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Optimization of thiamethoxam adsorption parameters using multi-walled carbon nanotubes by means of fractional factorial design

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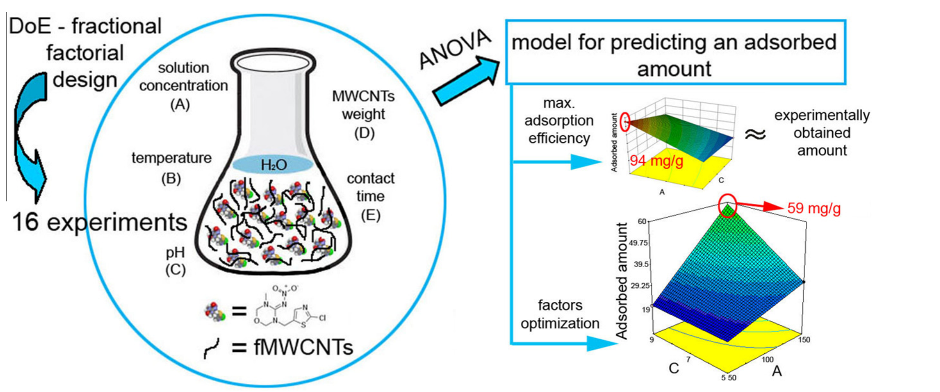
HIGHLIGHTS

- Adsorption potential of CNTs was studied in a thiamethoxam-in-water model system.
- Significant factors were evaluated using 2_V^{5-1} fractional factorial design.
- The obtained linear model was statistically tested using ANOVA.
- The initial solution concentration was found to be the most influencing parameter.
- Optimization was carried out by minimizing parameters usually critical in real life.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work was to evaluate significant factors affecting the thiamethoxam adsorption efficiency using oxidized multi-walled carbon nanotubes (MWCNTs) as adsorbents. Five factors (initial solution concentration of thiamethoxam in water, temperature, solution pH, MWCNTs weight and contact time) were investigated using 2_V^{5-1} fractional factorial design. The obtained linear model was statistically tested using analysis of variance (ANOVA) and the analysis of residuals was used to investigate the model validity. It was observed that the factors and their second-order interactions affecting the thiamethoxam removal can be divided into three groups: very important, moderately important and insignificant ones. The initial solution concentration was found to be the most influencing parameter on thiamethoxam adsorption from water. Optimization of the factors levels was carried out by minimizing those parameters which are usually critical in real life: the temperature (energy), contact time (money) and weight of MWCNTs (potential health hazard), in order to maximize the adsorbed amount of the pollutant. The results of maximal adsorbed thiamethoxam amount in both real and optimized experiments indicate that among minimized parameters the adsorption time is one that makes the largest difference. The results of this study indicate that fractional factorial design is very useful tool for screening the higher number of parameters and reducing the number of adsorption experiments.

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1. Introduction

In recent years, the interest for carbon nanotubes (CNTs) was emphasized in the field of different contaminants elimination from the environment (Pyrzynska, 2011). In order to solve problems related to environmental pollution, the application of CNTs as adsorbent was the subject of numerous studies. Pesticides are studied more than any other environmental contaminant due to their extreme toxicity to the fragile environment. Thiamethoxam ((EZ)-3-(2-chloro-1,3-thia-zol-5-ylmethyl)-5-methyl-1,3,5-oxadia zinan-4-ylidene(nitro)amine) is a broad-spectrum, systemic insecticide from the second generation of neonicotinoids (Jeschke and Nauen, 2008; Elbert et al., 2008). It acts on the level of nicotinic acetylcholine receptors in the central nervous system of insects. Thiamethoxam is worldwide used for foliar (marked Actara, Force, Celset) and seed-treatment (marked Cruiser). To date, it holds registration for 115 crop uses in more than 64 countries. Due to wide areas of thiamethoxam application, there is a growing need for its removal from the environment.

