Adsorption kinetics and thermodynamics of Azure C dye from aqueous solution onto activated charcoal

Kinetika a termodynamika adsorbce barviva Azure C z vodných roztoků na dřevěné uhlí

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Adsorption thermodynamics and kinetics of Azure C and from the aqueous solution on activated charcoal was examined. The charcoal was activated by concentrated sulphuric acid and the adsorption kinetic and thermodynamic was tested in batch experiment. An experiments used the adsorption batch method to observe the effect of the variable parameters, i.e. concentration of dye, time of contact, pH, temperature and adsorbent dose. The ideal dosage of adsorbent was 0.3 g for Azure C. The equilibrium state was reached within 60 min for dye Azure C at activated charcoal. The isotherms of equilibrium were investigated to characterize the adsorption operation. The data for the kinetics study were adjusted utilizing the equation of pseudo-second-order and the model of diffusion (intra-particle). All data were evaluated by means of equilibrium Freundlich, Langmuir and Temkin isotherm on activated charcoal surface. Based on the adsorption isotherm evaluation on activated charcoal the result was 4S by using Giles classification. The thermodynamic factors like ΔH, ΔG and ΔS were estimated.

Adsorpční rovnováhy a kinetika barviva Azure C z vodného roztoku na dřevěné uhlí jsou předmětem tohoto příspěvku. Dřevěné uhlí bylo aktivováno koncentrovanou kyselinou sírovou a adsorbce byla sledována pomocí vsázkové metody. V rámci práce byl sledován vliv proměnných parametrů, tzn. koncentrace barviva, doba kontaktu, pH, teplota a navážka adsorbentu. Ideální navážka baly stanovena na 0.3 g v daném uspořádání. Rovnovážný stav byl dosažen po 60 minutách. Adsorbční izotermy byly stanoveny za účelem charakterizace adsorbce. Data byla zpracována s použitím "pseudo-druhého řádu" a difúzního modelu. Všechna data byla hodnocena pomocí Freundlichovy, Langmuirovy a Temkinovy izotermy. Adsorbce byla ohodnocena třídou 4S za použití Gilesovy klasifikace. Byly stanoveny termodynamické parametry adsorbce ΔH, ΔG a ΔS.

INTRODUCTION

The processing of sewage and it was one of important problem of conservation, especially when such toxic materials, e.g. dyes [1]. Reactive dyes offer over a range of various chemical compositions and powerful reaction with many surface of artificial, there are utilized for coloring silk , cotton and wool [2,3]. Thiazine dyes it is one from a cationic dyes which contains a group of base main that acquires a proton under acidic condition by the dye medium [4-7]. The adsorption study for this dyes is important for different physic-chemical operations and for understanding of phenomena such as explanation and de pollution of industrial liquid wastes [8,9]. Adsorption of different kinds of dyes on the activated carbon and by using a number of adsorbent have been studied [10,11] by using the experiment, that we found the modified charcoal was an active Azure C derivatives adsorbent, the rates of adsorption kinetic were calculate and cause for the choose the proper distinctive expressions average of possible mechanisms. So, the analyses kinetic of adsorption for the done editing charcoal may be of a highly value for the practical for the application of thiazine dyes elimination from the waste water solution.

EXPERIMENTAL

All spectra and absorbance were completed on Shimadzu UV-1650, UV-VIS recording spectrophotometer. Shaking inductor HetoLab-equipment, centrifuge Megafuge 1.0 Herouse Epatech and advanced pH-meter AWTW-720 were utilized. The charcoal specimen utilized as adsorbent was provided from Thomas Barker and activated by using 5 ml of conc. sulphuric acid for 10 mg of charcoal, washed several times with deionized water, filtered and the dried temperature was 150 ^oC for 3 hour and stored [12]. The Azure C dye formula is given in Fig. 1.

