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## KINETICS OF BIS (2-CHLOROISOPROPYL) ETHER ADSORPTION FROM AQUEOUS SOLUTION

### KINETYKA ADSORPCJI ETERU BIS (2-CHLOROIZOPROPYLOWEGO) Z ROZTWORU WODNEGO

#### Abstract

A pseudo-first order rate equation describing the kinetics of adsorption of bis (2-chloroisopropyl) ether from aqueous solution onto activated carbon at different initial concentrations, dose adsorbent, temperature, particle diameter and rate of stirring have been developed. The rate constant was calculated. The rate constant correlation in good mixing conditions was described as a function of the molecular diffusion coefficient calculated by the Wilke-Chang method and the surface area of mass transfer.

*Keywords: bis (2-chloroisopropyl) ether, activated carbon, adsorption, kinetics, sewage*

#### Streszczenie

Kinetykę adsorpcji eteru bis (2-chloroizopropylowego) z roztworu wodnego na węglu aktywnym dla różnych stężeń początkowych, temperatur, średnic ziarna i szybkości mieszania można opisać równaniem reakcji pierwszego rzędu. Wyznaczono stałą szybkości procesu. Stałą szybkości w dobrych warunkach mieszania skorelowano zależnością współczynnika dyfuzji molekularnej oraz powierzchni kontaktu. Współczynnik dyfuzji molekularnej eteru bis (2-chloroizopropylowego) wyznaczono z równania Wilkego-Changa.

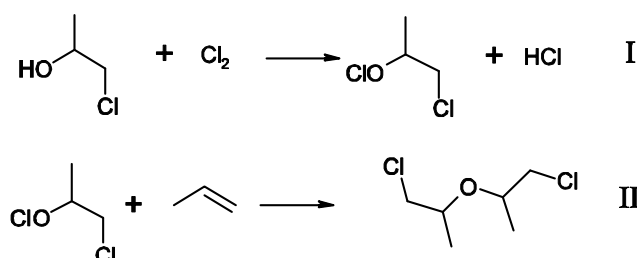
*Słowa kluczowe: eter bis (2-chloroizopropylowy), węgiel aktywny, adsorpcja, kinetyka, ścieki*

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## 1. Introduction

Wastewaters containing bis(2-chloroisopropyl) ether (BCIPE) are discharged in a large amount from a propylene oxide production plant.

BCIPE is formed as a by-product during the propylene oxide production by using the chlorohydrin method. The BCIPE formation proceeds according to the chemical equations



Because of its significant resistance to biodegradation and its carcinogenic and mutagenic properties, its removal is purposeful [1, 2]. So far there have been practically no works connected with BCIPE removal from aqueous solution.

High degree of purification can be achieved by means of the adsorption method on the activated carbons [3–8].

The adsorption processes are usually carried out on industrial scale in the columns packed with adsorbents or batch reactors. The fundamental information concerning the process is achieved experimentally by the investigation of the systems with a constant volume of the treated liquid. The equilibrium and major kinetic parameters relating to mass transfer can be determined on the basis of these studies [4].

The rate of adsorption process is determined by diffusion or convection in the solution, diffusion across the boundary layer surrounding the particle, as well as by intraparticle diffusion and diffusion in pores volume. Diffusion and convection in the solution have no influence on the process rate in systems where good mixing of the solution was ensured. Diffusion through a film takes place at the initial stage of the process, then it transforms into the intraparticle diffusion [5].

Depending on the system and hydrodynamic conditions, external mass transfer coefficient and intraparticle diffusion are taken into consideration, or one kinetic coefficient crucial for the rate of mass transfer.

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, several kinetic models are used to test the experimental data. The large number and array of different functional groups on the activated carbon surface imply that there are many types of adsorbent-solute interactions. Thus, any kinetics or mass transfer representation is likely to be global. From a system design viewpoint, a lumped analysis of the adsorption rates is thus sufficient for practical operations.