Elimination of any pollutant by means of adsorption is influenced by many factors, such as temperature and pH of solution, initial solution concentration, and adsorbent dosage. A common way to study the influence of adsorption parameters and optimize them is to use one-factor-at-a-time experimental approach which considers testing the response against one factor maintaining all others at constant values. This approach is time-consuming and expensive due to the many required experiments that have to be performed (Rahmanian et al., 2011). Moreover, this method is not able to determine the effects of interaction between the parameters, making the conclusion regarding the optimization unreliable. In order to circumvent the drawbacks of this conventional method, the design of experiments (DoE) approach can be used. Within the scope of DoE, factorial design and response surface methodology are important tools to determine the effects of process parameters, their interactions, as well as to optimize the process conditions (Gheshlaghi et al., 2008). A so-called full factorial design includes screening of the changes in response obtained in all possible combinations of the levels of the factors in all replications (Montgomery, 2001; Box et al., 2005; Antony, 2003). The observed effects are categorized as main effects (influence of primary factors) and joint effects of several primary factors, i.e. two-factor interactions (2fi), three-factor interactions (3fi), etc. 2^k factorial design, where each factor takes value on two levels ("high" and "low"), is widely used in investigations. Full factorial design is useful for studying the systems with small number of factors, but when the number of factors is large ($k \geqslant 4$), the required number of experiments becomes unreasonable (Lundstedt et al., 1998). Also, the interactions of order greater than 2fi are usually insignificant, therefore, it is often unnecessary to run all possible combinations of factor levels. A practical solution to overcome this problem is to use a fractional factorial design, which includes the performing of limited number of experiments in comparison with the full factorial design (Montgomery, 2001; Box et al., 2005). The goal of this experimental approach is to gather the largest possible amount of information with the smallest number of experiments.

The aim of this work was to study the effects of five process parameters (initial solution concentration, temperature, solution pH, weight of adsorbent, contact time) on the adsorbed amount of thiamethoxam from an aqueous solution using oxidized carbon nanotubes as adsorbents. Screening the factors and their interactions, as well as the optimization of adsorption conditions, was performed using the fractional factorial design.

2. Experimental

2.1. Synthesis and oxidation of multi-walled carbon nanotubes (MWCNTs)

MWCNTs were produced by catalytic chemical vapor deposition (CCVD) of ethylene over a 5%Fe–Co/Al_2O_3 catalyst prepared by metal precipitation on commercial γ-Al_2O_3 (Ketjen Catalysts) support (Ratkovic et al., 2009). The MWCNTs synthesis was carried out for 2 h in flow of ethylene/nitrogen mixture (1:1) at 700 °C, using *in situ* pre-reduced catalyst, in a home-made reactor setup that was described earlier (Ratkovic et al., 2009, 2011). The catalyst performed with high activity and selectivity to MWCNTs, measured as carbon yield of 264% and with no traces of amorphous carbon. In order to remove catalyst contamination, the raw product was purified by means of liquid oxidation, i.e. sequential boiling the raw MWCNTs under reflux in 3MNaOH and in concentrated HNO_3 solutions.

2.2. Characterization of oxidized multi-walled carbon nanotubes (MWCNTs)

The structure and morphology of purified MWCNTs were characterized by transmission electron microscopy (FEI TECNAI G2 20X-TWIN Transmission Electron Microscope). The sample texture was investigated by means of specific surface area determined by BET, mean pore diameter and pore volume determined from desorption part of the N_2 isotherm and calculated by Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951). Pores were classified according to Brunauer–Deming–Deming–Teller method based on hysteresis loops of adsorption–desorption isotherms (Lowell et al., 2004). Corresponding data for textural characterization were obtained by dynamic low temperature N_2 adsorption/desorption (LTNA) method, with He as a carrier gas, using Micromeritics ASAP 2010. FTIR spectroscopy was carried out on BRUKER Vertex 70 IR spectrometer in the wavenumber range of 4000–1000 cm^{-1} with the resolution of 2 cm^{-1}. Prior to FTIR characterization, the MWCNTs sample was prepared using the KBr method for solid samples by mixing it with spectroscopically pure KBr in 1:10 ratio.

2.3. Definition of model system and design of experiments

The focus of interest is purification of a model system – water polluted with thiamethoxam, by means of adsorption using MWCNTs. In order to get a broader picture of the chosen factors and their range on adsorption efficiency, an optimal number of experiments were determined by DoE.

2.3.1. Two-level fractional factorial design

Adsorption experiments were performed to determine the effects of 5 factors: initial solution concentration (thiamethoxam in water), temperature, solution pH, MWCNTs weight and contact time on the adsorbed amount of thiamethoxam. The DoE was used assuming a linear response generated by all the factors. By using two-level fractional factorial design and setting each parameter to "low" and "high" values in a 2_V^{5-1} arrangement it was possible to narrow down the number of runs to 16 instead of 32 required for full factorial design (Kukovecz et al., 2005). The applied resolution V results in a meaningful model providing a unique estimation of all main effects and 2f-interactions (Montgomery, 2001).

The independent factors and their levels applied in 2_V^{5-1} fractional design are described in Table 1. The chosen range of applied