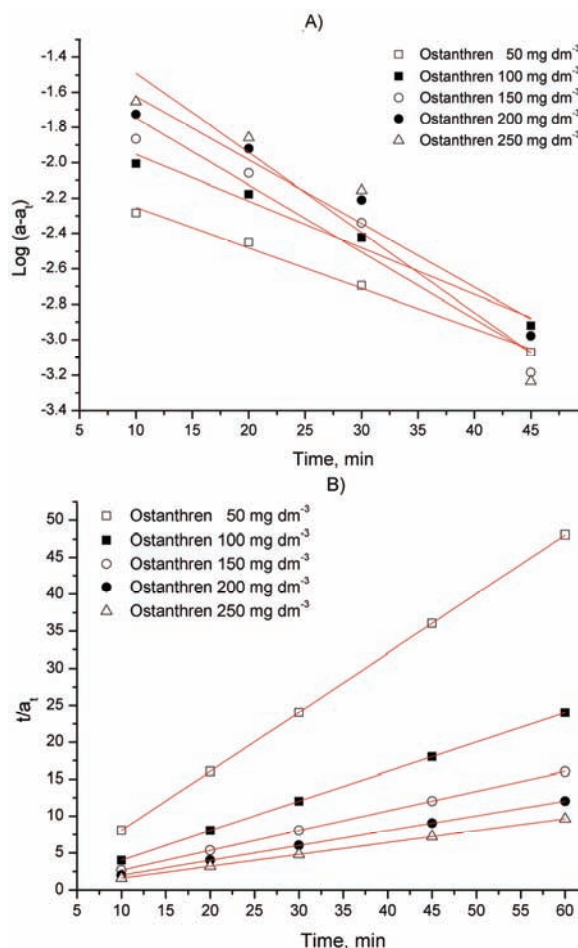


Fig. 11. Sorption kinetics of vat dye with the maximum studied adsorbent quantity; A) pseudo-first order; B) pseudo-second order.

TABLE II. Kinetic parameters of vat dye adsorption on ash ( $R^2 = 1$ , for pseudo-second order)

Absorbent quantity, g/100 cm <sup>3</sup>	Initial dye concentration, mg dm <sup>-3</sup>	$a_{max,exp}$ mg g <sup>-1</sup>	Pseudo-first order			Pseudo-second order	
			$k_1 / \text{min}^{-1}$	$a_{max,cal}$ mg g <sup>-1</sup>	$R^2$	$k_2$ g mg <sup>-1</sup> min <sup>-1</sup>	$a_{max,cal}$ mg g <sup>-1</sup>
1	50	4.99	0.042	0.035	0.997	3.59	5.00
	100	9.99	0.041	0.070	0.997	1.80	9.99
	150	15.0	0.041	0.11	0.998	1.20	15.0
	200	20.0	0.045	0.14	0.997	0.935	20.0
	250	25.0	0.046	0.18	0.998	0.764	25.0
2	50	2.50	0.040	0.018	0.998	7.15	2.50
	100	4.99	0.047	0.036	0.996	3.82	5.00
	150	7.49	0.051	0.055	0.994	2.60	7.49
	200	9.98	0.055	0.076	0.990	2.00	9.99
	250	12.5	0.056	0.095	0.989	1.63	12.5



TABLE II. Continued

Absorbent quantity, g/100 cm <sup>-3</sup>	Initial dye concentration, mg dm <sup>-3</sup>	$a_{\max, \text{exp}}$ mg g <sup>-1</sup>	Pseudo-first order			Pseudo-second order	
			$k_1 / \text{min}^{-1}$	$a_{\max, \text{cal}}$ mg g <sup>-1</sup>	$R^2$	$k_2$ g mg <sup>-1</sup> min <sup>-1</sup>	$a_{\max, \text{cal}}$ mg g <sup>-1</sup>
3	50	1.66	0.050	0.012	0.982	11.6	1.67
	100	3.33	0.057	0.025	0.971	6.05	3.33
	150	4.99	0.067	0.041	0.952	4.22	4.50
	200	6.66	0.075	0.060	0.936	3.20	6.66
	250	8.32	0.087	0.085	0.908	2.64	8.33
4	50	1.25	0.051	0.0090	0.992	15.9	1.25
	100	2.50	0.058	0.019	0.981	8.35	2.50
	150	3.74	0.080	0.034	0.944	6.10	3.75
	200	4.99	0.077	0.044	0.953	4.49	5.00
	250	6.24	0.094	0.065	0.917	3.81	6.24

As opposed to this, the pseudo-second order kinetics model had in all cases  $R^2 = 1$ , whereby full functionality was achieved and the model can be fully used to describe the adsorption process of vat dye on ash. Moreover, the differences between the calculated  $a_{\max, \text{cal}}$  and the experimental  $a_{\max, \text{exp}}$  were insignificant for this model.

