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Application of the electrosorption technique to remove Metribuzin pesticide

O. Kitous[a], A. Cheikh[a], H. Lounici[a], H. Grib, A. Pauss[b], N. Mameri[b,*]

[a] Laboratoire des Biotechnologies Environnementales et génie des procédés, Ecole Nationale Polytechnique d'Alger, B.P. 182, El-Harrach, 16200, Algeria
[b] University of Technology of Compiègne, Département Génie Procédés industriels, B.P. 20.509, 60205 Compiègne Cedex, France

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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.

* Corresponding author at: University of Technology of Compiègne, Département Génie chimique, B.P. 20.509, 60205 Compiègne Cedex, France.
Tel.: +33 3 44 23 44 57; fax: +33 3 44 23 52 16.
E-mail address: nabil.mameri@utc.fr (N. Mameri).

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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

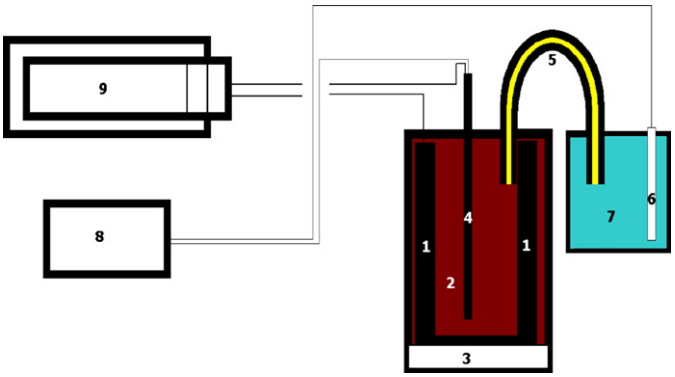

Fig. 1. Electrosorption apparatus, (1) auxilliary electrode, (2) granular activated carbon, (3) wool barrier, (4) working electrode, (5) salt bridge, (6) reference electrode, (7) saturated KCl, solution (3 M), (8) millivoltmeter and (9) potentiostat.

of a Tacussel PRT 20-2X potentiostat. The electrochemical potential applied during each experiment has been measured by means of saturated calomel electrode (SCE), taken as reference, and the working electrode. To avoid water dissociation phenomenon, the electrochemical potential has been limited in the range of −600 to +600 mV/SCE.

A synthetic Metribuzin solution has been prepared with distilled water and Metribuzin purchased at Bayer©(Germany). This solution has been fed by the topside of the column, and the filtrate has been collected at the bottom by means of a peristaltic pump (Watson Marlow 503U with two channels).

Experiments in batch mode have been carried out in a reactor with a volume of 500 ml. A known mass of GAC has been maintained in contact with Metribuzin solution. The equilibrium curves have been established by following the evolution of the residual Metribuzin concentration at equilibrium (C_e). The Metribuzin concentration in water solution has been determined with the spectrophotometer SHIMATZU, 1240CE (Japan) at wave length, $\lambda = 293$ nm (wave length at which the measured absorbance has been maximum).

For the continuous system for adsorption of Metribuzin on GAC column (with and without the electrochemical system), the pesticide concentration has been determined at regular interval (30 min) during each experiment for the determination of the breakthrough curve.

The effects of electrochemical potential, volumetric flow rate and initial concentration of Metribuzin on the process efficiency have been performed under various experimental conditions.

3. Results and discussion

3.1. Adsorption of Metribuzin on GAC in batch mode

The determination of the pesticide adsorption mechanism on the GAC has been performed by establishing the equilibrium curve via Metribuzin adsorption into the GAC kinetic curves (Fig. 2a and b). The results obtained, indicate that the Metribuzin adsorption into the GAC may be represented by the type I isotherm, indicating monolayer adsorption on active sites until their saturation, as described by Ruthven [14]. The determination of GAC limiting pesticide adsorption capacity (Q_m) by means of the linearized Eq. (2) has given values in the range of 210 $mg_{pesticide}\ g_{GAC}{}^{-1}$ (Fig. 2c).

