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KINETICS OF SIMULTANEOUS ADSORPTION OF WATER CHLOROORGANIC POLLUTANTS ON ACTIVATED CARBON

KINETYKA ADSORPCJI CHLOROORGANICZNYCH ZANIECZYSZCZEŃ WODY Z ROZTWORÓW WIELOSKŁADNIKOWYCH NA WĘGLU AKTYWNYM

Abstract: A comparative study of adsorption kinetics in the systems multicomponent aqueous solutions of selected chlorophenols (2-CP, 3-CP, 4-CP) and chlorophenoxy herbicides (2,4-D, MCPA) - activated carbon (F-300) has been performed. The concentrations of all adsorbates in the aqueous phase were determined using high performance liquid chromatography (HPLC). The applicability of two kinetic models, the pseudo-first and pseudo-second order models, for the experimental data was examined. The adsorption kinetics was better described by the pseudo-second order model with correlation coefficients $R^2 \geq 0.997$ for all adsorbates.

Keywords: adsorption, activated carbon, chlorophenols, chlorophenoxy herbicides, adsorption kinetics

Chlorophenols are one of the most common environmental contaminants. These compounds cause distasteful taste and odor of drinking water and can exert negative effects on different biological processes. Amongst the several techniques of chlorophenols removal, adsorption has been found to be a proficient and economic method. Large amount commercial systems currently use activated carbon as adsorbent to remove chlorinated phenols in wastewater because of its exceptional adsorption capability. Increasingly stringent legislation on the purity of drinking water has created a growing interest in the decontamination of water, wastewaters and polluted trade effluents using activated carbon. The applicability of this adsorbent for chlorophenols (4-CP, 2,4-DCP, 2,4,6-TCP from aqueous phase was investigated [1-6].

Water pollution by pesticides, particularly herbicides, has been recognized in agricultural areas for many years. A majority of the herbicides used in Europe are acidic herbicides, and phenoxy acid herbicides such as *2,4-dichlorophenoxyacetic acid (2,4-D)*, *2-methyl-4-chlorophenoxyacetic acid (MCPA)*, *dichlorprop (DCPP)* and *mecoprop (MCPP)* are among the 10 most important pesticides. Due to their high solubility in water, phenoxy herbicides easily enter surface or groundwaters through natural drainage or infiltration. Conventional water treatment processes have been reported to be more effective in removing less water soluble and easily degradable pesticides. Since there is a wide variety of herbicides varying in physical and chemical properties, it is difficult to apply a single method. Adsorption on activated carbon is one of the well-established and effective techniques for the removal of herbicides (CPA, 2,4-D, MCPA) from water [7-9].

The objective of the present study is to investigate and describe kinetics of simultaneous adsorption of selected chlorophenols and chlorophenoxy herbicides from aqueous solutions.

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Experimental

The commercial *granular activated carbon* Filtrasorb 300 (Chemviron) was chosen for this study. Prior to use, the as-received GAC was washed several times with distilled boiling water. Ash content decreased in that way from 8.05 to 7.85% wt. The main properties characterizing so prepared carbon are as follows: $S_{\text{BET}} = 938 \text{ m}^2/\text{g}$, $\text{IN} = 927 \text{ mg/g}$, NaOH neutralization ability 0.07 mmol/g , surface oxygen content from EDS - 4.57% wt.

As adsorbates three chlorophenols 2-CP, 3-CP, 4-CP and two chlorophenoxy herbicides 2,4-D and MCPA were selected. The kinetic experiments were conducted for initial concentration of aqueous solution $C_0 = 100 \text{ mg/dm}^3$ at temperature of 25°C . After putting in Erlenmeyer flask 0.2 g activated carbon and 100 cm^3 solution its content was agitated and hour by hour analyzed concentration of each adsorbate using HPLC with diode array detector (Shimadzu LC-20, Kyoto, Japan). Separation of analytes was performed using a Phenomenex Luna C_{18} ($4.6 \times 150 \text{ mm}$, $3 \mu\text{m}$) column (Torrance, CA, USA).

The amount of adsorption at time t , q_t [mg/g], was calculated by: $q_t = (C_0 - C_t)V/m$ where C_t is the adsorbate concentration at any time t [mg/dm³], V is the volume of the solution [dm³] and m is the mass of the adsorbent [g]. It was observed, that after about 6-7 hours adsorption equilibrium was achieved (Fig. 1). For description of curves $q_t = f(t)$ equations pseudo-first and pseudo-second order were considered.

