



Removal of pesticide from wastewater: Contact time optimization for a two-stage batch stirred adsorber



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ABSTRACT

In the present paper, an experimental and model-based analysis is carried out to optimize the contact times of a batch stirred adsorber to remove the herbicide MCPA, a herbicide that causes serious environmental concerns due to its persistence in the environment. Mesoporous Al_2O_3 has been used as sorption material.

The study shows that a two-stage adsorber offers a satisfactory option to obtain high herbicide removal fractions with short treatment times. An interesting result is that, for high percentages of removal, the optimal first stage contact time can be considered constant and is approximately two thirds of the total contact time for the case in examination.

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Introduction

The reduction of the potential toxic, carcinogenic and mutagenic effects caused by pesticide contamination of soils and water bodies is nowadays an important political and environmental question, taking into account the viable importance of water in many areas of the world. The Council Directive 98/83/CE sets the following requirement for drinking water: it allows a maximum residue of $0.1 \mu\text{g L}^{-1}$ for a single active substance and $0.5 \mu\text{g L}^{-1}$ for the sum of pesticides and their degradation products [1].

Consequently, different methods have been studied so far to remove pesticides from waters, including membrane technologies (ultrafiltration [2], nanofiltration [3], and reverse osmosis [4]), solid phase extraction, ozone and chemical oxidation, Fenton degradation, photocatalysis and adsorption on various supports

[5]. In particular, several studies have been focused on the adsorption process, that is the most widespread technology used for wastewater treatment. As a matter of fact, adsorption offers high flexibility in design and regeneration of adsorbent materials, low maintenance costs, high efficiency, and simple operability.

This study is concerned at the holistic design of a pesticide adsorber; we focused on the adsorption of a post-emergence phenoxy acid herbicide (MCPA) on the mesoporous metal oxide Al_2O_3 .

MCPA, 4-chloro-2-methylphenoxyacetic acid, is widely used to control annual and perennial weeds in cereals, grasslands, trees, and turf. MCPA is a herbicide that causes serious environmental concerns due to its persistence in the environment; it can be found in different forms (free acid, salts and esters), all soluble in water, releasing acid as the active ingredient [6].

Being a mesoporous material, Al_2O_3 can offer large adsorption capacity, good selectivity and improved recoverability for the removal of toxic compounds from aqueous solutions [7–9].

The study deals in particular with the contact time optimization of a two-stage batch stirred adsorber.

Batch adsorbers represent a simpler and less expensive solution compared to continuous systems. Stirred adsorbers, on the other hand, offer a series of advantages in comparison to (non-stirred) fixed bed systems. First of all, mixing increases the adsorption rate, reducing mass transfer resistances. In addition to this, the pressure drop in a stirred plant is very low in comparison to a fixed bed, and the binding and the fouling of adsorbent particles are reduced as well [10,11]. Nevertheless, only a limited number of papers has been so far focused on the design of stirred adsorption systems.

Abbreviations: c_{sol} , amount of herbicide sorbed (measurements) ($\mu\text{mol kg}^{-1}$); \hat{c}_{sol} , amount of herbicide sorbed (model estimates) ($\mu\text{mol kg}^{-1}$); $c_{\text{sol,eq}}$, amount of herbicide sorbed at equilibrium ($\mu\text{mol kg}^{-1}$); c_{liq} , liquid phase adsorbate concentration ($\mu\text{mol L}^{-1}$); k_1 , pseudo-first order rate constant of adsorption (min^{-1}); k_2 , pseudo-second order rate constant of adsorption ($\text{kg } \mu\text{mol}^{-1} \text{min}^{-1}$); M , adsorbent mass (kg); r^2 , coefficient of determination; R_k , percentage of removal for i th stage (%); R_{tot} , total percentage of removal for the adsorber; t , time (min); t_i , contact time for i th stage (min); t_{tot} , total contact time for the adsorber (min); t_1' , 1st stage contact time that minimizes the adsorber total contact time (min); V_1 , system volume (L).

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These papers are about the adsorption of dyes [11–17], Pb^{2+} and Cd^{2+} ions [18–23], arsenate [24], phosphate [25].

It has been recently shown by our group that a two-stage adsorber may allow a significant reduction of the overall required adsorbent amount compared to a single-stage system having the same total volume which justifies the higher cost of the two-stage plant. On the contrary, the adoption of a three-stage system allows only a limited reduction of adsorbent in comparison to a two-stage system having the same total volume [26]. As far as we know, no other papers have been so far published about the design of stirred adsorption systems for the removal of herbicides [26].

Several authors, dealing with stirred systems in which the adsorption equilibrium is reached within a short time, or expensive sorbents are to be used, or the adsorption capacity of the adsorbent is small, have obtained the mass of adsorbent and optimized the number of stages of a multi-stage adsorber by using a steady-state analysis: with equilibrium data it is possible to determine the minimum mass of adsorbent required to remove a given amount of herbicide from a given volume of wastewater [9,10,12,13,26,27].

In the present paper, an alternative approach has been followed, based on a transient analysis: experimental MCPA single-stage adsorption kinetics has been analyzed to optimize the contact times of the system, considering that an optimal contact time is not long enough to reach an equilibrium state [11,15,16,20,22–25].