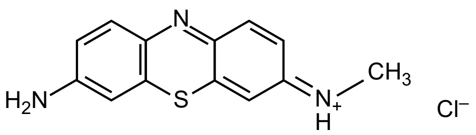

Fig. 1. Structural formula of Azure C dye
Obr. 1. Strukturní vzorec barviva Azure C

Tab. 1. Molecular weight and wavelength of dye / *Molekulární hmotnost a absorbční vlnová délka barviva*

Name	Molar mass	λ_{max}
Azure C	277.77	611.5 nm

General method for isotherms

Portions of dye (Azure C), 15 ml of known initial concentration 5-40 mg dm^{-3} and different measures of activated charcoal 0.02-0.4 g were mixed in volumetric flask. Investigation of Azure C in arrangements after equilibrium (60 min at 25 °C) were performed by method for an APEL-PD-303 UV-VIS spectrophotometer. Absorbance was resolved at 611.5 nm for color (see Fig. 2) related to the maximum absorption peak of dye. In order to decrease the errors of measurement, the absorption of visible light from each equilibrium solution test was measured three times and the average value was utilized to ascertain the concentration at equilibrium based on the standard calibration curve, which correlation coefficient square (R^2) was 0.993 for dye. Based on distinction between starting concentration and equilibrium, the quantities of Azure C dye absorbed were computed by the accompanying relation (Eq. 1).

$$Q_e = \frac{(C_o - C_e)\,V_{sol}}{M} \qquad (1)$$

where (Q_e) is quantity of dye adsorbed (mg g^{-1}), (C_0)/(C_e) are the concentrations at starting/equilibrium in (mg dm^{-3}) individually. The adsorbent (M) was in (g) unit and (V_{sol}) is the solution volume in (ml). The adsorption ability was resolved with the impact of contact equilibrium to fit in the adsorption isotherm.

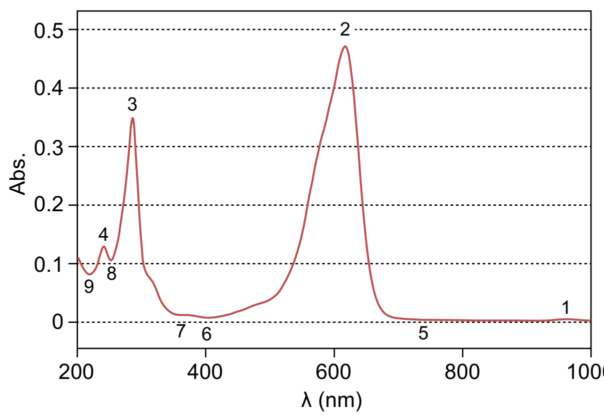

Fig. 2. UV-VIS spectrum of Azure C at 100 ppm
Obr. 2. UV-VIS spektrum barviva Azure C při 100 ppm

RESULTS AND DISCUSSION

Adsorption Isotherms

The Freundlich isotherm have been obtained to describe the adsorption ability for dyes poison utilizing activated charcoal as an adsorption by fitting the adsorption information Fig. 3.

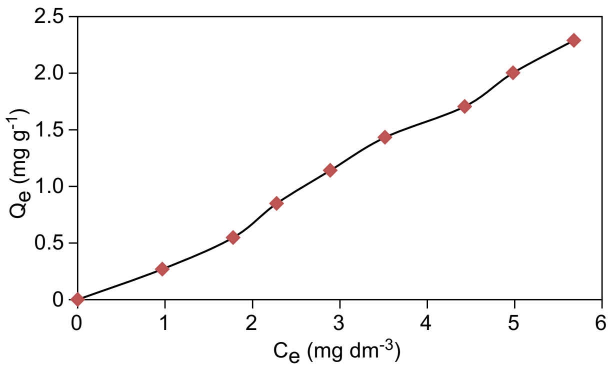

Fig. 3. Adsorption isotherm of dye Azure C at pH 7 and 25 °C
Obr. 3. Adsorbční izoterma barviva Azure C při pH 7 a 25 °C

The Freundlich isotherm have the general shape according to Eq. 2 [12].

$$Q_e = K_f\, C_e^{\ 1/n} \qquad (2)$$

where K_f is the Freundlich constant identified to the adsorption capacity (n) representing the degree of dependence of adsorption on equilibrium concentration, see Tab. 2 and Fig. 4.

