

LOW COST REMOVAL OF DIRECT DYE FROM AQUEOUS SOLUTION USING WASTE ASHES

UDC677.027.42+662.613:541.183.3

**Miodrag Smelcerovic¹, Dragan Djordjevic¹,
Milorad Cakic¹, Snezana Urosevic²**

¹University of Nis, Faculty of Technology, Leskovac, Serbia

²University of Belgrade, Technical Faculty, Bor, Serbia

Abstract. *The paper deals with the adsorption of direct dye from aqueous solution onto waste ashes prepared from the heating station of Leskovac (Serbia). Waste ashes are used removal of colour from textile wastewater. Based on the results, it can be said that the waste ashes are an efficient adsorbent for the removal of direct dye from aqueous solution. Prolonged contact time implies a greater amount of color on the adsorbent, i.e. the dye concentration in the solution decreases with the adsorption duration. The typical graphical representation obtained from the Freundlich equation shows that this model provides a sufficiently accurate description of the experimental data of dye adsorption on waste ashes as opposed to the Langmuir model.*

Key words: *waste ashes, direct dyes, adsorption, Langmuir model, Freundlich model.*

1. INTRODUCTION

The first bigger challenge in the field of adsorption modeling is the selection of the most promising types of adsorbate and adsorbent, mainly in terms of higher capacity and adsorption rate, high selectivity and low cost. The next real challenge is to clearly identify the mechanism of adsorption, particularly of interactions that are involved in the adsorbent/adsorbate bond [1-4]. Adsorption properties and equilibrium data, known as adsorption isotherms, describe how the adsorbate reacts with the adsorbent, and therefore, they are crucial for the selection and wider application. A precise mathematical description of adsorption equilibrium is indispensable for the accurate prediction of adsorption

Received March 25, 2015 / Accepted February 5, 2016

Corresponding author: Dragan Djordjevic

Faculty of Technology, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia

E-mail: drag_64@yahoo.com

parameters and quantitative comparison of the adsorption behavior of different factors (or in different experimental conditions) within any of the suggested systems [5, 6].

This paper deals with the proceedings of the absorption of direct dye on ashes and can represent the model for decolourization - purifying of the dyed waste waters after cotton dyeing process, by the help of a cheap adsorbent, which by its own represents the waste material. The aim is to acquire an undyed influent, observed visually, and which could be released out in the environment. A dye that is relatively frequently used for dyeing of natural cellulose fibers of textile materials has been deliberately used in darker tints, taking into account that the hue of the waste water is visually detectable, on one hand and the fact that the darker tints are harder to remove from the lighter tints, on the other hand.

2. EXPERIMENTAL

2.1. Materials and methods

As an adsorbent, bottom ash from the city heating station was used obtained from brown coal combustion. After collecting and draining, a sifting was carried out scaling its particles to 0,3 mm. To increase functionality demineralization of ash was performed by treating it with 7 % H_2SO_4 for 120 min followed by copious rinsing with water, repeated treating with acid and eventually adjusting pH of water ash slurry between 7 and 8.

The dye used belongs to the group of direct dyes, C.I. Direct Blue 71, soluble in water, 10 g/L (60°C), 20 g/L (97°C) and exists in the anionic form, soluble in ethanol and insoluble in other organic solvents, Fig. 1. It is used for dyeing cotton and viscose fibers, rayon, paper, leather and, to a lesser extent, nylon [7, 8].

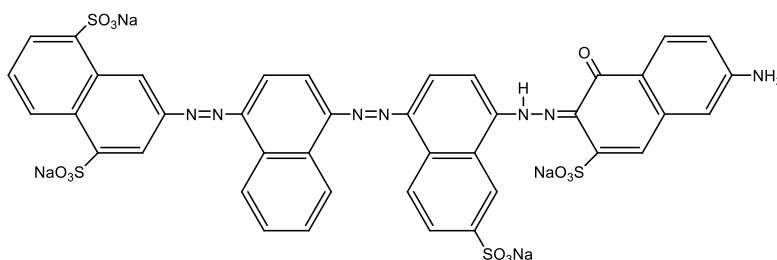


Fig. 1 Structure of direct dye

The process of adsorption was carried out in the glass Erlenmeyer flasks into which an adsorbent in the solution of a dye, adsorbate, was suspended. Erlenmeyers were set on the agitator-shaker operating on 135 rpm on certain temperature and were kept for certain time. The amount of ash was 4 g, while the solution, in the constant amount of 100 mL, comprised dyes of concentration, 50, 100, 150, 200, 250 mg/L, respectively. The time of processing, along with the constant mixing, was 5, 10, 20, 30, 40 min, while the pH of the solution varied from 2 to 10, regulated by adding 1M of sulphuric acid solution or sodium hydroxide.