A simple kinetic analysis of adsorption is the pseudo-first-order equation [6, 7]

$$\frac{da}{dt} = k(a^* - a) \quad (1)$$

where:

- $a$  – adsorption amount at the time moment (mg/g),
- $a^*$  – equilibrium adsorption amount (mg/g),
- $k$  – constant rate (1/min),
- $t$  – time (min).

The values of  $a^*$  must be obtained independently from equilibrium experiments.

After the definite integration by applying the initial conditions:  $a = 0$  at  $t = 0$ , eq. (1) becomes

$$\ln(a^* - a) = \ln(a^*) - kt \quad (2)$$

or

$$\ln\left(\frac{a^*}{a^* - a}\right) = kt \quad (3)$$

## 2. Experimental

### 2.1. Adsorption method

The sorption of BCIPE onto activated carbon was studied by batch experiments. The examined factors were: initial BCIPE concentration, activated carbon dose, particle diameter, mixing rate and temperature.

All the tests were conducted in capped flasks (240 cm<sup>3</sup>), by proportioning the BCIPE stock solution to the activated carbon suspension and mixing in a shaker. Samples were withdrawn at the suitable time intervals and analyzed.

### 2.2. Analytical method

The concentration of the studied compound was determined chromatographically on a Thermoquest GC 8000<sup>Top</sup> instrument with a flame ionization detector (FID). The determinations were carried out isothermally at the temperature 100°C. A capillary column DB-WAX (J&W) 30m × 0,5mm × 0,5 μm was used.

### 2.3. Materials

The adsorbent used in these studies was activated carbon of DTO type supplied by GRYFSKAND SA (Poland). This adsorbent was sieved into several discrete particle size ranges. The 0.91–0.63; 0.4–0.63 and 0.40–0.25 mm size range of activated carbon were used. The sieved activated carbon was washed by distilled water to remove fines and then dried in an oven for 24 h at 110°C. The carbon particles were assumed to be spheres having a diameter given by arithmetic mean value between respective mesh size (average particle diameters  $d_z$  were 0.77, 0.53 and 0.33 mm). The properties of DTO activated carbon are presented in Table 1. BCIPE (>99%) used in these studies was obtained by distillation from heavy ends after propylene oxide distillation. The purity was determined by using GC method.

Table 1

**Properties of DTO activated carbon**

Bulk density (g/dm <sup>3</sup> )	400
Apparent density (g/dm <sup>3</sup> )	860
Total surface (N <sub>2</sub> BET method) (m <sup>2</sup> /g)	943
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.53
Pore volume < 1.5 nm (cm <sup>3</sup> /g)	0.25
Porosity	0.45

### 3. Results

Figure 1 shows the examples of BCIPE kinetic curves onto the DTO activated carbon from aqueous solution. The pseudo-second reaction model was used to check all the results but the correlation coefficient is not high. However, the rate law for a first-order order could be fixed with very high correlation coefficient. The sorption of BCIPE onto the activated carbon could be a pseudo-first order process rather than the second-order.