#### CONCLUSIONS

Dye adsorption as a purification method has some advantages, because other processes, which include alteration or destruction of the chromophore dyes to decolorize the solution, do not remove residuals from waste waters that, as such, can still be detrimental for the environment. As opposed to this, adsorption removes the complete molecule without leaving any parts in the water. This is especially important with dyes containing metals, where bound metal (*e.g.*, Cr, Co, Cu) would remain in the waste water in cases of treatment methods other than adsorption, perhaps even in more harmful forms.

Removal of a vat dye with waste ash obtained from the “Heating Station – Leskovac” was studied under various conditions. The adsorption depended on the contact time, initial dye concentration and solution pH. The equilibrium state was achieved after a contact time of 60 min, while the % adsorption on ash was reduced on increasing the initial dye concentration in the solution, although the actual quantity of adsorbed dye was increased. A Langmuir isotherm describes the adsorption characteristics of the adsorbent in a satisfactorily manner.

The pseudo second order kinetics model fitted very well with the dynamic behavior of vat dye adsorption on natural waste ash under various conditions, with the remark that the adsorption is a very complex process.

Based on the obtained results, it can be concluded that brown coal ash is an efficient adsorbent for the removal of vat dyes from water solutions with a reasonable possibility of application on an industrial scale.

*Acknowledgment.* The financial support of the Serbian Ministry of Science and Technological Development (Project No. TP-19040A) is gratefully acknowledged.

## ИЗВОД

ДЕКОЛОРИЗАЦИЈА ТЕКСТИЛНЕ РЕДУКЦИОНЕ БОЈЕ АДСОРПЦИЈОМ  
НА ОТПАДНОМ ПЕПЕЛУ

МИОДРАГ ШМЕЛЦЕРОВИЋ, ДРАГАН ЂОРДJEВИЋ, МИЛЕ НОВАКОВИЋ и МИРЈАНА МИЗДРАКОВИЋ

*Универзитет у Нишу, Технолошки факултет, Булевар ослобођења 124, 16000 Лесковац*

Адсорпциони процес уз помоћ јефтених адсорбента могао би се декларисати као једноставна, селективна и јефтина алтернатива за пречишћавање обојених отпадних вода у односу на конвенционалне физичко-хемијске поступке. У раду је истраживана примена природног отпадног адсорбента – пепела за одстрањивање редуковане текстилне боје Ostanthren blue GCD заостале после бојења памучног текстила. Пепео добијен сагоревањем мрког угља у топлани у Лесковцу као отпадни материјал, коришћен је за пречишћавање отпадне воде текстилне индустрије, тј. отпадне воде настале после процеса бојење. Истраживан је утицај количине пепела, почетне концентрације боје, рН и времена мешања на адсорпцију. За описивање адсорпционе изотерме примењен је Ленгмиров модел. На основу аналитичког израза Ленгмировог модела нађене су константе, адсорпциони капацитет и енергија адсорпције. Кинетички модели псеудо првог и другог реда су испитивани ради оцене кинетичких података.

(Примљено 24. јула 2009, ревидирано 15. фебруара 2010)