After the adsorption, the solutions of dyes and ashes were filtrated through the filter paper. What follows is the determination of the solution adsorption on the spectrophotometer UV-VIS spectrophotometer (Cary 100 Conc UV-VIS, Varian) on 616 nm.

SEM measurements were carried out on the device VEGA TS 5130mm (Tescan) by using the detector for secondary electrons. The used ashes is a relatively fine-diffused material with heterogeneous particles, dismembered shape and form which are derived from the agglomerate of certain minerals, generally below 10 μm in size. Micrograph from the Fig. 2 gives the view with the amplification of 500 times.

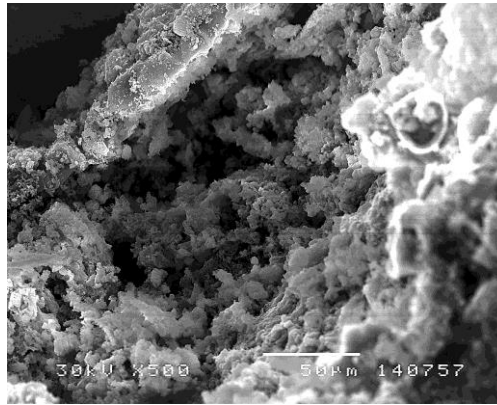


Fig. 2 Micrograph of the adsorbent used (waste ashes)

The degree of dye removal was calculated based on the dye concentration before and after treatment [9, 10]:

$$R = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (1)$$

where C_0 and C_t are the initial and final concentrations of dye solutions, respectively.

The amount of dye adsorbed (adsorbate) per unit mass of waste ashes (adsorbent), q_t (mg/g), was determined as follows [9, 10]:

$$q_t = \frac{(C_0 - C_t) \cdot V}{M} \quad (2)$$

where: M , g – mass of adsorbent, V , L – volume of solution from which adsorption is carried out.

For the processing of the experimental data *Langmuir* adsorption isotherms was used in the following form [11, 12]:

$$q_e = \frac{Q_0 \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (3)$$

where: q_e , mg/g is the adsorbed amount of adsorbate per unit mass of adsorbent, C_e , mg/L is the equilibrium molarity of adsorbate in solution; Q_0 , mg/g is *Langmuir* equilibrium constant or the maximum amount of adsorbate that can be bonded to adsorbent; b , L/mg is *Langmuir* equilibrium constant representing the relation of the adsorption rate constants and desorption rate constants of the adsorbate

Also, adsorption was analyzed using *Freundlich model* [11, 12]:

$$q_e = K_F \cdot C_e^{1/n} \quad (14)$$

where K_F - *Freundlich* constant, n - constants characteristic of the observed system: adsorbent, adsorbate and solvent.

3. RESULTS AND DISCUSSION

It is well known that the surface of ashes acquires a positive charge absorbing hydrogen ion (H^+) after immersion in water. In case of low pH and increased concentration of H^+ ions in the system, the ashes surface intensively acquires a positive charge [11]. In our case, the adsorption maximum occurred at pH 2 - 3 for dye solution, i.e. in strongly acidic media, Figure 3.

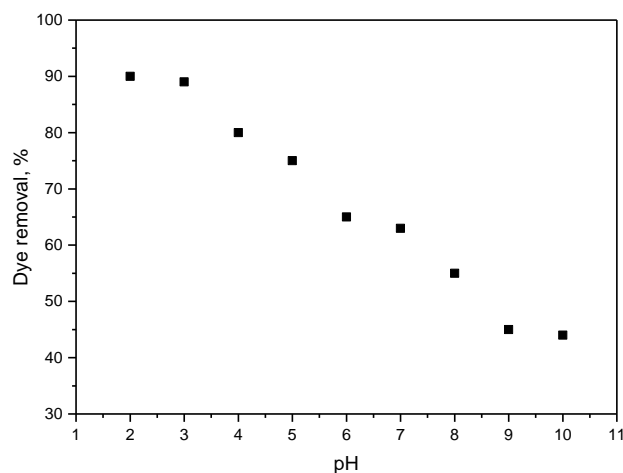


Fig. 3 The influence of pH on the removal of direct dye from aqueous solution by adsorption on waste ashes (adsorption time 40 min, dye concentration 250 mg/L)