Tab. 2. Freundlich and Langmuir constant of dye in aqueous solution utilizing activated charcoal as an adsorption / *Freundlichova a Langmuirova konstanta barviva na dřevěném uhlí*

dye	Freundlich parameters			Langmuir parameters		
	K_f (mg g^{-1})	n	R^2	b	Q_{max}	R^2
Azure C	0.2897	0.8203	0.993	-0.0599	-4.8309	0.637

The Langmuir isotherm has the general structure according to Eq. 3 [14].

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \qquad (3)$$

where (C_e) is the concentration of equilibrium solution, (Q_e) is amount of adsorbed dye to weight unit of adsorbent, (b) and (Q_{max}) are constant of Langmuir straight line. They were fitted by means of least square method.

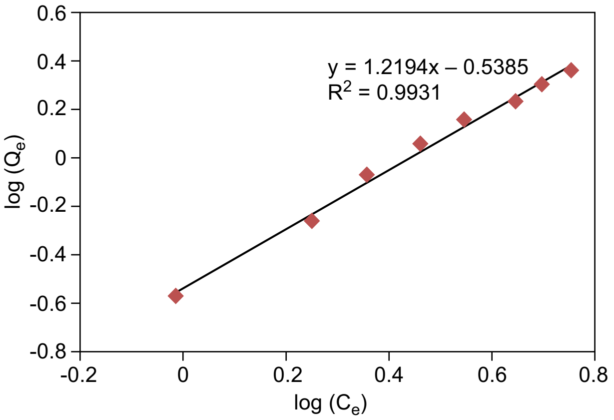

Fig. 4. Freundlich isotherm of dye Azure C with charcoal at pH 7
Obr. 4. Freundlichova izoterma barviva Azure C na dřevěném uhlí při pH 7

The slope was ($1/Q_{max}$), the intercept was ($1/bQ_{max}$). A straight lines acquired had profoundly critical correlation coefficients (R^2). The Langmuir constants and adsorption isotherms are given in Tab. 2 and Fig. 5.

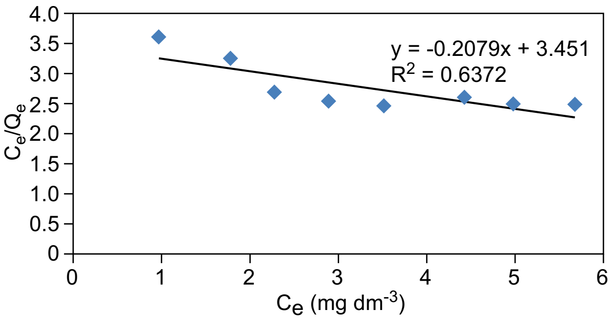

Fig. 5. Langmuir isotherm of dye Azure C with charcoal at pH 7
Obr. 5. Langmuirova izoterma barviva Azure C na dřevěném uhlí při pH 7

The Tempkin isotherm is regularly determined by Eq. 4.

$$q_e = \ln (K_T C_e) \quad (4)$$

The Tempkin isotherm (Eq. 4) can be simplified to the following Eq. 5 [15].

$$q_e = \beta \text{Ln} K_T + \beta \text{Ln} C_e \quad (5)$$

where $\beta = RT/b$, (T) is the thermodynamic temperature in Kelvin degrees and (R) was the universal gas constant, 8.314 J mol^{-1} K^{-1}. The consistent (b) is identified with the adsorption heat. The straight constants of isotherm and coefficient of determination are shown in Tab. 3. The coefficient od determination (R^2) acquired from Tempkin model were similar to those got for the Langmuir and Freundilch relations, which demonstrates the pertinence of Tempkin model to the adsorption of (Azure C) dyes onto activated charcoal (Fig. 6).

