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Application of the electrosorption technique to remove Metribuzin pesticide

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ABSTRACT

The present work deals with the removal of Metribuzin from aqueous solutions in a batch and continuous mode using electrosorption technique. This technique is based on the combination of two processes: the adsorption of Metribuzin into activated granular carbon (GAC) column and the application of the electrochemical potential. The effects of various experimental parameters (electrochemical potential, volumetric flow rate and initial Metribuzin concentration) on the removal efficiency were investigated. The pesticide sorption capacity at the breakthrough point of the GAC column reached 22 $mg_{pesticide}\ g_{GAC}{}^{-1}$. It was increased by more than 100% when the desired electrical potential (−50 mV/SCE) was applied in comparison with the conventional GAC column in similar experimental conditions without electrical potential. Evenmore, the electrosorption technique reduced considerably the drastic decrease encountered when passing from batch mode to continuous column mode.

1. Introduction

The intensive utilisation of various and recalcitrant organic compounds composing the pesticides in agriculture induces serious health problem to the population [1–3]. This situation leads to severe norms in terms of pesticides concentrations in water or food destined to the consummation.

Several techniques have been developed, for the last decade, in the treatment of pesticides. One can note, as an example, processes based on advanced oxidation, on the electrocoagulation, the membranes techniques etc.[4–7]. These processes have been efficient in terms of removal of the pesticide. On the other hand, it has been observed that these techniques are unable to permit the treatment of the contaminated water without transferring the pollutants or with risk of formation of undesirable organo-chlorine compounds [8]. The conventional adsorption on granular activated carbon bed column appeared to be an attractive simple technique to remove pesticides and various organic matters contained in water but more expensive in terms of treatment cost.

The electrosorption has been used in the present study to enhance the adsorbent capacity. An increase of the adsorption capacity reduces the quantity of the adsorbent used and then decreases the cost of the treatment. In a previous work, the authors demonstrated that the electrosorptive technique could be introduced to increase the adsorption capacity of activated alumina adsorbent during defluoridation of water [9].

Most of the previous electrosorption studies were conducted to determine the sorption capacity of a variety of ions and of neutral organic compounds on metallic electrodes [10–13].

1.1. Adsorption

Equilibrium isotherms may be attributed to theoretical or empirical models proposed by many authors who have established a relationship between a fixed adsorbed mass and the solution concentration (C_e) at the equilibrium state [14].

Isotherms are usually interpreted by monolayer adsorption or by multilayer adsorption. The monolayer adsorption may be represented by the Langmuir Eq. (1) which can be transformed to linear form (Eq. (2))

$$\frac{X}{m} = \frac{Q_m b c_e}{1 + b c_e} \quad (1)$$

$$\frac{c_e}{X/m} = \frac{1}{Q_m b} + \frac{c_e}{Q_m} \quad (2)$$

Adsorption through a packed bed may be explained by the exchange zone method (EZM) developed for a fixed bed ion exchange [15] and extended to the fixed bed adsorbent [16]. This model is based on a simplified method of interpreting the kinetic data in a fixed bed represented by the characteristic *S* curve commonly called the breakthrough curve.

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Nomenclature

b	equilibrium constant which characterizes the granular activated carbon ($dm^3\ mg^{-1}$)
C_0	Metribuzin initial concentration ($mg\ dm^{-3}$)
C_e	Metribuzin residual concentration at equilibrium ($mg\ dm^{-3}$)
C_p	Metribuzin residual concentration at breakthrough time ($mg\ dm^{-3}$)
C_s	Metribuzin residual concentration at saturation ($mg\ dm^{-3}$)
D	filtrate volumetric flow ($v\ v^{-1}\ h^{-1}$)
E	electrochemical potential (V)
E_0	potential of zero charge (V)
GAC	granular activated carbon
m	adsorbent mass on the packed column (g)
Q_m	limiting pesticide adsorption capacity ($mg_{pesticide}\ g_{GAC}{}^{-1}$)
SCE	saturated calomel electrode
t_p	breakthrough time (min)
t_s	saturation time (min)
T	temperature (°C)
t	experimental time (min)
v	filtrate volume collected at time t (m^3)
V_p	filtrate volume collected at breakthrough point, t_p (m^3)
V_s	filtrate volume collected at saturation point, t_s (m^3)
X	mass of solute fixed by the granular activated carbon (mg)
X_p	adsorption capacity at breakthrough point of the fixed bed ($mg_{pesticide}\ g_{GAC}{}^{-1}$)
X_s	adsorption capacity at saturation point of the fixed bed ($mg_{pesticide}\ g_{GAC}{}^{-1}$)