Anyway, the increase or decrease in the percentage of dye removal depending on the pH of the solution should be considered in light of changes in the dye structure and condition of the ashes surface layer. As in the acidic condition the positive charge on the surface of the adsorbent is dominant and there is a significant electrostatic attraction between the positively charged surface of the adsorbent and anions from direct dye.

The effect of contact duration on adsorption, i.e. changes in adsorbate amounts adsorbed on the adsorbent with time for different initial concentrations of direct dye, is shown in the diagram in Figure 4.

Based on the results from the above mentioned diagram, it can be confirmed that the amount of dye adsorbed on waste ashes increases with time, i.e. the dye concentration in the solution decreases with the duration of the adsorption. Therefore, there is continuity in change over time, i.e. a longer period of time gives a larger amount of adsorbed dye per unit mass of adsorbent. Also, at the highest concentration of dye there is the highest adsorption, as expected. At lower concentrations, there is a higher percentage of dye removed. On the other hand, a general look at the parameters, the percentage of adsorbed dye and dye concentration, shows that the amount of dye adsorbed by waste ashes is actually higher at the highest initial concentration.

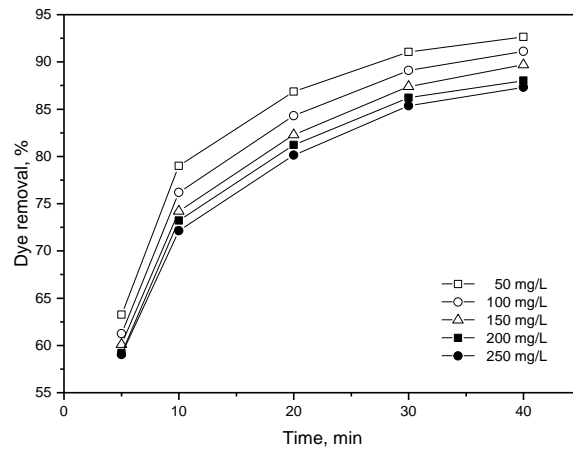


Fig. 4 The effect of adsorption time on the amount of direct dye removed

Figure 5 shows dye concentration in the solution depending on the duration of the adsorption on waste ashes. It can be noticed that in all cases the longer duration of the process reduces the dye concentration in the solution, as was expected, and somewhat more intensely at higher initial concentration of dye. Also, the amount of residual dye after a period of 40 min (equilibrium time) was higher at higher initial concentrations.

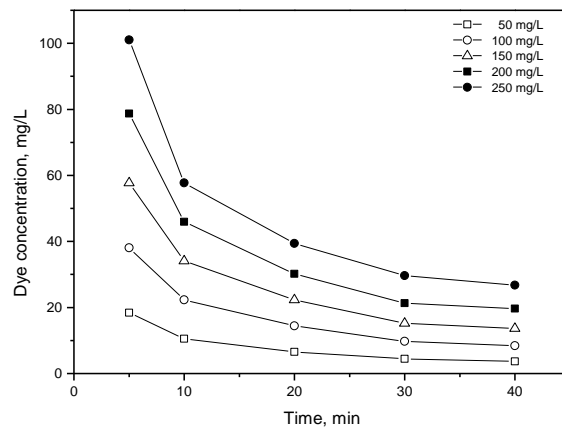


Fig. 5 Variations of direct dye quantity in the solution during adsorption on waste ashes

The results of changes in the adsorbed quantity of adsorbate on the adsorbent with time for different initial concentrations of both dyes and different amounts of ashes are shown in the diagram in Figure 6. There is a continuity of changes in time, i.e. longer periods of time bring larger amounts adsorbed per unit mass of adsorbent. Also, the largest adsorption occurs at the highest dye concentration.