## REFERENCES

1. E. Demirbas, M. Koboya, M.T. Sulak, *Bioresour. Technol.* **99** (2008) 5368
2. X. F. Sun, S. G. Wang, X. W. Liu, W. X. Gong, B. Y. Gao, H. Y. Zhang, *Bioresour. Technol.* **99** (2008) 3475
3. N. Emanuel, G. Kumar, *Environ. Chem. Lett.*, DOI 10.1007/s10311-0080182-x
4. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, A. A. Pelaez-Cid, *Colloids Surf. A* **254** (2005) 107
5. M. M. Nassar, M. S. El-Geundi, *J. Chem. Technol. Biotechnol.* **50** (1991) 257
6. K. R. Ramakrishna, T. Viraraghavan, *Water Sci. Technol.* **36** (1997) 189
7. O. J. Hao, H. Kim, P.-C. Chiang, *Crit. Rev. Environ. Sci. Technol.* **30** (2000) 449
8. T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol.* **77** (2001) 247
9. A. Krysztalkiewicz, S. Binkowski, T. Jesiouowski, *Appl. Surf. Sci.* **199** (2002) 31
10. R. M. Liversidge, G. J. Lloyd, D. A. J. Wase. C. F. Forster, *Process Biochem.* **32** (1997) 473
11. T. Robinson, B. Chandran, P. Nigam, *Environ. Int.* **28** (2002) 29
12. G. Annadurai, R.-S. Juang, D.-J. Lee, *J. Hazard. Mater. B* **92** (2002) 263
13. R. Sivaraj, C. Namasivayam, K. Kadirvelu, *Waste Manage. (Oxford)* **21** (2001) 105
14. T. Robinson, B. Chandrai, P. Nigam, *Water Res.* **36** (2002) 2824
15. V. K. Gupta, D. Mohan, S. Sharma, M. Sharma, *Sep. Sci. Technol.* **35** (2000) 2097
16. M. S. El-Geundi, *Water Res.* **25** (1991) 271
17. M. M. Nassar, M. F. Hamoda, G. H. Radwan, *Water Sci. Technol.* **32** (1995) 27
18. M. M. Nassar, Y. H. Magdy, *Chem. Eng. J.* **66** (1997) 223
19. M. M. Nassar, *Water Sci. Technol.* **40** (1999) 133
20. L. C. Morais, O. M. Freitas, E. P. Goncalves, L. T. Vasconcelos, C. G. Gonzalez, *Water Res.* **33** (1999) 979

21. I. Bouzaida, M. B. Rammah, *Mater. Sci. Eng. C* **21** (2002) 151
22. G. Sun, X. Xu, *Ind. Eng. Chem. Res.* **36** (1997) 808
23. J. Shore, *Colorants and auxiliaries: organic chemistry and application properties*, Society of Dyers and Colourists, Bradford, 2002, p. 45
24. Lj. Vračar, A. Despić, V. Dražić, K. Đorđević, D. Jovanović, S. Jovanović, M. Maksimović, B. Nikolić, D. Ovcin, D. Šepa, *Experimental Physical Chemistry*, Faculty of Technology and Metallurgy, Belgrade, 1987, p. 237 (in Serbian)
25. [http://www.eps.rs/publikacije/Zastita\\_zivotne\\_sredine/EPS\\_Zastita\\_zivotne\\_sredine.pdf](http://www.eps.rs/publikacije/Zastita_zivotne_sredine/EPS_Zastita_zivotne_sredine.pdf)
26. A. Jakob, S. Stucki, P. Kuhn, *Environ. Sci. Technol.* **29** (1995) 2429
27. M. S. Wang, L. C. Wang, C. C. Wang, *J. Hazard. Mater.* 133 (2006) 177
28. S.I. Shih, Y.F. Wang, J.E. Chang, J.S. Jang, F.L. Kuo, L.C. Wang, G.P. Chang-Chien, *J. Hazard. Mater.* **137** (2006) 1817
29. B. Bayat, *Water Air Soil Pollut.* **136** (2002) 69
30. G. Gupta, N. Torres, *J. Hazard. Mater.* **57** (1998) 243
31. J. Ayala, F. Blanco, P. Garcia, P. Rodriguez, J. Sancho, *Fuel* 77 (1998) 1147
32. B. Bayat, *J. Hazard. Mater.* **3** (2002) 251
33. B. Bayat, *J. Hazard. Mater.* **3** (2002) 275
34. Y. M. Kuo, T. C. Lin, P. J. Tsai, *J. Hazard. Mater.* **133** (2006) 75
35. C. A. Johnson, S. Brandenberger, P. Baccin, *Environ. Sci. Technol.* **29** (1995) 142
36. S. Aricke, T. Van Gerven, C. Vandecasteele, *J. Hazard. Mater.* **137** (2006) 235
37. J. Iori, J. Balg, *Residue Treat.* **6** (1995) 9
38. S. Sakai, M. Hiraoka, N. Takeda, T. Tsunemi, *Water Sci. Technol.* **22** (1990) 329
39. J. P. Young, H. Jong, *J. Hazard. Mater. B* **9** (2002) 89
40. V. Gundula, *Color Technol.* **122** (2006) 317
41. A. Mishra, M. Bajpai, *Bioresour. Technol.* **97** (2006) 1055.