The breakthrough point P is attained after a time t_p. For industrial application, adsorption columns are used in a series and a column is used in the process up to its saturation at time t_s, when the effluents concentration reaches the feed concentration. Parameters t_p and t_s are linked by a linear relationship to the breakthrough volume (V_p) and the saturation volume (V_s) which are collected at the bottom of the adsorbent column at time t_p and t_s, respectively. The interpretation of the operation and performance of the fixed bed may be evaluated by several characteristic parameters determined by using the breakthrough curves and graphical integration of Eqs. (3) and (4). Thus, the adsorption capacities at the breakthrough point (X_p) and saturation point (X_s) of the fixed bed have been used to interpret the performance of the sorption column. X_p and X_s may be defined as the ratio of the quantity of the solute adsorbed at the breakpoint and saturation point, respectively.

$$X_p = \frac{\int_0^{V_p}(c_0 - c)\,dv}{m} \quad (3)$$

$$X_s = \frac{\int_0^{V_s}(c_0 - c)\,dv}{m} \quad (4)$$

The purpose of this work is to determine the efficiency of the electrosorption technique for removal of pesticides encountered in dilute and concentrate liquid wastes.

In this work, stainless steel electrodes (working and auxiliary) have been only used to create an electric field in the GAC column. The electric field effect on the mechanism and the performance of the uptake have been tested under various experimental conditions by varying electrochemical potential, volumetric flow and initial Metribuzin concentration.

Table 1
Physicochemical characteristics of the Metribuzine [3]

Molecular weight	$M = 214.3$ g
Water solubility at $T = 20$ °C	1.2 g dm^{-3}
Vapour pressure	1.310^{-3} Pa
Division coefficient n-octanol-water	1.70
Fusion temperature	125 °C
Density d^{25} at $T = 25$ °C	1.28

2. Material and methods

The Metribuzine is a complex macromolecule with formula $C_4H_{14}N_7OS$ and systematic name 4-amino-6-tert-buthyl-3-méthylthio1,2,4-triazine-5(4H)-one. The main physicochemical characteristics of this pesticide are given in Table 1.

The main physicochemical characteristics of activated granular carbon NFEN12915 purchased by OTV©(France) are presented in Table 2. It can be noted that the GAC adsorbent had a specific surface of about 1180 $m^2\ g^{-1}$. It was soaked overnight in distilled water before the beginning of each experiment.

The adsorption and electrosorption of Metribuzin on GAC column was achieved in flow continuous mode. The comparison of the performance of the electrosorption process and current GAC column has been achieved by means of two adsorption cells which have similar dimensions (diameter: 1.5 cm and length: 25 cm). These cells have been realized in the laboratory (Fig. 1). The electrosorption cell has been equipped with two stainless steel electrodes utilized as working and auxiliary electrodes. These electrodes have been introduced in the PVC column (2 cm diameter and 20 cm length) to produce an electrical field in the GAC bed. Electrochemical potential has been maintained constant by means

Table 2
The main physicochemical characteristics of GAC

Characteristics	Value	Standard error
Moisture (%)	4.2	±0.1
Porosity (%)	27.0	±0.3
Iodine indice ($mg\ g^{-1}$)	1440	±25
Ash (%)	5.2	±0.1
Real density ($g\ cm^{-3}$)	1.59	±0.03
Apparent density ($g\ cm^{-3}$)	0.50	±0.02
Total porous volume ($cm^3\ g^{-1}$)	1.38	±0.01
Specific area ($m^2\ g^{-1}$)	1180	±54
Particles size (mm)	1.5	±0.3

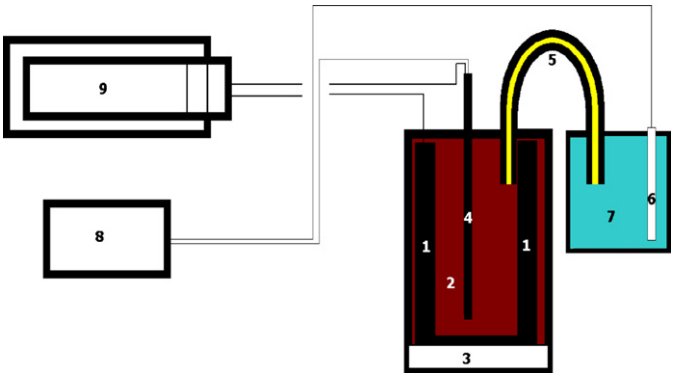

Fig. 1. Electrosorption apparatus, (1) auxilliary electrode, (2) granular activated carbon, (3) wool barrier, (4) working electrode, (5) salt bridge, (6) reference electrode, (7) saturated KCl, solution (3 M), (8) millivoltmeter and (9) potentiostat.