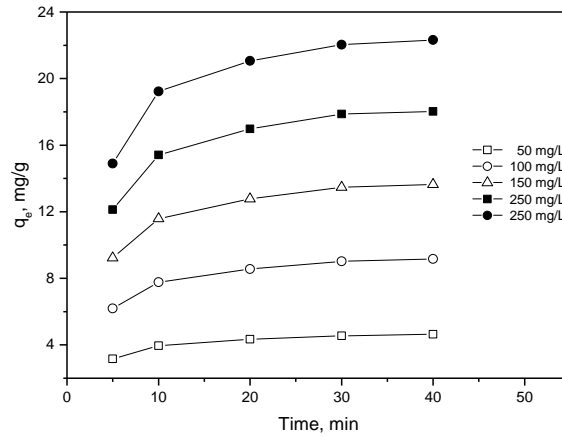


Fig. 6 Adsorbed amount of adsorbate on the adsorbent for various initial direct dye concentrations in a period of time

The diagrams in Figure 7 show *Langmuir* adsorption isotherms in various forms to describe the adsorption of direct dye on the waste ashes.

It is evident that here, too, the adsorption curves are smooth and continuous, which leads to saturation at different concentrations on the interphase of the adsorbent materials.

In Figure 8, the diagram to the right, i.e. from the slope and intercept of the functional straight line obtained by the fitting procedure, the values of *Langmuir* constants Q_0 and b were determined for the adsorption of direct dye on the ashes.

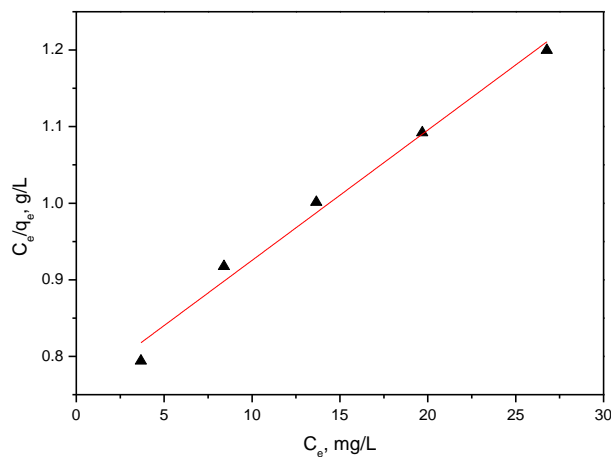


Fig. 7 Langmuir adsorption isotherms in case of direct dye – waste ashes system

The results related to the coefficients of *Langmuir* isotherm for the given experiment are provided in Table 1. The table also shows the values of the determination coefficient R^2 for *Langmuir* diagram $C_e/q_e - C_e$. The determination coefficient mentioned is a relative measure of the representativeness of the regression line, or measures of usefulness of *Langmuir* model. In cases where $R^2 = 1$, the bond is functional or linear, i.e. all the points in the scatter diagram lie on the regression line. Consequently, the model is more representative when the determination coefficient is closer to 1 [13].

According to the results, *Langmuir* model may be acceptable ($R^2 > 0.98$) for the description of the adsorption of direct dye on the waste ashes. Practically, this sorption model is used to determine the maximum value of uptake or total capacity of adsorbent for dye (Q_0) and the constant b , which represents the affinity between the adsorbent and adsorbate. The parameter b – energy (rate) of adsorption can be correlated with the variation of the surface and porosity of adsorbent. This parameter is related to the free energy of adsorption, ΔG ($b \propto e^{-\Delta G/RT}$), and shows the affinity of adsorbent for dye binding. Higher values of b obtained for the direct dye - waste ashes system mean stronger binding of dye to ashes [14].

Table 1 Langmuir equation and coefficient for direct dye – waste ashes system

Equation	Coefficients		
	Q_0 (mg/g)	b (L/mg)	R^2
$C_e/q_e = 0.755 + 0.017 \times C_e$	58.79	0.022	0.987

Characteristics of *Langmuir* isotherm can be expressed by a dimensionless constant, the equilibrium parameter R_L [13], $R_L = 1/(1 + bC_0)$.

The value of R_L indicates whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). From the values of b (Table 2) and the highest initial dye concentration (250 mg/L) it follows that R_L is 0.15, i.e. between 0 and 1, i.e. the adsorption is suitable for the adsorbent used.

