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Sorption equilibrium prediction of competitive adsorption of herbicides 2,4-D and MCPA from aqueous solution on activated carbon using ANN

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Abstract The simultaneous adsorption of two herbicides—2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA)—from their aqueous binary mixtures onto granular activated carbon was studied. The quantities adsorbed were determined by HPLC with UV detection. The experimental data were analysed using the Freundlich adsorption isotherm. The high correlation coefficients indicated that the adsorption equilibrium fitted the Freundlich isotherm well. A multilayer perceptron (MLP) (an artificial neural network model—ANN) was applied to describe the adsorption equilibrium in multicomponent systems. This enabled sorption isotherms to be predicted for all possible combinations of the two herbicides. The experimental results and the calculated data obtained from MLP for the solutions of the individual components and their mixtures suggest that MCPA is better adsorbed onto activated carbon than 2,4-D.

Keywords Chlorophenoxy herbicides · Activated carbon · Adsorption · ANN

List of symbols

ANN	Artificial neural network
b_1, b_2, b_3, b_4	Biases—the signals shifting according to Fig. 1 (dimensionless)
C_0	The initial concentration of the adsorbate in solution (mmol/dm^3)
C_e	The equilibrium concentration of the adsorbate in solution (mmol/dm^3)
D	2,4-D; 2,4-dichlorophenoxyacetic acid
GAC	Granular activated carbon
K_F	Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mmol/g)·(dm^3/mmol)$^{1/n}$
m	The mass of the adsorbent (g)
M	MCPA; 4-chloro-2-methylphenoxyacetic acid
MLP	Multilayer perceptron
n	Freundlich constant indicative of the intensity of the adsorption (dimensionless)
N	The number of calculated coefficients in MLP network (dimensionless)
P	The number of experimental data, (dimensionless)
q_e	The amount of solute adsorbed per unit mass of adsorbent at equilibrium (mmol/g)
r^2	Squared coefficient of determination (dimensionless)
R^2	Squared correlation coefficient (dimensionless)
S_{BET}	Brunauer–Emmett–Teller surface area (m^2/g)
S_{me}	Mesopore surface area (m^2/g)
V	The volume of the solution (dm^3)
V_{me}	Mesopore volume (cm^3/g)
V_{mi}	Micropore volume (cm^3/g)
w_{kj}	Weights of signal between neuron k and j according to Fig. 1 (dimensionless)

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1 Introduction

The widespread use of pesticides has led to many possible sources of contamination by these compounds in the

environment. Chlorinated phenoxyacetic acid herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA), are among the most commonly used herbicides (Stoytcheva 2011; Legrouri et al. 2005; Derylo-Marczewska et al. 2010; Foo and Hameed 2010). They are preferred because of their low cost and good selectivity; nevertheless, they represent a potential risk to water resources as they are poorly biodegradable and quite mobile in aqueous systems because of the acidic carboxyl group they contain. Moreover, a consequence of their large-scale application is that they are present throughout the environment, contaminating *inter alia* surface and ground waters (Stoytcheva 2011). The toxicity of pesticides and their degradation products renders such chemicals potentially hazardous to the environment and human health. Thus, it is important to prevent their release into the environment.