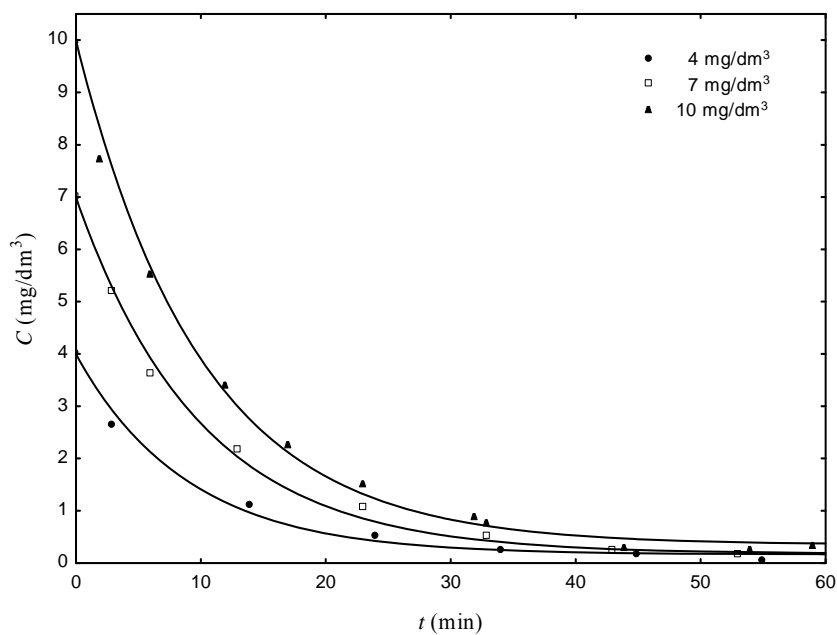


Fig. 1. Kinetic curves of BCIPE adsorption

Rys. 1. Krzywe kinetyczne adsorpcji BCIPE

### 3.1. Effect of initial DCP concentration

Figure 2 shows the kinetic curve in a linear form for three different initial concentrations. According to Fig. 2, within the examined range of the initial concentration (4–10 mg/dm<sup>3</sup>), the concentration does not affect in an essential way the BCIPE adsorption kinetics from aqueous solution onto the DTO activated carbon. For those values of the adsorbate initial concentrations, the duration needed to obtain equilibrium state is approximate and averages out about 60 minutes.

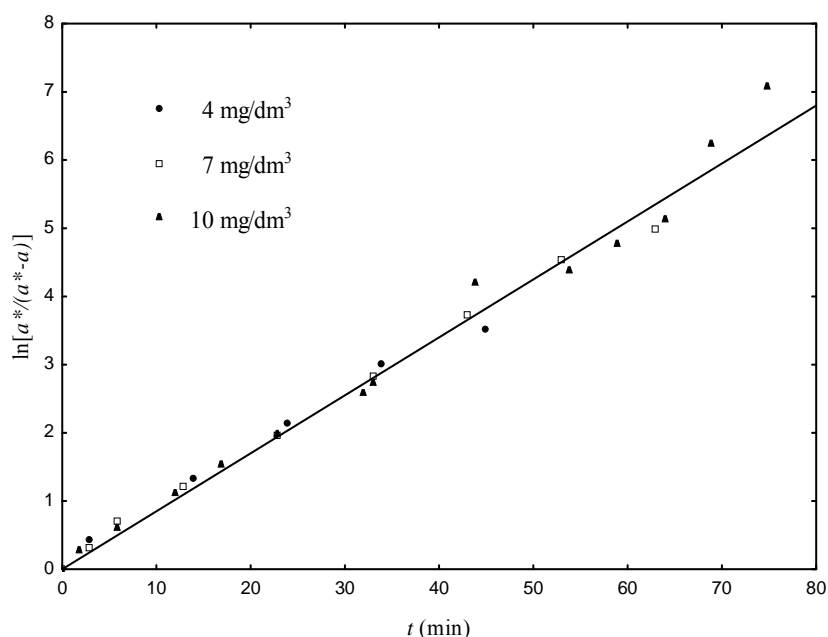


Fig. 2. Kinetic curves of BCIPE adsorption for various initial concentration

Rys. 2. Krzywe kinetyczne adsorpcji BCIPE dla badanych stężeń początkowych

### 3.2. Effect of adsorbent dose

Figure 3 shows kinetic curves in a linear form for three different adsorbent doses. The influence of carbon mass is consistent with the expectations, the increase of the process rate, together with the increase of carbon amount, is observed. The rate increase is proportional to the adsorbent concentration, and what follows, to the surface area of mass transfer. Moreover, in the system where there are more grains, turbulence is higher and it is possible that in the result of interstitial shearing the boundary layer in a certain range is reduced. That is why the molecules of the adsorbate penetrate to surface of the grains easier and faster.

