Kinetics Study of Methylene Blue Adsorption Onto Activated Carbon by Means of Spectrophotometry

Dijana Jelić[1], Jelena Penavin-Škundrić[2], Željka Marjanović-Balaban[3], Vesna Antunović[1], Nataša Radulj[1]

[1]University of Banjaluka, Medical faculty, Pharmacy department, Boulevard Vojvode Petra Bojovica 1a, 78000 Banja Luka, Bosnia and Herzegovina, e-mail: dijana_jelic@hotmail.com
[2]University of Banjaluka, Technology faculty, Boulevard Vojvode Stepe Stepanovica 73, 78000 Banja Luka, Bosnia and Herzegovina
[3]University of Banjaluka, Forestry faculty, Boulevard Vojvode Stepe Stepanovića 75a, 78000 Banja Luka, Bosnia and Herzegovina

Abstract: Goal of this work is to explore adsorption phenomenon of methylene blue on activated carbon. The adsorption process was monitored at 30 ⁰C and 50 ⁰C. We used spectrophotometric method for concentration estimation and on the basis of obtained results we proposed kinetics mechanism and equilibrium isotherms. Adsorption has been found to be an efficient and economically cheap process to remove pollutants such as colors, dyes and metal impurities. Adsorption processes using activated carbons are widely used to remove pollutants from wastewater. By fitting experimental results, pseudo-second order and Elovichev model gave very satisfactory results with the correlation coefficient R = 0.99994 and R = 0.99973, successively. Equilibrium isotherms of the methylene blue on the activated carbon were determined and correlated with common isotherm equation Freundlich, Langmuir and Temkin model. Rate of adsorption increased with increase in experimental temperature, which goes in favor of endothermic process. Adsorption of methylene blue onto activation carbon is happening probably through chemisorption path.

Keywords: activated carbon, methylene blue, kinetics, adsorption.

Introduction

Dye pollution presents a significant problem in industry. Dyes have been used in paper, cosmetics, textile, plastics, pharmaceuticals and food industries for a long time. It is estimated that 10-15% of dye is dicharged into wastewater. This water contains a variety of organic compounds and toxic substance which are very harmful to fish and other aquatic organism. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganism and may cause direct destruction or inhibition of their catalytic capabilities. Among the various types of dyes, the highest rates of toxicity were found among basic and diazo direct dyes. Methylen blue, a cationic dye is used in microbiology, surgery, diagnostics and as a sensitizer in photo-oxidation of organic pollutants. Methylen blue dye causes eye burn, if ingested produces vomiting, mental confusion and methemoglobinemia.

Many treatment methods have been used to remove the dyes from wastewater. These methods can be divided into physical, chemical and biological methods (Seshardi et al., 1994) (Ciardelli & Ranier,i 2001) (Issac, 1996). Among variouos methods, adsorption is an effective process for a wide variety of application. It is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewater. Dye removal from wastewater has received considerable attention with several adsorbents and several classes of dyes being investigated. The removal of dye wastewater, particulary, by

activated carbon has been reported widely (Seshardi et al., 1994) (Ciardelli & Ranier,i 2001) (Issac, 1996) (Tang & Huren 1995) (Ramakrishna & Viraraghavan 1997) (Avom et al., 1997). Activated carbon is well known for its high surface area due to the presence of micro and meso pores. Since, activated carbon is expensive, there are many less expensive materials proposed, such as bamboo grass, corncob, plum kernels, jute fiber, rice husks, olive stones, palm-tree cobs, fruit stones and nutshells (Issac, 1996) (Tang & Huren 1995) (Ramakrishna & Viraraghavan 1997) (Avom et al., 1997) (Wu et al., 1999). Concerning literature, removal of dyes by activated carbon is economically favorable and technically easy. Adsorption processes using activated carbon are widely used to remove pollutants from wastewater. The successful prediction of adsorption isotherms of dyes on activated carbon has been reported. Y. Zhu et al., (Y. Zhu et al., 2009) described methylen blue adsorption on activated carbon by Langmuir model the best, determing the adsorption capacity on 30 ^{0}C - 58,48 mg/g, 40 ^{0}C - 64.10 mg/g and 50 ^{0}C - 69.93 mg/g. It was suggested that investigated adsorption state is between chemical and physical adsorption. Z. Shahryari et al. (Z. Shahryari et al. 2010) calculated thermodynamic parameters, such as ΔG°, ΔH° and ΔS°. Obtained negative value of free Gibbs energy goes in favor of spontaneous process in nature and the positive value of enthalpy presents endothermic character of a adsorption process. Sips isotherm model was found to fit the best. It has been reported in available literature that over 25 kinetics models have been referenced, all in attempt to describe quantitatively the kinetic behaviour of adsorption process (Santhly & Selvapathy, 2006). Even though, adsorption process of methylen blue on activated carbon is still ambigous, for each adsorption kinetic model has its own limitation and it is largely conected with certain experimental and theoretical assumption.