Several methods are used to remove chlorinated phenoxyacetic acid herbicides from water, including biodegradation (Onbasili and Aslim 2011; Evangelista et al. 2010; Sanchis et al. 2013), photocatalytic (Zertal et al. 2004; Djebbar et al. 2006; Abramovic et al. 2009; Sojic et al. 2010) and electrochemical (Boye et al. 2003; Brillas et al. 2004; Fontmorin et al. 2012) degradation, oxidation by Advanced Oxidation Processes (AOPs) (Benitez et al. 2004; MacAdam and Parsons 2009; Garcia-Segura et al. 2011; Rivera-Utrilla and Sanchez-Polo 2012; Sanchis et al. 2013). However, adsorption has proven to be one of the most attractive and effective methods for removing these herbicides from water, due to its low maintenance costs, high efficiency and simplicity of operation. Activated carbons are the most frequently used adsorbents for this purpose. Sometimes, as adsorbents other materials are also used, e.g. carbon nanotubes and metal oxide nanoparticles (De Martino et al. 2012) or clay (Prates Ramalho et al. 2013). Most of the cited papers relate to the adsorption of just one of the two herbicides examined in the present work: either 2,4-D (Aksu and Kabasakal 2004; Chingombe et al. 2006; Hameed et al. 2009; Salman and Hameed 2010; Njoku and Hameed 2011; Salman et al. 2011) or MCPA (Gimeno et al. 2003; De Martino et al. 2012; Prates Ramalho et al. 2013). Only a few describe the adsorption of both 2,4-D and MCPA (Derylo-Marczewska et al. 2010; Kim et al. 2008; Ignatowicz 2009; Ocampo-Perez et al. 2012; Vergili and Barlas 2009; Kusmierek et al. 2014). However, these adsorption studies focused on the uptake of a single adsorbate. Structurally very similar, 2,4-D and MCPA are used for the same purposes. The difference between them lies in the replacement in 2,4-D of one chlorine atom in position 2 by a $-CH_3$ group. Therefore, agricultural or industrial effluents may at once contain 2,4-D, MCPA and the derivatives of both. Hence, a study of the simultaneous adsorption of these pollutants is required. To the best of our knowledge, no information is available in the literature on the simultaneous removal by activated carbon of 2,4-D and MCPA from their aqueous binary mixtures.

The aim of this study is to acquire an understanding of the simultaneous adsorption of the two herbicides 2,4-D and MCPA on granular activated carbon from aqueous solutions. A multilayer perceptron (MLP) (an artificial neural network model—ANN) was used to describe the adsorption equilibrium in multicomponent systems.

2 Experimental

2.1 Materials

98 % 2,4-Dichlorophenoxyacetic acid (2,4-D) and >99 % 4-chloro-2-methylphenoxyacetic acid (MCPA) were from Sigma-Aldrich (St. Louis, MO, USA). HPLC-grade acetonitrile and 99.5 % acetic acid were obtained from POCH (Gliwice, Poland). The granular activated carbon Filtrasorb 400 (GAC) was purchased from Chemviron (Feluy, Belgium). Prior to use, the GAC was de-ashed using conc. HCl and HF acids and rinsed several times with deionised water, after which it was dried in an oven at 130 °C to constant weight and stored in a desiccator. The GAC specific surface area according to the BET equation was $S_{BET} = 997\ m^2/g$, micropore volume $V_{mi} = 0.310\ cm^3/g$, mesopore volume $V_{me} = 0.113\ cm^3/g$, mesopore surface area $S_{me} = 41\ m^2/g$ (Biniak et al. 2006).

2.2 Adsorption procedure

For the determination of adsorption isotherms, 0.03 g of granular activated carbon and 40 cm^3 of solutions containing a known concentration of 2,4-D and/or MCPA (from 0.05 to 0.5 $mmol/dm^3$) were placed in an Erlenmeyer flask and shaken at 25 °C for 8 h. After mixing, the solutions were passed through a 0.2 μm pore size filter and analysed chromatographically. Adsorbates were adsorbed onto granular activated carbon from single (100 % of 2,4-D or MCPA) and binary mixtures containing 25/75, 50/50 or 75/25 of 2,4-D and MCPA (ratio of the initial molar concentrations of the components in the solution). The uptake of the adsorbate at equilibrium, q_e (mmol/g), was calculated from the equation:

$$q_e = V\frac{C_0 - C_e}{m} \quad (1)$$

where C_e is the equilibrium concentration of adsorbate ($mmol/dm^3$) in solution.

2.3 Analytical method

HPLC with UV detection (Shimadzu LC-20, Kyoto, Japan) was used to determine 2,4-D and/or MCPA. The

