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Kinetic and equilibrium studies of simultaneous adsorption of monochlorophenols and chlorophenoxy herbicides on activated carbon

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ABSTRACT

Adsorption on activated carbon is one of the well-established and effective techniques for the removal of chloroorganic pollutants from surface water, groundwater, and drinking water. Since these water contaminants occur often together in the present study, kinetics and equilibria of simultaneous adsorption of selected chlorophenols and chlorophenoxy herbicides from aqueous solutions are investigated and described. For investigations, three monochlorophenols (2-chlorophenol, 3-chlorophenol, and 4-chlorophenol), as well as chlorophenoxy hebicides (2,4-dichlorophenoxyacetic acid and 2-methyl-4-chlorophenoxyacetic acid), are chosen. As adsorbent granular-activated carbon Filtrasorb 300 (938 m^2/g) was used. Adsorption quantities were determined by HPLC method. Kinetics of adsorption was described by pseudo-second-order model and adsorption equilibria by Freundlich equation. Proposed method can be used for adsorption from multicomponent aqueous solutions.

Keywords: Chlorophenols; Chlorophenoxy herbicides; Activated carbon; Adsorption kinetics; Adsorption equilibria

1. Introduction

Halogenated organic contaminations of surface water, groundwater, and drinking water are a serious threat to living organisms. They include in particular chlorophenols and chlorophenoxy herbicides [1,2]. Among chlorophenols can be distinguished groups of isomers of equal number of chlorine atoms in the molecule, for example three monochlorophenols. They differ in the position of the chlorine atom in the aromatic ring: 2-chlorophenol, 3-chlorophenol, and 4-chlorophenol. In the published works, the adsorption of chlorophenols on activated carbon is rarely used for comparing two isomers [3–8] or even three [9,10] of one Cl atom in molecule. These studies were carried out separately for each adsorbate [11–16], mainly for 4-CP. In the case of chlorophenoxy herbicides, most commonly studied by adsorption is 2,4-D (two Cl atoms in the aromatic ring) [17–25]. In the few works is also MCPA used for comparison [26–30]. The difference between them lies in the replacement in the 2,4-D one chlorine atom in the 2-position by a –CH_3 group. Chlorophenols are formed as by-products often during the production of herbicides, and therefore both groups may be present very common in the environment (especially in surface water and groundwater) simultaneously. However, in the literature,

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both chlorophenols and herbicides are examined separately. To the best of our knowledge, a direct comparison of the adsorption kinetic and equilibrium of chlorophenols and herbicides onto activated carbon has not been described.

The objective of the present study is to investigate and describe kinetics and equilibria of simultaneous adsorption of selected chlorophenols (2-, 3-, and 4-chlorophenol) and chlorophenoxy herbicides (2,4-D and MCPA) on granular-activated carbon from aqueous solutions.

2. Materials and methods

2.1. Chemicals and reagents

2-Chlorophenol, >99% (2-CP), 3-chlorophenol, 98% (3-CP), and 4-chlorophenol, >99% (4-CP) were from Sigma (St Louis, MO, USA). 2,4-Dichlorophenoxyacetic acid, >99% (2,4-D), 2-methyl-4-chlorophenoxyacetic acid, 99% (MCPA), and acetic acid were obtained from POCH (Gliwice, Poland). HPLC-grade acetonitrile was from Acros Organics (Geel, Belgium).

2.2. Adsorbent

The granular-activated carbon Filtrasorb 300 used in this study was purchased from Chemviron (Feluy, Belgium). Prior to use, the carbon was pretreated by washing in distilled water several times. Ash content decreased in that way from 8.05 to 7.85 wt.%. Finally, the activated carbon was dried in an oven at 120°C for 6 h and stored in a desiccator until use. The main properties characterizing the prepared carbon are as follows: the BET surface area of the carbon = 938 m^2/g, iodine number = 927 mg/g, NaOH neutralization ability 0.07 mmol/g, and surface oxygen content from EDS—4.57 wt.% [12].