Materials and methods

Materials

The 4-chloro-2-methylphenoxyacetic acid (MCPA) was purchased from Sigma–Aldrich (99.0% purity). All solvents were of HPLC grade (Carlo Erba). All other chemicals were obtained from Sigma–Aldrich. γ -Aluminum (Al_2O_3) nano-sized oxide were purchased from IoliTec Nanomaterials (Denzlingen, Germany; 99.9 and 99.5% purity for Al_2O_3 and Fe_2O_3 , respectively).

Physical analysis of Al_2O_3 and Fe_2O_3

The specific surface area (SSA) of Al_2O_3 and Fe_2O_3 was calculated by the BET method [24]. N_2 adsorption–desorption isotherms at 77 K were obtained by a Micromeritics Gemini II 2370 apparatus.

Analytical determination of herbicides

MCPA was analyzed by an HPLC apparatus (Agilent 1200 Series), equipped with a DAD and a ChemStation Agilent Software.

Adsorption equilibrium and kinetics tests

Stock solutions of herbicide were prepared by dissolving 100 mg of MCPA in 500 mL of 0.03 M KCl (final concentration $1000 \mu\text{mol L}^{-1}$). The adsorption studies of MCPA on the selected oxide were conducted in batch conditions. The experiments were performed at a solid/liquid ratio of 1 mg mL^{-1} , obtained by adding 20 mg of Al_2O_3 to a final volume of 20 mL, with a herbicide concentration of $10 \mu\text{mol L}^{-1}$, at pH value of 4.0 (Al_2O_3).

Adsorption isotherms were obtained using initial herbicide concentrations ranging from 0.05 to $200 \mu\text{mol L}^{-1}$ for MCPA. After incubation in a rotatory shaker at 20°C , the samples were centrifuged at 7000 rpm for a fixed time. The amount of herbicide sorbed on the oxides was calculated as the difference between the quantity of herbicide initially added and that present in solution. Blanks were made using herbicides in the absence of sorbent, in order to check herbicide stability and adsorption to vials.

Kinetic tests were conducted at 30°C . After centrifugation, the supernatants were analyzed as described above.

Statistical analysis of the data

All the experiments were performed in triplicate, and the relative standard deviation was lower than 4%.

Adsorption kinetics modeling

Adsorption kinetics was analyzed with pseudo-first order (PFO) and pseudo-second order (PSO) kinetics, which are the most-used estimation models in the scientific literature for processing adsorption kinetics data under non-equilibrium conditions [11,16,23].

The pseudo-first order kinetic equation (PFO), proposed by Lagergren [28], can be expressed as follows:

$$\frac{d\hat{c}_{\text{sol}}}{dt} = k_1 (c_{\text{sol,eq}} - \hat{c}_{\text{sol}}) \quad (1)$$

where $c_{\text{sol,eq}}$ and $c_{\text{sol}} = c_{\text{sol}}(t)$ are the amounts of herbicide sorbed ($\mu\text{mol kg}^{-1}$) at equilibrium and at time t , respectively, k_1 is the pseudo-first order adsorption rate constant (min^{-1}), and t is the time (min). Eq. (1) can be integrated adopting the boundary condition $t=0$, $c_{\text{sol}}=0$ and rearranged in the following form, which represents the non-linear pseudo-first order kinetic model:

$$\hat{c}_{\text{sol}}(t) = \hat{c}_{\text{sol,eq}}(1 - e^{-k_1 t}) \quad (2)$$

An alternative to the previous method is given by the pseudo-second order kinetic equation, proposed by Blanchard et al. [18], developed by Ho [19] and theoretically derived by Azizian [29], it can be represented by:

$$\frac{d\hat{c}_{\text{sol}}}{dt} = k_2 (c_{\text{sol,eq}} - \hat{c}_{\text{sol}})^2 \quad (3)$$

in which k_2 is the pseudo-second order adsorption rate constant ($\text{kg } \mu\text{mol}^{-1} \text{ min}^{-1}$). Eq. (3) can be integrated adopting the boundary condition $t=0$, $c_{\text{sol}}=0$ and rearranged in the form:

$$\hat{c}_{\text{sol}}(t) = \frac{k_2 c_{\text{sol,eq}}^2 t}{1 + k_2 c_{\text{sol,eq}} t} \quad (4)$$

which represents the non-linear pseudo-second order kinetic model.

The PFO and the PSO kinetic models (Eqs. (2) and (4)) are commonly linearized. In this study, the non-linear forms have been used to fit the experimental data, as it has been observed [13,30] that transformations of non-linear adsorption kinetic equations to their linear forms implicitly alter their error structure and as a consequence, may distort the estimates of model parameters.

In both cases model rate constants are to be derived by fitting experimental data with the estimation model, that is to find the model parameters k_1 and k_2 that minimize the discrepancy between the measurements c_{sol} and the model estimates \hat{c}_{sol} , for example, by the use of a least-squares algorithm. Consequently, given the analytical expression of the estimation model (e.g., Eq. (2) or (4)) the amount of herbicide adsorbed can be estimated with the function F :

$$\hat{c}_{\text{liq}}(t) = F(t, k, c_{\text{sol,eq}}) \quad (5)$$

The problem is to find the constant k that minimize the summed square of residuals for the function F (a measure of the

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