The aim of this work is to evaluate mechanism and to determine equalibrium isotherms of methylen blue adsorption on activated carbon on two different temperatures. In order to understand the process of adsorption, knowledge of kinetics is essential. Three kinetic models and three equalibrium isotherms were used. All the adsorption data were obtained by means of spectophotometric method, which were fitted in theoretical models in order to see which kinetic model and which isotherms describes the process of adsorption the best.

Materials and Methods

In experimental work we used methylen blue (Merck, molar mass - 320 g/mol) and activated carbon (for analysis, molar mass - 12.01 g/mol). Ultrapure water was used for preparing all the solutions and reagents. A stock of solution of methylen blue was prepared by dissolving 1.0 g in 1 L of ultrapure water and the solutions for adsorption process were prepared from the stock solution to the desired concentration by successive dilutions. The experiments were carried out in a set of erlenmayer flasks where proper amount od activated carbon and 50 mL dye solutions of desired concentration were added. Samples were kept for 6 h at isothermal conditions 30 ^{0}C and 50 ^{0}C in order to reach equalibrium of the solid-solution mixture. Initial concentration of methylen blue were in range of 100 - 500 mg/L. The concentration of methylen blue were determined by spectophotometric measurement at 650 nm by Shimadzy 1800 UV. The amount of adsorption at equalibrium was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where C_o and C_e are the concentration of methylen blue at initial and equilibrium state. V is the volume of the solution and W is the mass of activated carbon.

D. Jelić, et al.:
Kinetics Study of Methylene Blue Adsorption Onto Activated Carbon by Means of Spectrophotometry
Quality of Life (2014) 5(3-4):107-113

Adsorption isotherms and kinetic models

The following models were used to describe the adsorption kinetics behaviour: Pseudi-first order, pseudo-second order and Elovich model.

- Pseudo first order is expressed by equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where $(g\ mg^{-1}\ min^{-1})$ is constant rate and (min) is the time. After integration process (t = 0 to t = t, q = 0 to q = q$_t$) we got:

$$q_t = q_e\,(1 - e^{-k_1 t}) \tag{3}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The adsorption rate constant can be experimentally determined by the slope of linear plots $\ln(q_e - q_t)$ vs. t.

- Model of pseudo-second order is expressed by:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

After few mathematical steps final form of pseudo-second order is as follows:

$$\frac{t}{q_t} = \frac{1}{q_e^2} \times \frac{1}{k_2} + \frac{1}{q_e}t \tag{6}$$

where k_2 $(g\ mg^{-1}\ min^{-1})$ is adsorption rate constant of pseudo-second order. By plotting t/q_t vs. t, q_e and k_2 can be determined as slope and intercept.

- One of the most useful models to describe gas/liquid adsorption on solid surface is Elovich model. This model is presented by equation 7, which after integration is expressed in the form of equation 8.

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{7}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{8}$$

where α $(mg\ g^{-1}\ min^{-1})$ is the initial adsorption rate and β $(g\ mg^{-1})$ is desorption constant during each experiment.

Adsorption isotherms

Adsorption isotherms can provide very valuable information concerning description of how adsorbates will react with adsorbent and are essential for optimizing the use of adsorbent. Several mathematical models can be used to describe adsorption phenomenon. We employed Langmuir, Freundlich and Temkin isotherms for interpretation of obtained adsorption data.

- The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent. This mathematical form of isotherm was found to describe the best monolayer adsorption. The Langmuir isotherm can be written in the form of:

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

where q$_m$ and K$_L$ are related to the adsorption capacity and energy of adsorption, successively.

- Freundlich isotherm describes the best heterogeneous systems by equation:

$$qe = K_F Ce^{1/n} \tag{10}$$

K_F is a constant which represents adsorption capacity of the adsorbent and n is an empirical constant related to the magnitude of the adsorption driving force.

- Temkin isotherm takes into account the interaction of sorbate/adsorbate and because of these interaction the heat of adsorption of all molecules in the layer will decrease linearly with coverage. Temkin isotherm has following mathematical form:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \tag{11}$$

where K_T is the equilibrium binding constant related to the heat of adsorption.