2.3. Adsorption procedure

The kinetic experiments were carried out with following procedure. A fixed amount of the activated carbons (0.2 g) and a 100 ml of the solutions containing a initial concentration of adsorbates $C_0 = 100$ mg/l were placed in an Erlenmeyer flask, shaken at 25 °C, and theirs concentrations were analyzed after 1, 2, 3, 4, 5, 6, and 7 h. The amount of adsorption at time t, q_t (mg/g), was calculated by equation:

$$q_t = V\frac{C_0 - C_t}{m} \tag{1}$$

where C_0 and C_t are the initial concentration and adsorbate concentration at time t (mg/l), respectively, m is the mass of the adsorbent (g), and V is the volume of the solution (l).

For the determination of adsorption isotherms, a fixed amount of the activated carbons (0.2 g) and a 100 ml of the solutions containing a known concentration of monochlorophenols and chlorophenoxy herbicides (ranged from 5 to 100 mg/l) were placed in an Erlenmeyer flask and shaken at 25 °C for 6 h. After mixing, solutions were filtered through a 0.2 μm pore-size filter and analyzed. The uptake of the adsorbates at equilibrium, q_e (mg/g), was calculated by the following equation:

$$q_e = V\frac{C_0 - C_e}{m} \tag{2}$$

where C_e is the equilibrium concentration of adsorbates (mg/l) in solution.

2.4. Chromatographic analysis

The concentration of monochlorophenols and chlorophenoxy herbicides in water solutions was measured by high-performance liquid chromatography with diode-array detector (Shimadzu LC-20, Kyoto, Japan). Separation of analytes was performed using a Phenomenex Luna C_{18} (4.6 × 150 mm, 3 μm) column (Torrance, CA, USA). For separation of the adsorbates, gradient elution was used. The elution profile was as follows: 0–10 min 25–55% B; 10–12 min 55% B; where elution solvent (A) was water adjusted to pH 3.0 with acetic acid and (B) acetonitrile. The temperature was 25°C, the flow rate 1.0 ml/min, and the detector wavelength was from 274 to 283 nm. Twenty μl of the sample was injected into the chromatographic column.

3. Results and discussion

3.1. Chromatography

Under applied chromatographic conditions, eluted peaks were distinctly separated. Typical chromatogram is shown in Fig. 1. Identification of peaks was based on comparison of retention times and diode-array spectra, taken at real time of analysis, with corresponding set of data obtained for authentic compounds. The calibration curves were constructed by plotting peak height vs. analytes' concentration and the curves were fitted by least squares linear regression analysis. The calibration range was 0.2–100 mg/l for all compounds. The equations for the linear regression lines and regression coefficients are presented in Table 1.

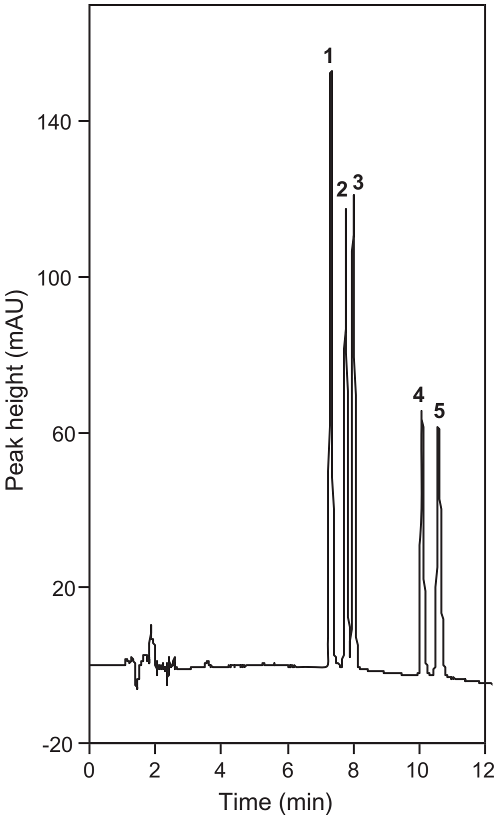

Fig. 1. Chromatogram of a starting monochlorophenols and chlorophenoxy acids mixture in water before the adsorption measurements; concentration of each compound 50 mg/l; chromatographic conditions as described in text: Peaks: (1) 2-CP; (2) 4-CP; (3) 3-CP; (4) MCPA; (5) 2,4-D.