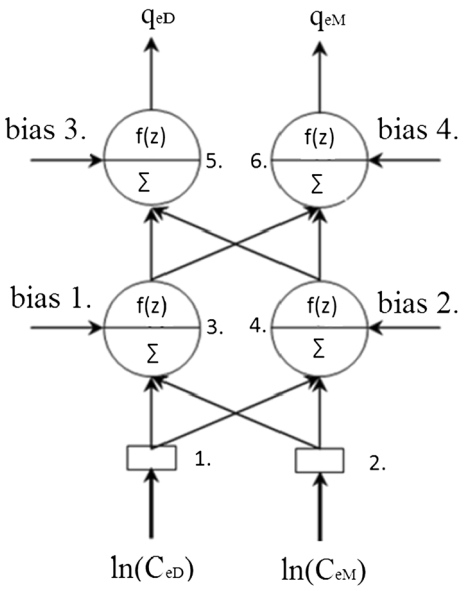

Fig. 1 Diagram of the ANN

chromatographic analysis was carried out under isocratic conditions on a Phenomenex Luna C18, 4.6 × 150 mm, 3 μm column (Torrance, CA, USA) thermostatted at 40 °C. The mobile phase consisted of acetonitrile and water adjusted to pH 3.0 with acetic acid (65/35, v/v); the flow rate was 0.7 cm^3/min and the detection wavelengths were 283 and 278 nm for 2,4-D and MCPA respectively.

2.4 Artificial neural network

Artificial Neural Networks (ANN) offer a qualitative approach to process modelling. Shaped after biological neural systems, these networks are composed of multiple interconnected non-linear processing elements. The computational capabilities of ANNs result from their ability to learn, i.e. to form an internal representation of process input–output parameters represented by experimental data. In addition, these networks can approximate precisely an arbitrary, continuous non-linear mapping function of many variables. Thus, there is a firm theoretical basis for using ANNs as universal models of non-linear multi-dimensional systems.

Examples of application of ANN to predict sorption isotherms are as follows: sorption of phenol on activated carbon from aqueous solutions (Shahryari et al. 2013a), sorption of methylene blue onto multiwalled carbon nanotubes (Shahryari et al. 2013b), sorption of a mixture of heavy metal on clinoptilolite from an aqueous solution (Tomczak and Kaminski 2012) and, the competitive adsorption isotherm of 2-phenylethanol and 3-phenylpropanol in liquid chromatography (Wu et al. 2014).

In the present work, an ANN—a multilayer perceptron MLP with feed forward connections—was used to predict the competitive sorption equilibrium of two herbicides from aqueous solution. After the preliminary calculations and analysis of network topologies (number of hidden neurons, determination of the transfer function), the network illustrated in Fig. 1 was obtained.

It was assumed that the inputs to the network were the natural logarithms of the concentrations of herbicides D and M in the solution. If any of the components was not present in solution, the value of the corresponding input was equal to $C_e = 10^{-5}$ mmol/dm^3. This complied with the detection limit concentration. Each connection between neurons was assigned a weight. A logistic function in the neurons in the hidden layer and the output layer was adopted as the transfer function. The total transfer functions (input–output) took the form:

$$q_{eD} = f(w_{35} \cdot f(z_1) + w_{45} \cdot f(z_2) + b_3) \quad (2)$$

$$q_{eM} = f(w_{36} \cdot f(z_1) + w_{46} \cdot f(z_2) + b_4) \quad (3)$$

where

$$z_1 = w_{13} \cdot \ln(c_{eD}) + w_{23} \cdot \ln(c_{eM}) + b_1 \quad (4)$$

$$z_2 = w_{14} \cdot \ln(c_{eD}) + w_{24} \cdot \ln(c_{eM}) + b_2 \quad (5)$$

f(z)—logistic transfer function, which limits the output results to between 0 and 1.

$$\mathrm{f(z)} = \frac{1}{1 + \exp(-\mathrm{z})} \quad (6)$$

Equations (2)–(5) include 4 biases and 8 weights, a total of 12 unknown coefficients, which were matched to the experimental data in the learning procedure. Total number of experimental points was 30 and 21 points were use for training and the other 9 randomly selected were used for validation. The Levenberg-Marquard learning method was applied. The calculations were performed in the MATLAB environment. The learning process started from randomly selected coefficients. The Levenberg-Marquard method (second order) was used to find the global minimum of the objective function, and the sum of the deviations of experimental and calculated values. Because the location of the minimum of the objective function depends on the starting point, the calculations were repeated 150 times in order to find the best solution (global minimum). The resulting weights of the network after the learning process are summarised in Table 1.

3 Results and discussion

3.1 Equilibrium studies—traditional description

The adsorption isotherms of 2,4-D and/or MCPA on granular activated carbon from water were studied.