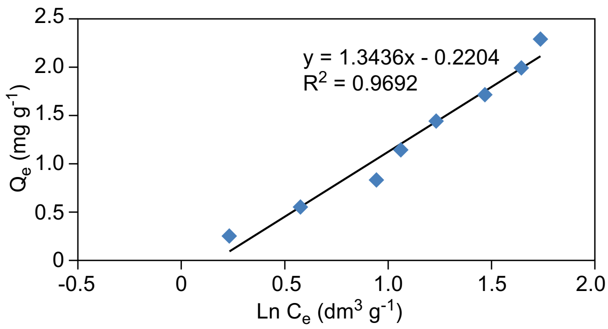

Fig. 6. Temkin isotherm for Azure C adsorption by charcoal at 25 °C
Obr. 6. Temkinova izoterma barviva Azure C na dřevěném uhlí při 25 °C

Tab. 3. Coefficients and isotherm parameters for Azure C dye adsorption onto charcoal / *Koeficienty a parametry izoterm barviva Azure C na dřevěném uhlí*

Dyes	Tempkin parameters		
	K_T (dm^3 g^{-1})	β (mg dm^{-3})	R^2
Azure C	0.802	1.343	0.969

Effect of pH

In order to study the hydrogen ion concentration (pH) effect on Azure C adsoprtion onto activated charcoal, the dye solution was set up in the extent of 5-40 mg dm^{-3} and adjusted to various pH values (2, 4, 7 and 10) utilizing HCl (0.1N) and NaOH (0.1N). The results are given in Fig. 7. Obviously the quantity of discolored dyes differs at various pH. pH 10 gives a huge adsorbed amount for dye Azure C. At acidic solution pH, the discoloration ability was decreased, as the adsorbent was positively charged and the dyes were transformed to neutral charged.

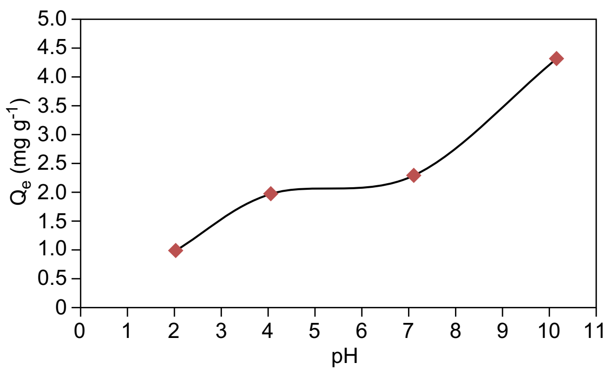

Fig. 7. Discoloration of aqueous solution of Azure C dye at different pH
Obr. 7. Odbarvení roztoků barviva Azure C při různých úrovních pH

Contact Time

An effect of the contact time on the adsorption ability of dye by adsorbent charcoal was carried out in batch experiments to accomplish the equilibrium, see Fig. 8.

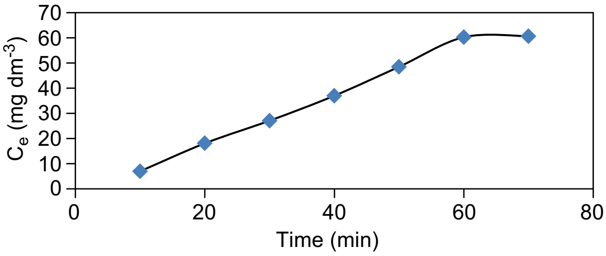

Fig. 8. Adsorption ability against contact time of dyes Azure C with activated charcoal
Obr. 8. Adsorbční schopnost v závislosti na čase pro barvivo Azure C na dřevěném uhlí

The adsorption ability increases with the prolonged contact time. The equilibrium was accomplished by subsequent shaking for sufficient time, i.e. 70 min for Azure C dye. In this manner every experiment was shaken for 60 min.

Adsorbent dosage

Keeping in mind the final goal, to think about the impact of adsorbent measurements on dyes removal (the adsorption ability, temperature, pH and shaking time on activated charcoal as an adsorbent) various weight of dose was utilized (0.02 , 0.05 , 0.1, 0.15, 0.2, 0.25, 0.3 and 0.4 g). The best removal of dyes was seen with the dose 0.3 g (see Fig 9 utilized for all the next experiments.