Kinetics of adsorption of methylen blue

In order to get insight in the kinetics of adsorption of methylen blue on activated carbon, three models were used, namely pseudo-first order, pseudo-second order and Elovich model. By fitting experimental data, pseudo-second order and Elovich model gave satisfactory results. Figure 1 and 2 present pseudo-second order and Elovich model. Table 1 and Table 2 present all the relevant constants for pseudo-second order and Elovich model according to equation 5 and 8, successively.
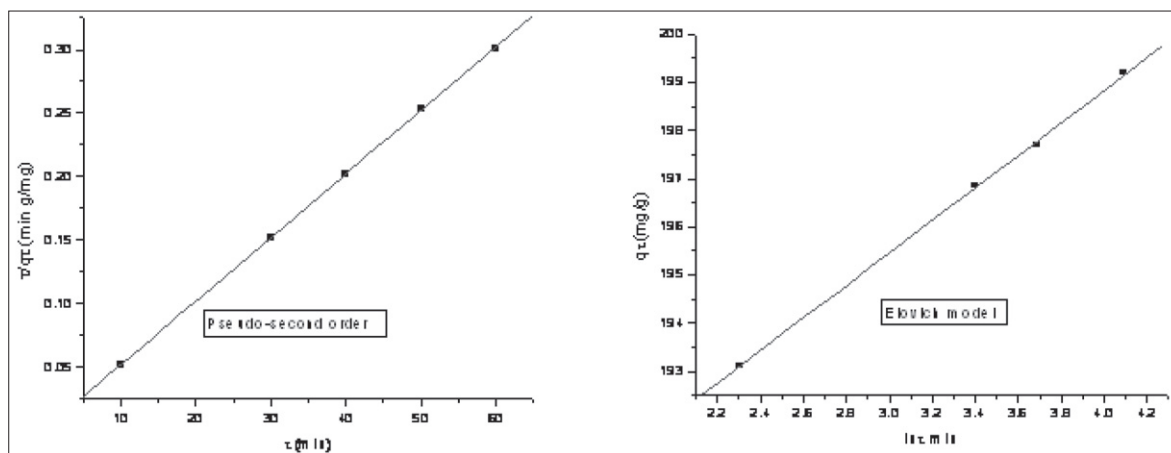

Figure 1 and Figure 2. Kinetics of pseudo-second order (left) and Elovich model (right) for methylen blue onto activated carbon

Table 1. Kinetics constants for pseudo -second order

Parameter	Value
q_e	200
k_2	0.01163
R	0.99994

Table 2. Kinetics constants for Elovich model

Parameter	Value
β	0.296
α	185.35
R	0.99973

Adsorption isotherms

As presented in introduction, three equilibrium isotherms were used: Langmuir, Freundlich and Temkin. On the basis of R value (Table 3) we can conclude that Langmuir isotherm gave the best fit between theory and experimental data. This goes well with literature data concerning adsorption kinetics of methylen blue on activated carbon (Zhu Y et al. 2009) (Yasin Y et. al., 2007).

Table 3. Correlation coefficient for Langmuir, Freundlich and Temkin isotherms

Temperature	Langmuir	Freundlich	Temkin
30 ^{0}C	0.99138	0.93917	0.9656
50 ^{0}C	0.99758	0.95992	0.9713

Langmuir isotherm provides calculation of parameter R_L which describes the adsorption process. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). R_L values for 30 ^{0}C and 50 ^{0}C were 0.3736 and 0.4340, successively, there for we can conclude that adsorption process onto activated carbon is favorable one. Even though, Langmuir isotherm gave the best fit between experimental data and theory model, other two isotherms Freundlich and Temkin gave also satisfactory results. Therefore we have calculated all relevant parameters obtained by all three equilibrium isotherms employed. Table 4 summarized our results.

Table 4. Kinetics constants for Langmuir, Freundlich and Temkin isotherms

Parameter	30 ^{0}C	50 ^{0}C
	Langmuir	
K_L	238.66	303.95
α_M	0.7756	1.0668
	Freundlich	
K_F	1.139	2.111
n	2.1358	2.1514
	Temkin	
b	158.39	149.65
K_T	47.71	59.257