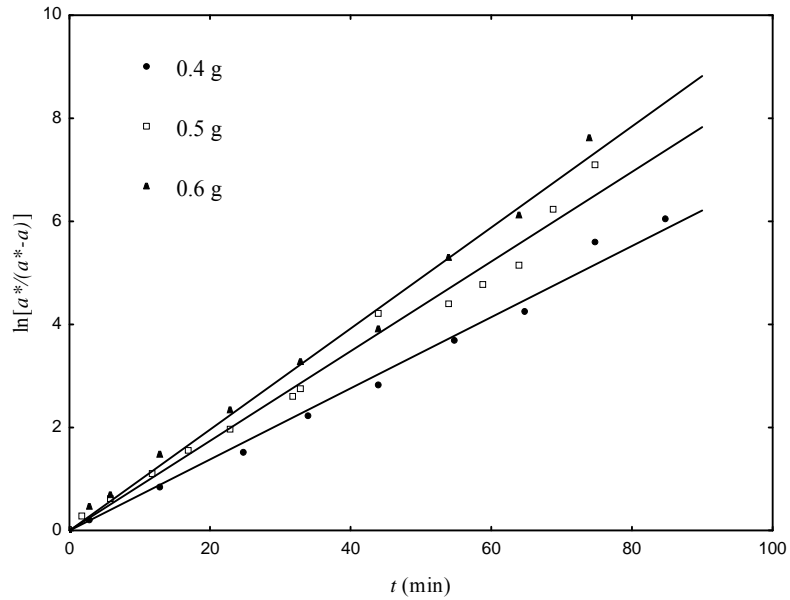


Fig. 3. Kinetic curves of BCIPe adsorption for various adsorbent doses

Rys. 3. Krzywe kinetyczne adsorpcji BCIPe dla badanych dawek adsorbentu

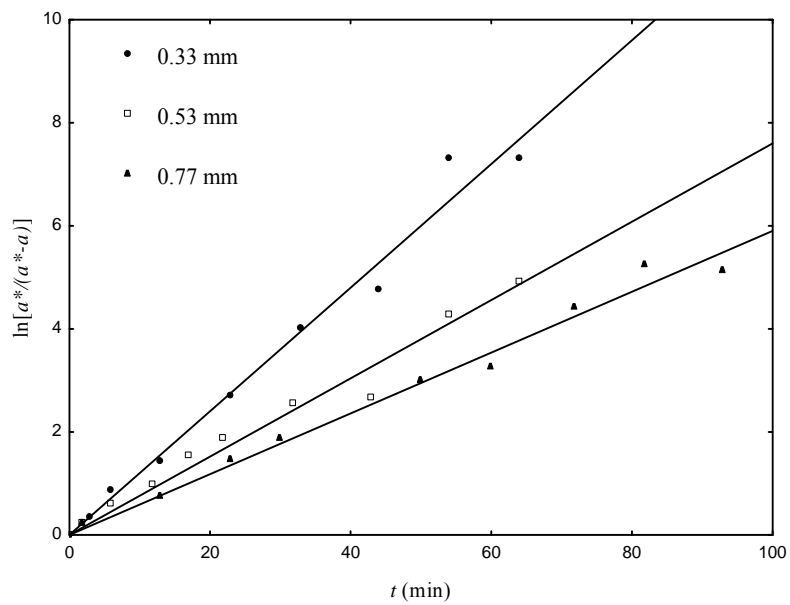


Fig. 4. Kinetic curves of BCIPe adsorption for a various particle diameters of activated carbon

Rys. 4. Krzywe kinetyczne adsorpcji BCIPe dla badanych średnic ziarna węgla aktywnego

### 3.3. Effect of particle diameter

Figure 4 shows kinetic curves in a linear form for three different diameters of the adsorbent particles. Along with the reduction of the particle diameter, the rate of the process increased. The rate is proportional to the increase of the surface area of mass transfer between the adsorbent and the bulk solution. Such action is also confirmed by the effect of the increase of the adsorbent mass.