Table 1
Calibration and validation results

Compounds	Linear regression equation $y = ax + b$	Regression coefficient R^2	Analytical wavelength (nm)
2-CP	$y = 3.4409x + 0.7268$	0.9993	274
3-CP	$y = 2.8759x + 0.2958$	0.9994	274
4-CP	$y = 3.1748x - 0.3761$	0.9994	281
2,4-D	$y = 0.8755x + 2.6746$	0.9975	283
MCPA	$y = 0.9850x + 0.5845$	0.9971	278

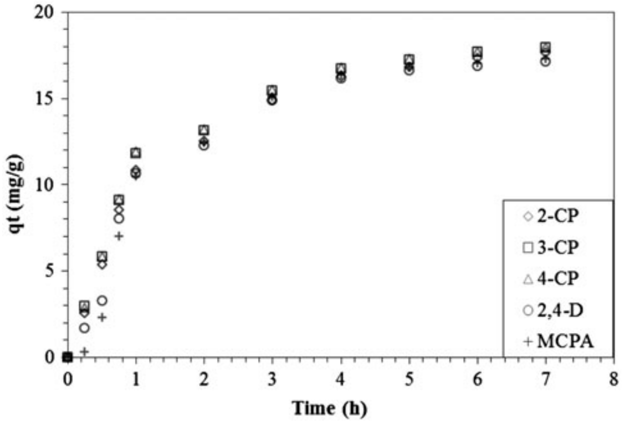

Fig 2. Adsorption kinetics of selected phenols and herbicides on granular-activated carbon Filtrasorb 300 at 25˚C, initial concentration 100 mg/l.

Table 2
The pseudo-first and pseudo-second-order-rate constants of selected phenols and herbicides on granular-activated carbon Filtrasorb 300 at 25˚C; initial concentration 100 mg/l

Compounds	Pseudo-first-order		Pseudo-second-order	
	k_1 (1/h)	R^2	k_2 (g/mg h)	R^2
2-CP	0.689	0.989	21.241	0.997
3-CP	0.725	0.987	17.560	0.998
4-CP	0.714	0.986	17.316	0.997
2,4-D	0.811	0.986	18.842	0.997
MCPA	0.830	0.988	19.172	0.997

3.2. *Adsorption rate constant*

Fig. 2 shows the adsorption kinetics of selected chlorophenols and herbicides on granular-activated carbon Filtrasorb 300 at 25˚C. In order to investigate the kinetics of adsorption of selected chloroorganic compounds on activated carbon, the rate constants were determined in terms of the pseudo-first-order and pseudo-second-order models. The pseudo-first-order kinetic model is expressed as [31]:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - \frac{k_1}{2.303}t \qquad (3)$$

where q_e and q_t are the amounts of adsorption at equilibrium (mg/g) and at time t (h), respectively, and k_1 is the rate constant of adsorption (1/h). Values of k_1 were calculated from the plots of $\log(q_\mathrm{e} - q_t)$ vs. t for different concentrations of selected adsorbates.

If the sorption follows pseudo-second-order mechanism, the equation has the form [32]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_\mathrm{e}^2} + \frac{1}{q_\mathrm{e}}t \qquad (4)$$

where q_e and q_t are the amounts of adsorption at equilibrium and at time t, respectively, and k_2 is the rate constant of second-order adsorption (g/mg h). Values of k_2 were calculated from the intercept and slope of the plots of t/q_t vs. t. The results are summarized in Table 2.