Table 1 Weights and biases in MLP network

$w_{13} = -0.33718841$	$w_{23} = -0.06489582$
$w_{14} = -0.27829006$	$w_{24} = -0.14626705$
$b_1 = -1.9692488$	
$b_2 = -2.0931238$	
$w_{35} = -21.218444$	$w_{45} = +11.179416$
$w_{36} = +67.319396$	$w_{46} = -72.956190$
$b_3 = +1.4924107$	
$b_4 = -0.70732469$	

Table 2 Freundlich adsorption isotherm model parameters and correlation coefficients R^2 for the adsorption of chlorinated phenoxyacetic acid herbicides onto granular activated carbon

2,4-D				MCPA			
% in mixture	K_F	n	R^2	% in mixture	K_F	n	R^2
100	2.235	1.255	0.993	0	–	–	–
75	1.393	1.176	0.997	25	0.973	1.368	0.983
50	1.266	1.302	0.988	50	1.492	1.356	0.995
25	1.190	1.359	0.987	75	1.701	1.425	0.981
0	–	–	–	100	3.521	1.190	0.995

The Langmuir and Freundlich models were used to fit the experimental data but the better results were obtained using the second one. The Freundlich isotherm (Freundlich 1906), for single component is given by Eq. (7):

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

which can be linearized to

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

where K_F (mmol/g)·(dm^3/mmol)$^{1/n}$ and n are Freundlich equation constants relating to the sorption capacity and sorption intensity of the adsorbent. Straight line plots of ln q_e against ln C_e were constructed and the curves were fitted by least squares linear regression. Values of K_F and 1/n were obtained from the intercept and slope in the linear regression. In that way it was possible to obtain four different equations describing equilibrium state for each herbicide 2,4-D and MCPA alone and in the mixture and appropriate coefficients are listed in Table 2.

The linear regression correlation coefficients show that the equilibrium data obtained for both herbicides were well represented by the Freundlich isotherm model—Eq (8). The Freundlich constant K_F calculated for solutions containing only a single adsorbate (100 %) was much higher for MCPA (3.521 (mmol/g)·(dm^3/mmol)$^{1/n}$) than for 2,4-D (2.235 (mmol/g)·(dm^3/mmol)$^{1/n}$). This suggests that MPCA is better adsorbed onto activated carbon than 2,4-D.

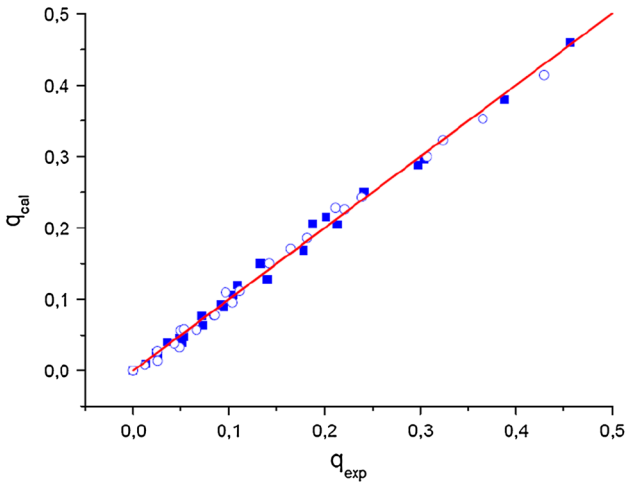

Fig. 2 Comparison of experimental and calculated values (*circle*-herbicide M, *squares*-herbicide D) for pure components and the mixtures

Table 3 Statistical evaluations for the: 2,4-D (D) and MCPA (M) herbicides

Name	Fisher test	Squared coefficient of determination r^2	Root mean square error sqrt ($\sum(q_{exp}-q_{cal}^2/p)$
Herbicide D	186.37	0.996	0.00809
Herbicide M	148.87	0.995	0.00799

3.2 Equilibrium studies—MLP description

As a result of the calculations using the MLP, sorption equilibria were obtained depending on the solution composition and concentration at equilibrium state (30 points for 2,4-D and 30 points for MCPA). The experimental and calculated values are compared in Fig. 2.