Unlike the *Langmuir* isotherm, *Freundlich* model does not assume either homogeneous site energy or limited levels of sorption. This model, recognized as the earliest known empirical equation, is consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. It is an empirical equation used to describe multilayer adsorptions with interaction between the adsorbed molecules. The model predicts that the dye concentration on waste ashes would increase until there is an increase in dye concentration in the solution (not limited to the monolayer in the adsorbent). The model applies adsorption on heterogeneous surfaces with a uniform distribution of energy and reversible adsorption [14].

The diagram in Figure 8 represents the *Freundlich* model for the adsorption of direct dye on the ashes. There is an extremely high level of functionality of the variables, which was not the case with the *Langmuir* model. *Freundlich* constants were determined based on these diagrams, and they were also used to determine the eligibility of the model in order to describe the dye adsorption process in the ashes.

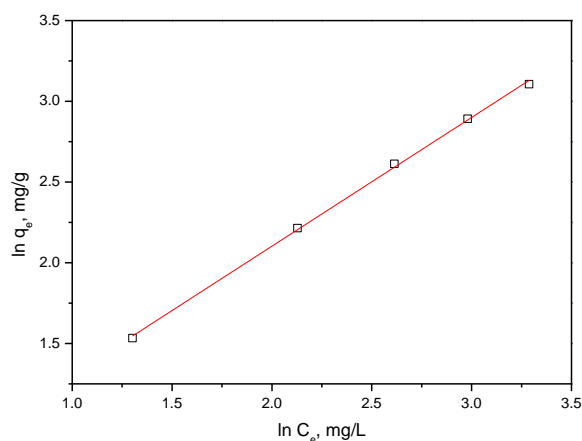


Fig. 8. Freundlich adsorption isotherm for direct dye – waste ashes system

One of the *Freundlich* constants, K_F , is used as a relative measure of adsorption capacity. Higher value of K_F indicates a higher adsorption capacity. The other *Freundlich* constant, n , is an empirical parameter that varies with the level of heterogeneity indicating the degree of nonlinearity between dye uptake and concentration of non-adsorbed color. In general, $1/n < 1$ illustrates that the adsorbate has been conveniently adsorbed on the adsorbent, that the adsorption capacity is growing and new adsorption sites have been formed. Also, it has been noticed that, the greater the value of n the greater the intensity of adsorption is. That is, if $n = 1$, the adsorption is linear, i.e. adsorption sites are homogeneous and there is no interaction between the adsorbed particles. If $1/n > 1$, the adsorption is unfavorable, the adsorption bonds become weaker and adsorption capacity decreases [14].

The results in Table 2 confirm that n is greater than 1, i.e. $1/n < 1$, which shows that direct dye adsorbs well to the adsorbent under all test conditions. Also, according to the results given in Table 2, the coefficient of determination of *Freundlich* isotherm is greater than those obtained for the *Langmuir* expression, reaching the value of 1 (0.999), which represents the absolute functionality. This means that the *Freundlich* isotherm or model that does not follow the ideal monolayer adsorption is given priority in this equilibrium study.

Table 2 Freundlich equation and coefficients in case of direct dye – waste ashes system

Equation	Coefficients		
	n	K_F	R^2
$q_e = 1.66 \times C_e^{0.797}$	1.25	1.66	0.999

4. CONCLUSION

Removal of direct dyes using waste ashes was investigated under various conditions. It was found that the adsorption depends pH on the solution, contact time and the initial dye concentration.

Based on these results, we can conclude that the waste ashes are an efficient adsorbent for removal of direct dye from aqueous solutions with a justified tendency of application in industrial conditions.

Based on the experimental results the following conclusions can be drawn:

- Differences in the dye adsorption depending on pH of the solution indicate that this parameter is of significant importance for the adsorption of the dye applied.
- Prolonged contact time means a greater amount of dye on the waste ashes, i.e. the dye concentration in the solution decreases with the duration of the adsorption.
- The percentage of the removed dye decreases the increase of the initial dye concentration in the solution, but the actual amount of the adsorbed dye increases with the increase of dye concentration.
- A typical representation obtained from *Langmuir* equation shows that this model provides a good but not exactly accurate description of the experimental data.
- A typical representation obtained from the *Freundlich* equation confirms that this model provides a sufficiently accurate description of the experimental data.

The results obtained in this work indicate the opportunity for a practical application of water coloration removal in the textile industry, thus providing the support to environmental protection both from economic and practical perspective.