The pseudo-second-order model fits the experimental data quite well for all adsorbates with the correlation coefficients greater than 0.99. These results indicate that the adsorption system belongs to the second-order kinetic model.

3.3. Adsorption isotherms

Adsorption isotherms of monochlorophenols and chlorophenoxy herbicides on the activated carbon are shown in Fig. 3. The experimental isotherms were modeled according to the Langmuir [33] and Freundlich [34] models. The Langmuir empirical model is represented by:

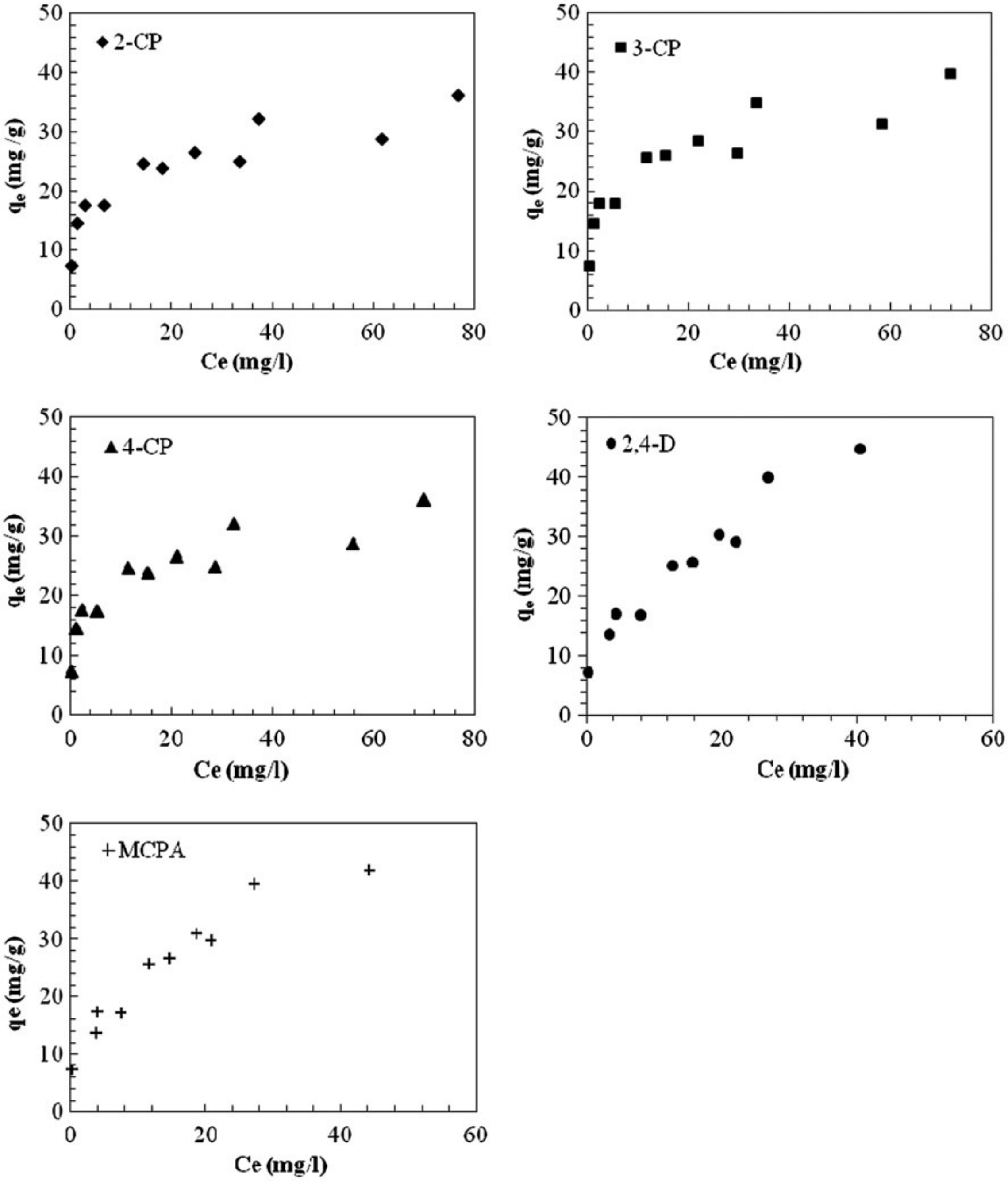

Fig 3. Adsorption isotherms of 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenoxyacetic acid, and 2-methyl-4-chlorophenoxyacetic acid on granular-activated carbon Filtrasorb 300 at 25 °C.

$$q_e = \frac{bq_m C_e}{1 + bC_e} \tag{5}$$

where b is the constant related to the free energy of adsorption (l/mg) and q_m the maximum adsorption capacity (mg/g). After integrating and applying the initial conditions, the integrated form of Eq. 4 becomes:

$$\frac{1}{q_e} = \frac{1}{bq_m}\frac{1}{C_e} + \frac{1}{q_m} \tag{6}$$

In order to obtain the rate constants and correlation coefficients, the straight-line plots of $1/q_e$ vs. $1/C_e$ for the selected adsorbates have been tested.

The experimental data were also fitted to the Freundlich equation:

$$q_e = K_F C_e^{1/n} \tag{7}$$

which can be linearized to linear form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

where K_F is a constant indicative of the relative adsorption capacity of the adsorbent ((mg/g) (l/mg)$^{1/n}$) and n is a constant indicative of the intensity of the adsorption. The straight-line plots of ln q_e against ln C_e were constructed. K_F and $1/n$ values were obtained from the intercept and slope in linear regression result.

The results are summarized in Table 3.