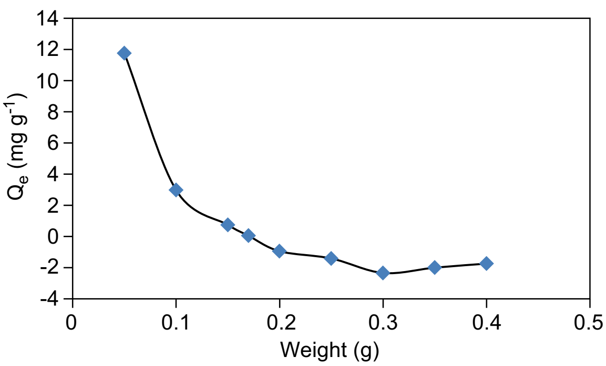

Fig. 9. The effect of the adsorbent dosage
Obr. 9. Vliv navážky adsorbentu

Kinetics of Adsorption

Fig. 10 and 11 show the kinetics of dye (Azure C) adsorption onto activated charcoal. The curves are given for starting concentration 25 mg dm^{-3}. The highly increase of q_t may be caused by adsorption of dyes on the activated charcoal. The slope was taken when more than 25 % adsorption happened. This was ascribed as the use of the active sites in the activated charcoal. The data from experimental were processed using pseudo-first-order Eq.10, pseudo-second-order Eq.11 [16]. The coeffcients of determination are given in Tab. 4.

$$\ln (q_e - q_t) = \ln q_e - K_1 T \qquad (6)$$

wherever (q_e) is the equilibrium concentration in (mg g^{-1}) of dye in activated charcoal, (q_t) is the average concentration for the dye at time t (min) in activated charcoal, K_1 is the rate constant for pseudo-first-order (min^{-1}).

Tab. 4. Kinetic coefficients of the adsorption of dye / *Kinetické koeficienty adsorbce barviva*

	Pseudo-first-order	Pseudo-second-order
Dyes	R^2	R^2
Azure C	0.761	0.920

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \cdot t \qquad (7)$$

where K_2 is the rate constant for the pseudo-second-order (mg g^{-1} min^{-1}).

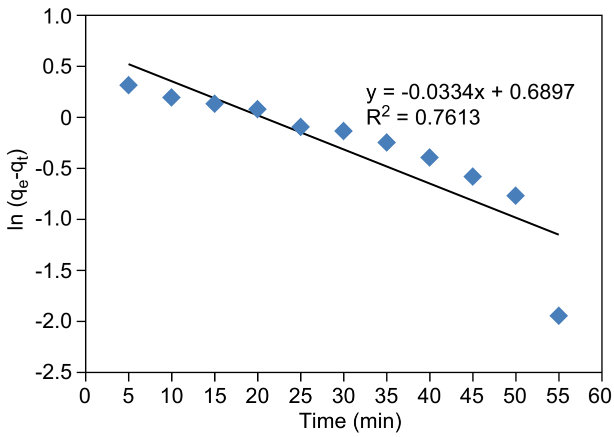

Fig. 10. Pseudo –first-order for Azure C dye by activated charcoal at 25 °C
Obr. 10. Závislost dle pseudo-prvního řádu pro barvivo Azure C na dřevěném uhlí při 25 °C

Tab. 5. Thermodynamics values for dyes Azure C in aqueous solution by utilizing charcoal activated as an adsorbent / *Termodynamické parametry pro barvivo Azure C ve vodném roztoku při použití dřevěného uhlí jako adsorbentu*

Dyes	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
Azure C	0.8136	2.252	4.827

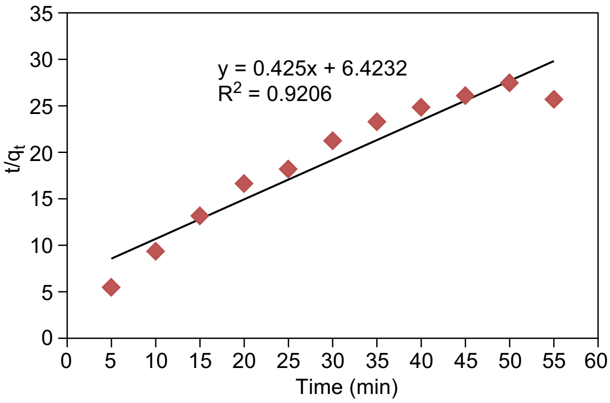

Fig. 11. Pseudo second-order for (Azure C) dye by activated charcoal at 25 °C
Obr. 11. Závislost dle pseudo-druhého řádu pro barvivo Azure C na dřevěném uhlí při 25 °C

Tab. 4 shows the kinetic data are well fitted the pseudo-second-order. The coefficients of correlation (R^2) for pseudo- second -order are larger than pseudo-first-order [15].