Langmuir isotherm graphs are presented below in Figure 3 and Figure 4 for two temperature employed, 30 ^{0}C and 50 ^{0}C. One can conclude that higher temperature gives better agreement between obtained experimental data and theoretical model for methylene blue adsorption on activated carbon.
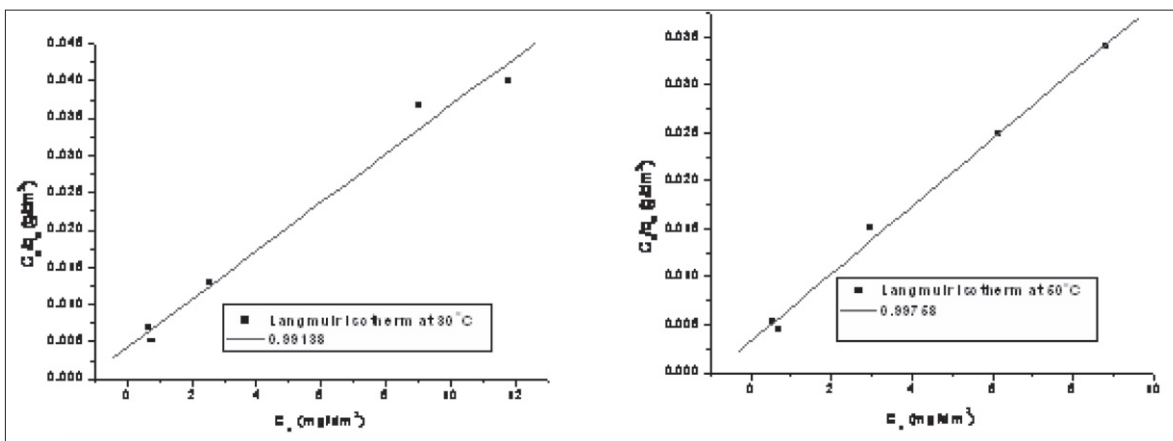
Figure 3. and Figure 4. Langmuir isotherm at 30° C (left) and at 50° C (right) for methylen blue onto activated carbon

In addition to our investigation concerning kinetics and equilibrium isotherms, valuable thermodynamics parameters were determined. Table 5 presents values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ for methylen blue adsorption on activated carbon. On the basis of obtained data we can conclude that this investigated adsorption phenomenon is spontaneous, since Gibbs free energy has negative value and is an endothermic one, because enthalpy change has positive sign.

Table 5. Thermodynamic data for adsorption of MB on activated carbon at 30° C and 50° C

Parameter	30 °C	50 °C
$\Delta H°$	34.794 kJ/mol	34.794 kJ/mol
$\Delta S°$	160 J/mol	160 J/mol
$\Delta G°$	-13.792 kJ/mol	-15.352 kJ/mol

Conclusions

- Kinetics and equilibrium of adsorption process of methylen blue onto activated carbon was investigated. From the kinetics point of view, pseudo-second order gave the best results, with R value 0.99994.
- Three equilibrium isotherms at 30 °C and 50 °C were used, from which Langmuir isotherm gave the best fit between obtained experimental results and theory model. We deal here, probably, with hemisorption process.
- Determined R_L value was in range between 0 and 1, which goes in favor of favorable adsorption process.
- The adsorption process under investigation is spontaneous and endothermic one based on thermodynamics data obtained.

References

Avom, J., Mbadcam, J. K., Noubactep, C., Germain, P. (1997). *Adsorption of methylen blue from an aqueous solution onto activated carbon from palm-trees*. Carbon, (35), 365-369.

Ciardelli, G., Ranieri, N. (2001). *The treatment and refuse of waste water in the textile industry by means of ozonization and electoflocculation*. Water Res., (35), 567-572.

Issac, R. A. (1996). *Disinfection chemistry*. Water Envior. Tecnol., (8), 47-51.

Ramakrishna, K. R., Viraraghavan, T. (1997). Dye removal using low cost adsorbents. Water Sci. Technolog., (36), (2-3), 189-196.

Santhly, K., and Selvapathy, P. (2006). *Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon*. Bioresource and Technology, (97), 1329-1336.

Seshardi, S., Bishop, P. L., Aga, A. M. (1994). *Anaerobic & aerobic treatment of selected azo dyes in waste water*. Waste manage., (15), 127-137.

Shahryari, Z., Goharriti, S. A., Azadi, M. (2010). *Experimental study of methylen blue adsorption from aqueous solutions onto acitvated carbon*. Int. J. of Water and Envir. Eng., (2)2, 016-028.

Tang, W., Huren, A. (1995). *UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions*. Chemosphere, (31), 4157-4170.

Wu, F.C., Tseng, R.L., Juang, R.S. (1999). Pore structure and adsorption perfomance of the activated carbons from plum kernels. J. Hazard Mater., (B69), 287-302.

Yasin, Y., Hussein, M. Z., Ahmad, F. H. (2007). *Adsorption of methylen blue onto treated activated carbon*. The Malaysian J. of Anal. Sci., (11),11 400-406.

Zhu, Y., Wang, D., Zhang, X., Qin, H. (2009). *Adsorption removal of methylen blue from aqueous soluution by using bamboo charcoal*. Fresenius Enviromental Bulletin, (18)3, 369-376.