In general, the linear regression correlation coefficient values show that the equilibrium data obtained for all adsorbates were better described by the Freundlich model than by the Langmuir isotherm model. The Freundlich constant K_F can be considered as an indicative parameter of the adsorption strength. The values of K_F determined from the Freundlich plots decreased in the order 4-CP > 3-CP > 2-CP > MCPA > 2,4-D. This suggests that chloroorganics adsorption by granular-activated carbon Filtrasorb 300 decreased in similar order. Moreover, chlorophenols are better adsorbed on activated carbon than chlorophenoxy hebicides.

Table 3
Langmuir and Freundlich equations correlation coefficients as well as K_F and $1/n$ parameters for the adsorption of selected phenols and herbicides on granular-activated carbon Filtrasorb 300 at 25˚C

Compounds	Langmuir	Freundlich		
	R^2	K_F*	$1/n$	R^2
2-CP	0.911	11.646	0.251	0.946
3-CP	0.961	12.554	0.260	0.946
4-CP	0.959	12.667	0.267	0.954
2,4-D	0.788	9.244	0.410	0.934
MCPA	0.881	9.708	0.391	0.947

*((mg/g) (l/mg)$^{1/n}$).

4. Conclusions

Selected adsorbates—three monochlorophenols and two chlorophenoxy herbicides—are typical water pollutants. In environmental conditions, most often in surface water, groundwater, and even drinking water, many pollutants are present simultaneously. Despite this, both groups of compounds (chlorophenols and herbicides) are generally considered and studied separately. In this work, it is shown that the investigation of simultaneous adsorption of several chloroorganic compounds from aqueous solution on activated carbon is possible. In the case of kinetic studies, it is stated that dependence of adsorption quantity on time follows better model: pseudo-second-order than pseudo-first-order. For all adsorbates, R^2 reaches high values. Chlorophenols are better adsorbed on the surface of activated carbon than herbicides. Adsorption equilibria are very well described by Freundlich equation for all adsorbates used.

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