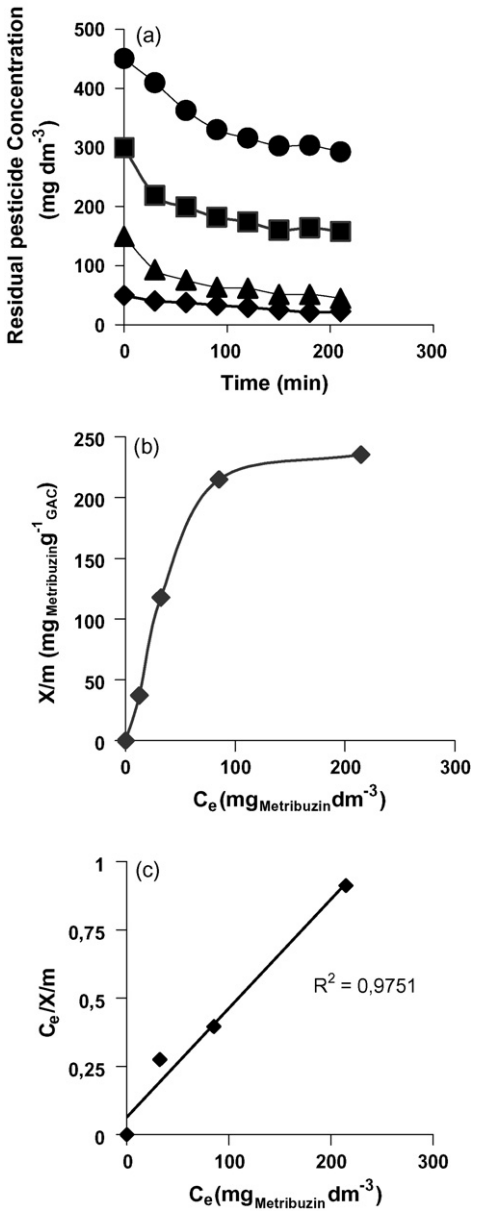

Fig. 2. Metribuzin adsorption on the GAC in batch reactor. M = 1 g GAC; reactor volume = 0.5 dm^{-3}; pH 7 and $T = 20\,^{\circ}C$. (a) Metribuzin adsorption kinetics on the GAC. (♦) $C_0 = 50\ mg\ dm^{-3}$, (▲) $C_0 = 150\ mg\ dm^{-3}$, (■) $C_0 = 300\ mg\ dm^{-3}$, (●) $C_0 = 450\ mg\ dm^{-3}$. (b) Adsorption isotherm of Metribuzin on GAC with contact time of about $t = 210$ min; (c) Linearized equation plot.

3.2. Effect of operational parameters on the electrosorption process in continuous mode

The influence of the electrochemical potential (E) on the performance of the granular activated carbon has been studied in continuous mode using the electrosorption column (Fig. 1). The variation in Metribuzin concentration of the filtrate against experimental time for different values of E is plotted in Fig. 3a.

The determination of calculated adsorption capacities X_p and X_s at various electrochemical potentials used (Fig. 3b) indicates that the curves have parabolic shape and present an interesting value with electrochemical potentials ranging from −100 to −50 mV/SCE. It can be noted that with a desired electrochemical potential of about −50 mV/SCE, value at which the process is more efficient, the adsorption capacity at the breakthrough point (X_p) of the fixed bed attained $X_p = 22\ mg\ g^{-1}{}_{GAC}$. This performance compared to the conventional adsorption ($E = 0$ mV/SCE) on column in similar conditions demonstrates that removal rate and removal efficiency have increased by about 100%. Indeed, a value of about $X_p = 11\ mg\ g_{GAC}{}^{-1}$ has been obtained in conventional mode.

It is clear that the electrosorption process successfully improves the Metribuzin removal reaction. Furthermore, the adsorption capacity at the saturation point (X_s) of the fixed bed has been of about $X_s = 150\ g\ g_{GAC}{}^{-1}$ under the desired condition of electrosorption mode. This result compared to those obtained by conventional GAC adsorption is twice in term of efficiency.