REFERENCES

1. Anastopoulos, I., Kyzas, G. Z., (2014), Agricultural peels for dye adsorption: A review of recent literature, *Journal of Molecular Liquids*, Vol. 200, Part B, 2014 pp. 381 - 389.
2. McKay, G., (1996), Use of Adsorbents for the Removal of Pollutants from Wastewaters, CRC Press, Boca Raton, pp. 125-150, 1996, Hardcover ISBN 0-8493-6920-7.
3. Jarusiripot, C., (2014) Removal of Reactive Dye by Adsorption over Chemical Pretreatment Coal based Bottom Ash, *Procedia Chemistry*, Vol. 9, 2014 pp. 121-130.
4. Pala, A., Tokat, E., (2002), Color removal from cotton textile industry wastewater in an activated sludge system with various additives, *Water Research*, Vol. 36, 2002 pp. 2920-2925.
5. Yagub, M. T., Sen, T. K., Afroze, S., Ang, H. M., (2014), Dye and its removal from aqueous solution by adsorption, A review, *Advances in Colloid and Interface Science*, Vol. 209, 2014 pp. 172-184.
6. Duta, A., Visa, M., (2015), Simultaneous removal of two industrial dyes by adsorption and photocatalysis on a fly-ash-TiO₂ composite, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 306, 2015 pp. 21-30.
7. Amin, N. K., (2009), Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, *Journal of Hazardous Materials*, Vol. 165, 2009 pp. 52-62.
8. Kuo, C. Y., Wu, C. H., Wu, J. Y., (2008), Adsorption of direct dyes from aqueous solutions by carbon nanotubes: Determination of equilibrium, kinetics and thermodynamics parameters, *Journal of Colloid and Interface Science*, Vol. 327, 2008 pp. 308-315.
9. El-Mekkawi, D., Galal, H. R., (2013), Removal of a synthetic dye "Direct Fast Blue B2RL" via adsorption and photocatalytic degradation using low cost rutile and Degussa P25 titanium dioxide, *Journal of Hydro-environment Research*, Vol. 7, 2013 pp. 219-226.
10. Cheng, Z., Zhang, L., Guo, X., Jiang, X., Li, T., (2015), Adsorption behavior of direct red 80 and congo red onto activated carbon/surfactant: Process optimization, kinetics and equilibrium, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol. 137, 2015 pp. 1126-1143.
11. Amin, N. K., (2008), Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith, *Desalination*, Vol. 223, 2008 pp. 152-161.
12. Isa, M. H., Lang, L. S., Asaari, F. A. H., Aziz, H. A., Ramli, N. A., Dhas, J. P. A., (2007), Low cost removal of disperse dyes from aqueous solution using palm ash, *Dyes Pigments*, Vol. 74, 2007 pp. 446-453.

13. Sun, D., Zhang, X., Wu, Y., Liu, X., (2010), Adsorption of anionic dyes from aqueous solution on fly ash, *Journal of Hazardous Materials*, Vol. 181, 2010 pp. 335-342.
14. Gimbert, F., Morin-Crini, N., Renault, F., Badot, P., Crini, G., (2008), Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: Error analysis, *Journal of Hazardous Materials*, Vol. 157, 2008 pp. 34-46.

JEFTINO UKLANJANJE DIREKTNE BOJE IZ VODENOG RASTVORA KORIŠTENJEM OTPADNOG PEPELA

Rad se bavi adsorpcijom direktne boje iz vodenom rastvoru na otpadnom pepelu dobijenom iz Leskovačke toplane (Srbija). Otpadni pepeo je korišćen za smanjenje obojenja tekstilnih otpadnih voda, na primer. Na osnovu rezultata, može se reći da je otpadni pepeo efikasan adsorbent za uklanjanje direktne boje iz vodenog rastvora. Duži vreme kontakta znači veću količinu boje na adsorbentu, odnosno koncentracija boja u rastvoru opada sa trajanjem adsorpcije. Tipični grafički prikaz dobijen iz Freundlich jednačine dokazuje da je ovaj model pruža dovoljno precizan opis eksperimentalnih podataka za adsorpciju boje na otpadnom pepelu nasuprot Langmuir modelu.

Ključne reči: *otpadni pepeo, direktna boje, adsorpcija, Langmuir model, Freundlich model.*