### 3.4. Effect of mixing rate

Figure 5 shows kinetic curves in a linear form for three different mixing rates. With the mixing rate of 200 cycle per minute (cpm) time needed to obtain the adsorption equilibrium state equals 360 min. The rate of establishing the adsorption equilibrium for 250 and 300 cpm equals about 60 min. Besides, the constant rates determined in such conditions are comparable. It states about a good mixing of the solution and no influence of external diffusion on the adsorption process.

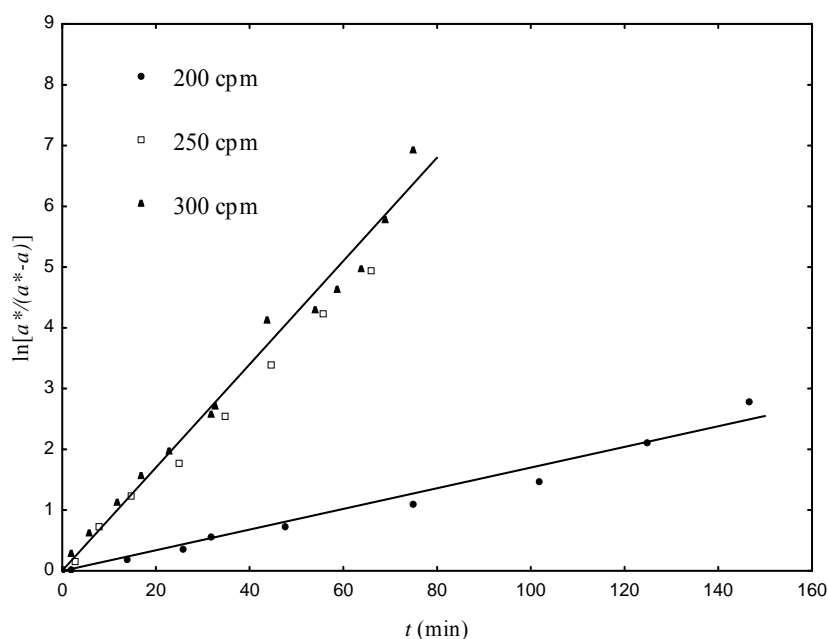


Fig. 5. Kinetic curves of BCIPE adsorption for various mixing rates

Rys. 5. Krzywe kinetyczne adsorpcji BCIPE dla badanych szybkości mieszania

### 3.5. Effect of temperature

Figure 6 shows kinetic curves in a linear form for three different temperatures. In a way from 293 K to 313 K the rate of adsorption of the examined compounds increases. At the

temperature of 313 K almost double increase of the adsorption coefficient rate was noted, in comparison with the values obtained at the temperature 293 K.