On the other hand, the values obtained at saturation point values X_s, ranging from 150 to 80 $g\ g_{GAC}{}^{-1}$, with both electrosorption and conventional processes are less efficient than GAC limiting pesticide adsorption capacity, previously presented, in batch mode. This phenomenon has been encountered during Zn(II) biosorption on *Streptomyses rimosus* biomass experiments. Drastic reduction of the capacity of the biosorbent has been reported when the experiments were transferred from batch mode to continuous column mode [17].

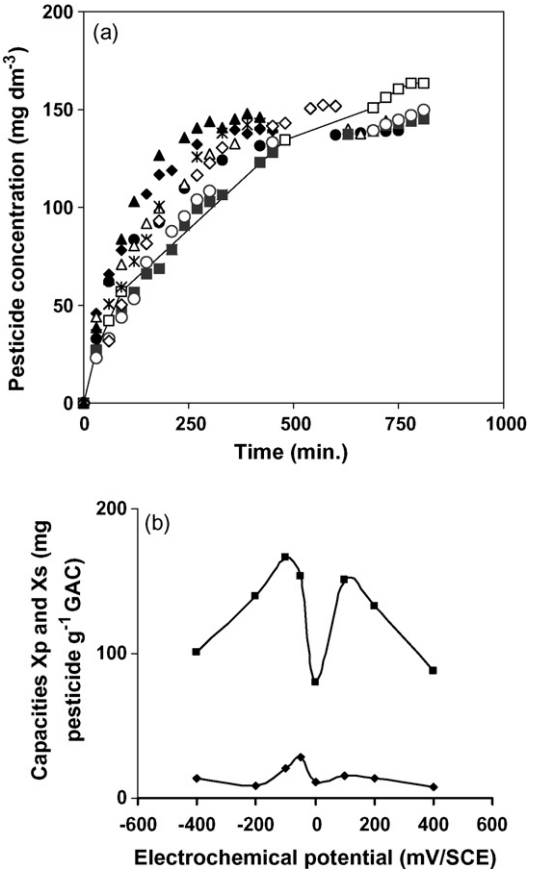

Fig. 3. Electrochemical potential effect on the performance of the GAC column. C_0 = 200 mg/l, m = 5 g, H = 5 cm, D = 10 ml/min and T = 20 °C. (a) Breakthrough curves: (◊) E = −600 mV/SCE, (*) E = −400 mV/SCE, (Δ) E = −200 mV/SCE, (■) E = −100 mV/SCE, (○) E = −50 mV/SCE, (▲) E = 0 mV/SCE, (●) E = +100 mV/SCE,(□) E = +200 mV/SCE and (♦) E = +400 mV/SCE. (b) Evolution of capacities at breakthrough point and saturated point under various electrochemical potential. (♦) at breakthrough point and (■) at saturated point.

The effect of application of electrochemical potential on the adsorbent capacity may be attributed to electric charge induced in activated carbon by the electrochemical technique by increasing the number of sites and then increasing the adsorbent efficiency. The electric charge of the activated carbon is the sum of acidic and basic surface functional groups. An assumption can be made that at given potentials, these charged sites are neutralized by an opposite potential, giving one electric charge to the surface. A combination of an electrostatic attraction and repulsion may explain the decrease of the pesticide adsorption capacity of the GAC at high potentials (anodic and cathodic). A similar explanation was proposed by Johns et al., who attributed the lowest adsorption values for six organic compounds to the presence of a large number of polar or charged groups on the meso-and macropore surfaces of the carbon that inhibit access of the small organics to the micropores [18].