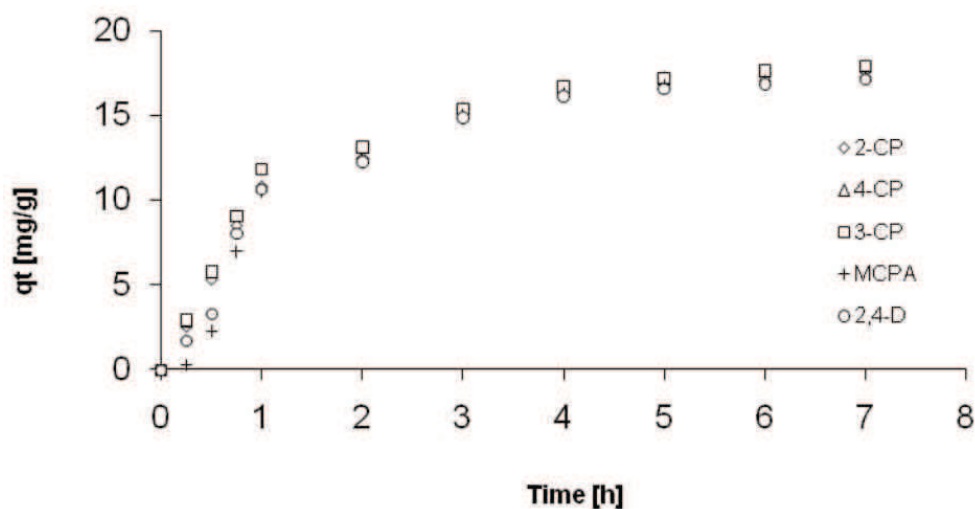


Fig. 1. Adsorption kinetics of selected chlorophenols and chlorophenoxy herbicides on activated carbon at 25°C , initial concentration 100 mg/dm^3

Results and discussion

In order to investigate the kinetics of adsorption of selected chlorophenols and chlorophenoxy herbicides on activated carbon, the rate constants were determined in terms of the pseudo-first order and pseudo-second order models.

The pseudo-first order equation has the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are the amounts of adsorption at equilibrium and at time t , respectively, and k_1 is the pseudo-first order rate constant. After integration and applying the initial conditions, the integrated form of Eq. (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

In order to obtain the rate constants, the straight line plots of $\log(q_e - q_t)$ vs t for the selected adsorbates have been tested.

If the sorption follows pseudo-second order mechanism, the equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where q_e and q_t are the amounts of adsorption at equilibrium and at time t , respectively, and k_2 is the pseudo-second order rate constant. Integrating Eq. (3) and applying the initial conditions we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The straight line plots of t/q_t against t have also been analyzed. The values of pseudo-second order rate constants were calculated from these plots.

The experimental results were described by the pseudo-first and pseudo-second order models equations. The rate constants (k_1 , k_2) and correlation coefficients R^2 for both kinetic models were calculated and listed in Table 1.

Table 1

The pseudo-first and pseudo-second order rate constants for adsorption of selected chlorophenols and chlorophenoxy herbicides on activated carbon at 25°C, initial concentration 100 mg/dm³

Compounds	Pseudo-first order model			Pseudo-second order model		
	k_1 [h ⁻¹]	k_1 [min ⁻¹]	R^2	k_2 [g mg ⁻¹ h ⁻¹]	k_2 [g mg ⁻¹ min ⁻¹]	R^2
2-CP	0.689	0.0115	0.989	21.241	0.0008	0.997
3-CP	0.725	0.0120	0.987	17.560	0.0010	0.998
4-CP	0.714	0.0120	0.986	17.316	0.0010	0.997
2,4-D	0.811	0.0138	0.986	18.842	0.0009	0.997
MCPA	0.830	0.0136	0.988	19.172	0.0009	0.997

The correlation coefficient values $R^2 \geq 0.997$ for pseudo-second order equation indicate the applicability of this model to describe the adsorption process of the all selected adsorbates on Filtrasorb 300 activated carbon. Literature survey has shown that pseudo-second order model suitably fitted experimental data and is more suitable than pseudo-first order model [2, 3, 5, 6].

Conclusions

The adsorption kinetics for all studied systems aqueous multicomponent solutions of selected chloroorganic adsorbates - activated carbon was found to follow pseudo-second order model with good correlation. The correlation coefficients of particular adsorbed chlorophenols or chlorophenoxy herbicides were very high. For the pseudo-first order model they are only slightly lower.

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KINETYKA ADSORPCJI CHLOROORGANICZNYCH ZANIECZYSZCZEŃ WODY Z ROZTWORÓW WIEŁOSKŁADNIKOWYCH NA WĘGLU AKTYWNYM

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Abstrakt: Wykonano badania porównawcze szybkości adsorpcji z wieloskładnikowych wodnych roztworów wybranych chlorofenoli (2-CP, 3-CP, 4-CP) i herbicydów chlorofenoksyoctowych (2,4-D, MCPA) na granulowanym węglu aktywnym (F-300). Stężenia wszystkich adsorbatów w fazie wodnej oznaczano za pomocą wysokosprawnej chromatografii cieczowej (HPLC). Zbadano przydatność dwóch modeli kinetycznych: pseudopierwszego i pseudodrugiego rzędu do opisu wyników eksperymentalnych. Uzyskane rezultaty pokazują, że kinetykę adsorpcji lepiej opisuje równanie pseudodrugiego rzędu, co potwierdziły większe wartości współczynnika korelacji dla wszystkich adsorbatów ($R^2 \geq 0,997$).

Słowa kluczowe: adsorpcja, węgiel aktywny, chlorofenole, herbicydy chlorofenoksyoctowe, kinetyka adsorpcji