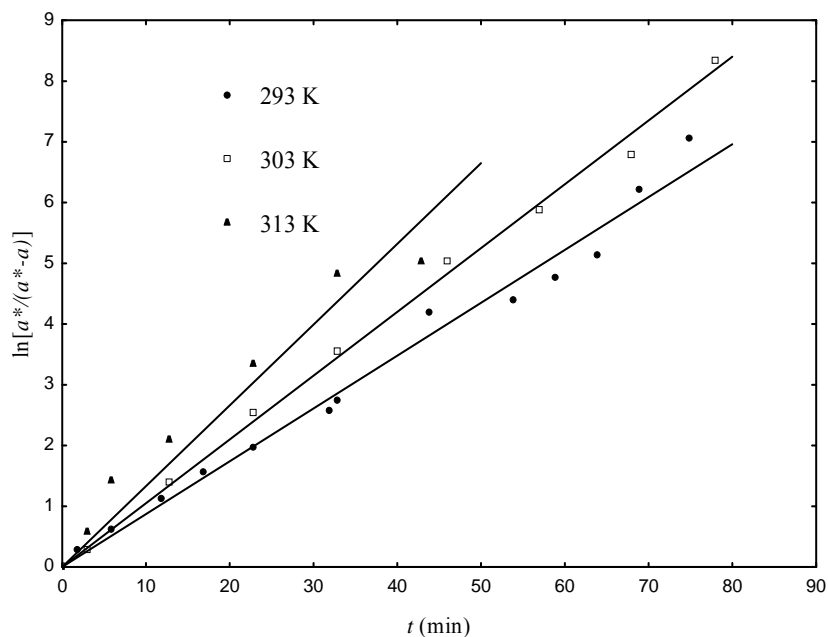


Fig. 6. Kinetic curves of BCIPE adsorption for various temperatures

Rys. 6. Krzywe kinetyczne adsorpcji BCIPE dla badanych temperatur

#### 4. Discussion

In Table 2 the constants rate ( $k$ ) determined for particular processes and values of the BCIPE molecular diffusion coefficients in water were presented. The molecular diffusion coefficients were calculated by the Wilke-Chang method [8].

It was found that  $k$  parameter depends on the contact surface area and the BCIPE molecular diffusion coefficient in water in a linear way. The linear dependence of  $k$  can be described by the equation below

$$k = k_0 DS \quad (4)$$

where:

$k_0$  – constant rate independent from temperature and adsorbent dose (1/min),

$S$  – surface area of mass transfer ( $\text{dm}^2$ ).

The surface area of mass transfer is defined as

$$S = m\alpha \quad (5)$$



where:

$\alpha$  – specific particle area (dm<sup>2</sup>/g),

$m$  – adsorbent mass (g).

The specific particle area was defined as

$$\alpha = \frac{A_z}{m_z} = \frac{\pi d^2}{\frac{\pi}{6} d^3 \rho} = \frac{6}{\rho d} \quad (6)$$

where:

$\rho$  – apparent density (g/dm<sup>3</sup>),

$A_z$  – particle area (dm<sup>2</sup>),

$d$  – particle diameter (dm),

$m_z$  – particle mass (g).

Table 2

**Obtained of the constant rates of BCIPE adsorption**

$m$	$D$	$k$	$k_0 \cdot 10^{-10}$	$\sigma$	
[g]	[dm <sup>2</sup> /min]	[1/min]	[1/min]	[%]	
0.4	3.83·10 <sup>-6</sup>	0.0691	0.0342	7.5	
0.5		0.0867	0.0344	7.9	
0.6		0.0981	0.0324	2.3	
$C_0$ , mg/dm <sup>3</sup>					
4		0.0835	0.0331	4.3	
7		0.0833	0.0330	4.1	
10		0.0867	0.0344	7.9	
$d$ , mm					
0.37		0.1199	0.0332	4.6	
0.53		0.0762	0.0302	4.8	
0.70		0.0592	0.0310	2.2	
$cpm$ , 1/min					
200		0.0226	0.0068	–	
250		0.0744	0.0225	11.0	
300		0.0867	0.0263	4.1	
$T$ , K					
293	4.97·10 <sup>-6</sup>	0.0867	0.0344	7.9	
303		0.1050	0.0321	1.3	
313		0.1329	0.0321	1.3	
an average of $k_0$			0.0513	4.1	

According to the Wilke-Chang equation, the molecular diffusion coefficient depends only on temperature for a given system.

Equation (4) allows to define the constant rate of the BCIPE adsorption onto DTO activated carbon in good mixing conditions for any temperature.

In Table 2 relative deviation  $\sigma$  between the defined average  $k_0$  and the values for particular measurements were shown

$$\sigma = \frac{|k_0 - \overline{k_0}|}{\overline{k_0}} \cdot 100\% \quad (7)$$

where:  $\overline{k_0}$  – average values of  $k_0$  (1/min).

The mean value of deviation equals 4.1%, which states about the good compatibility of eq. (5) with the experimental data.

## 5. Conclusion

The adsorption process BCIPE from aqueous solution in a shaker onto DTO activated carbon describes the model of the pseudo-first order reaction well. The rate constant correlation in good mixing conditions was described as a function of the molecular diffusion coefficient calculated by the Wilke-Chang method and the surface area of mass transfer. In the system with good mixing the equilibrium was established for no longer than 60 min., irrespective of the rest of the parameters.

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