The following estimations were used for the statistical evaluation: Fisher's test, the squared coefficient of determination and the root mean squares error. Fisher's test was applied to $p = 30$ the number of experimental data, $N = 12$ was the number of calculated coefficients, and the 99 % confidence level was equal to $F = 3.92$. The statistical calculations for the two herbicides are summarized in Table 3. The statistical data indicate very good fitting of the experimental data by means of MLP.

The experimental results and the calculated data obtained from the MLP for the solutions of the individual components and their mixtures are shown in Figs. 3 and 4. Figure 3 is for the herbicide 2,4-D alone and in the mixture and Fig. 4 is for MCPA alone and in the mixture.

When 2,4-D is present in the solution, the sorption isotherms of 2,4-D herbicide for mixtures containing from

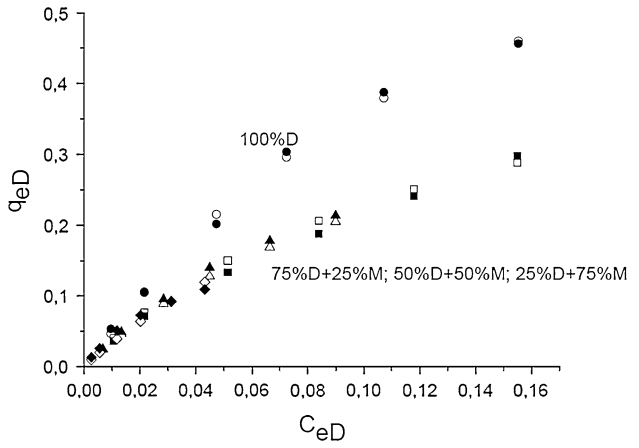

Fig. 3 Sorption isotherms for 2,4-D-component pure and in the mixtures (100 %D; 75 %D + 25 %M; 50 %D + 50 %M; 25 %D + 75 %M). Open symbol-calculated, solid symbol-experimental data

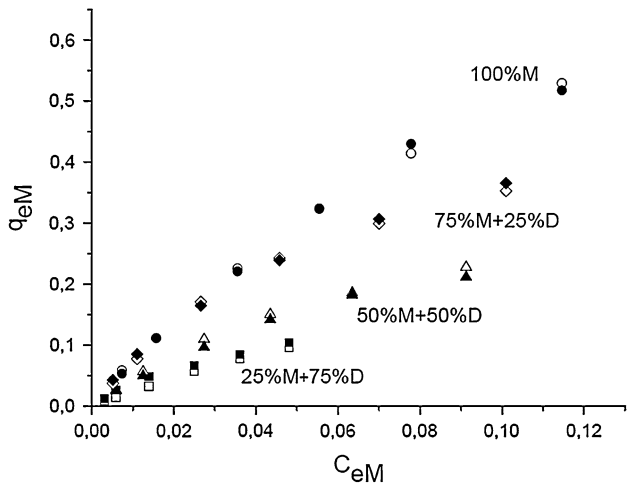

Fig. 4 Sorption isotherms for MCPA-component pure and in the mixtures (100 %M; 25 %D + 75 %M; 50 %D + 50 %M; 75 %D + 25 %M). Open symbol-calculated, solid symbol-experimental data

25 to 75 % are slightly different. This means that MCPA is preferentially adsorbed. Such an effect cannot be predicted for mixtures of components from the known theory of adsorption (Koopal et al. 1994; Crittenden et al. 1985).

4 Conclusions

1. Traditional approach to describe sorption isotherm using Freundlich model allows obtaining relationship between concentration for given component in the solution (C_e) and the amount of solute adsorbed per unit mass of adsorbent at equilibrium (q_e). However it is not possible to describe the sorption isotherms for multicomponent mixture applying Freundlich approach in one equation for all possible composition.
2. Predicting sorption isotherms for multicomponent mixtures on the basis of the sorption of the individual components and applying appropriate models of interactions may often lead to significant errors.
3. Adsorption of herbicides 2,4-D and MCPA from aqueous solutions demonstrates the competitiveness and the dominance of MCPA.
4. MLP can be used to calculate the adsorption isotherms of aqueous solutions of the herbicides 2,4-D and MCPA individually and for their mixtures.
5. The application of ANN for predicting equilibrium sorption is particularly useful for solutions containing many components. Among other things, this approach permits parallel processing of the data.

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