Temperature Effect

Adsorption isotherms were measured for the dyes in the temperature range of 298 to 328 K. The results are given in Fig. 12. The thermodynamic parameters ΔH, ΔG and ΔS were processed.

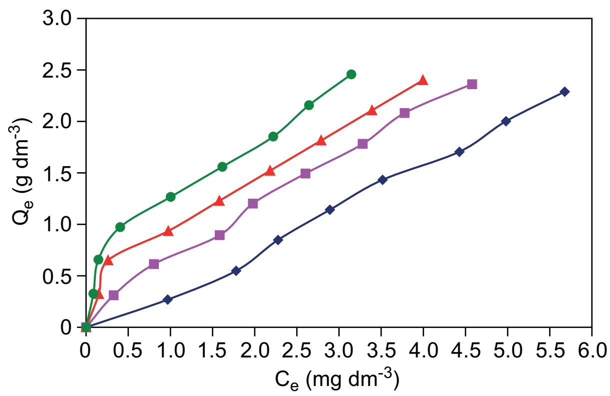

Fig. 12. Temperature effect on the ability of adsorption of dye Azure C with charcoal activated at pH=7
Obr. 12. Vliv teploty na adsorbční schopnost barviva Azure C na dřevěném uhlí při pH 7

With a specific final goal, to pick up knowledge into the instrument required in the adsorption procedure, thermodynamic parameters for the studied work were computed. (ΔH) enthalpy, (ΔG) Free energy and (ΔS) entropy were calculated utilizing the next relationships [18,19].

$$\Delta G = -RT \ln K \quad (8)$$

$$\ln K \; \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where (R) is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the thermodynamic temperature in Kelvin. Vant Hoff curves of (lnK) versus (1/T) were plotted. The estimations of ΔS and ΔH were resolved by the slopes and intercept separately. Tab. 4 lists the values of thermodynamic parameters. The capacity at higher temperatures is given in Fig. 13, which demonstrates that adsorption of dyes in this system was an endothermic procedure. Endothermic nature of this process is evidence of the absorption process as well as the adsorption process, increasing the temperature spread molecules adsorbed on the surface and inside the pores and increases the rate of deployment [11].

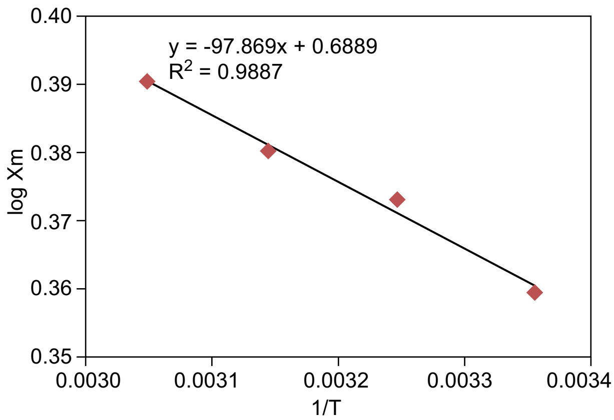

Fig. 13. The relation between Log Xm and 1/T to Azure C
Obr. 13. Vztah mezi log Xm a 1/T pro barvivo Azure C

Adsorption of dyes was observed to be non-spontaneous within the range of temperatures 298-328 K as showed by the positive value of ΔG. Nevertheless, Azure C dye is adsorbed on activated charcoal. This deviation is identified with higher proclivity of dye on the activated charcoal surface. Additionally this might be caused by an inclination of the dye molecule to get away from the activated charcoal to the liquid with increase of temperature of the solution [11].

CONCLUSIONS

Activated charcoal as an adsorbent for removal of Azure C from the aqueous solution has been studied. The results show that the dyes removal is very fast process. The equilibrium and kinetic of the dyes adsorption at activated charcoal was obtained by means of the equilibrium adsorption fit of the Freundlich, Langmuir and Tempkin isotherms. The kinetics shows the process of adsorption was driven by the pseudo-second-order equation.

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