The effect of the volumetric flow rate on the performance of the electrosorption process, shown in Fig. 4a and b, has been realized at desired electrochemical potential E = −50 mV/SCE, previously determined. The results obtained show that the volumetric flow rate influences slightly the efficiency of the process to remove the pesticide. Similar curves shape has been obtained in electrosorption or conventional adsorption mode. Indeed, an increase of D induces a reduction of residence time in the column. Then, taking into account the low adsorption kenitics, shown in Fig. 2a, the reduction of the efficiency of the process may be explained by the fact that the adsorbent has not enough time to bind the pesticide

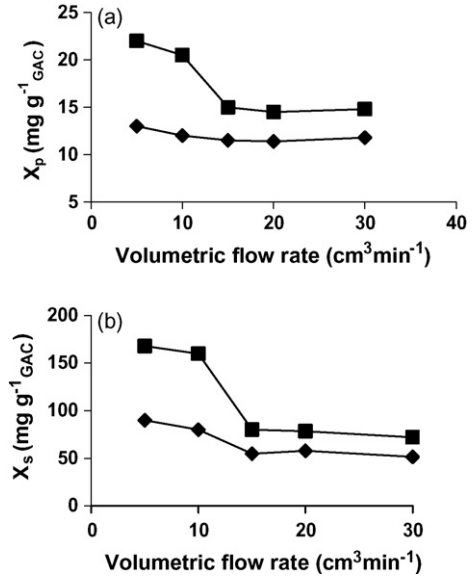

Fig. 4. Influence of the volumetric flow rate on the performance of the GAC column. C_0 = 200 mg/l, m = 5 g, H = 5 cm and T = 20 °C. (a) Evolution of capacities at breakthrough point (♦), X_p with electrosorption column at E = −50 mV/ECS and (■), X_p with current column. (b) Evolution of capacities at saturated point with the volumetric rate. (♦), X_p with electrosorption column at E = −50 mV/ECS and (■), X_p with current column.

since the residence time is too short. An interesting volumetric flow rate of about D = 10 cm^3 min^{-1} can be retained.

The influence of the initial concentration of Metribuzin on the performance of the electrosorption technique has been performed under desired conditions previously determined. The binding capacities of the GAC, shown in Fig. 5a and b, indicate that an increase of the pesticide concentration improves slightly the binding capacity of the GAC with the electrosorption and/or conventional techniques. These results may be explained by the fact that the breakthrough curves at various initial pesticide concentrations have been realized with an experimental time exceeding 12 h and by concentrate solution of Metribuzin. Then, the GAC column saturation of active sites has been practically achieved with the lowest concentration used.

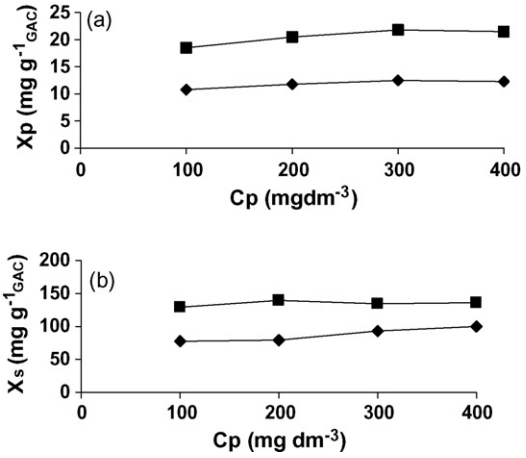

Fig. 5. Influence of the pesticide concentration on the performance of the electrosorption process. m = 5 g, H = 5 cm, D = 10 ml/min and T = 20 °C. (a) Evolution of capacities at breakthrough point (■), X_p with electrosorption column at E = −50 mV/ECS and (♦), X_p with current column. (b) Evolution of capacities at saturated point with the volumetric rate. (■), X_p with electrosorption column at E = −50 mV/ECS and (♦), X_p with current column.

4. Conclusion

The effects of various experimental parameters (electrochemical potential, volumetric flow rate and initial Metribuzin concentration) on the removal efficiency were determined. The results obtained showed that the process was more efficient than the classical one in all cases. Indeed, 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 at similar experimental conditions without electrical potential. Furthermore, the electrosorption process successfully improved the Metribuzin removal reaction. Indeed, the adsorption capacity at the saturation point (X_s) of the fixed bed was of about $X_s = 150\,g\,g_{GAC}{}^{-1}$ at the desired conditions under electrosorption mode. This result compared to those obtained with conventional GAC adsorption was twice in term of efficiency.

Evenmore, the electrosorption technique reduced considerably the drastic decrease of the efficiency process encountered when passing from batch mode to continuous column mode.

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