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The influence of activated carbon surface properties on the adsorption of the herbicide molinate and the bio-regeneration of the adsorbent

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Abstract

In the present study, the effect of the textural and surface chemistry properties of the activated carbon were evaluated in a combined treatment system to remove the herbicide molinate from waters. The process consists of an initial adsorption step followed by the bio-regeneration of the activated carbon through the utilization of a defined bacterial mixed culture (DC), previously described as able to mineralize molinate.

Molinate adsorption and partial bio-regeneration was favoured with activated carbons with larger pores, consisting mainly of meso and macropores. In order to study the effect of different surface chemical characteristics while maintaining the original textural properties, a commercial activated carbon was submitted to thermal and nitric acid treatments. The thermal treatment improved the molinate adsorption capacity of activated carbon. However, the bio-regeneration of the nitric acid oxidised activated carbon was slightly higher. With all the activated carbon materials used it was observed that the biological consumption of molinate present in the liquid phase displaced the equilibrium towards the activated carbon partial regeneration.

Keywords: Molinate; Activated carbon; Adsorption; Surface chemistry; Bio-regeneration

1. Introduction

Pesticides are used worldwide in agriculture to control plagues, in order to increase crops yields. The agricultural practices, accidental spillage or uncontrolled release of contaminated waters resultant of washing of pesticide containers or industrial effluents in the environment have been leading to the contamination of air, soils, surface and ground water and of living organisms. The environmental and trophic chain contamination with pesticides has serious negative impacts on the public health and on the biological diversity. In this way, remediation methods capable of minimizing the generalized environmental contamination have been developed.

The physical treatment of contaminated waters by adsorption onto activated carbon is a widely used technique. Despite the efficacy of the adsorption process, the main disadvantage of such methodology is that the activated carbon is contaminated with the pollutant at the end of the treatment. Several methods have been used to regenerate activated carbon, the thermal desorption being the most common process [1]. High temperatures promote the drying and loss of highly volatile compounds below 200 °C, vaporization and decomposition of unstable compounds at temperatures between 200 and 500 °C, and the pyrolysis of non-volatile adsorbents at temperatures over 500–700 °C [2]. In this context, the biological regeneration seems to be an effective alternative to costly traditional physicochemical techniques.

The most common process of bio-regeneration is designated by biological-activated-carbon (BAC) where adsorption of the pollutant is concomitant with biodegradation [e.g. 3–6]. Another procedure involves two stages of treatment: first the pollutant is removed and concentrated by adsorption and then bio-regenerated through the utilization of microorganisms able to degrade the pollutant [7–9]. The major advantage of this methodology is that the adsorption and the bio-regeneration steps of the treatment may occur in different locations and/or periods of time.

The major limitation of biological regeneration of the adsorbent is the irreversibility of pollutant desorption under the

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microbial growing conditions [9,10]. High adsorption capacity is expected for materials with high microporosity and surface chemical groups able to bind or attract the adsorbate. However, due to the high adsorption energies associated with adsorption, the adsorbate is not easily desorbed. In fact, in a previous work of this team [9] it was shown that an activated carbon with a large volume fraction of micropores could efficiently adsorb the thiocarbamate herbicide molinate. However, the adsorbed herbicide did not promote the growth of a defined bacterial mixed culture (mixed culture DC) able to mineralize free molinate [11,12], hampering its bio-regeneration [9]. Thus, characteristics of the adsorbent and adsorbate should be taken in consideration prior the implementation of a combined adsorption/bio-regeneration treatment system. In fact, the activated carbon adsorption capacity depends on quite different factors, namely adsorbate characteristics (molecular weight, polarity, pK_a, molecular size, functional groups) and solution conditions (pH, adsorbate concentration, presence of other possible adsorptives) [13–15]. It also depends on activated carbon texture (surface area, pore size distributions) and surface chemistry (surface functional groups) [16,17]. The nature of the surface groups can be modified through physical, chemical and electrochemical treatments. The most common are liquid phase treatments using HNO_3, gas phase oxidation with O_2 and heat treatment under inert gas to selectively remove some of the functional groups [18]. Different studies have shown that acid oxygen-containing surface groups decrease the adsorption of organic compounds in aqueous solution, while their absence favours adsorption [16,17]. There are two types of interactions between the adsorbate and the activated carbon: electrostatic and dispersive. The former appears when the adsorbate is dissociated under the experimental conditions used; the latter is mainly associated with the π–π dispersion interaction mechanism [16,17].

This study was designed to evaluate the influence of activated carbon surface properties on the adsorption and desorption of the herbicide molinate with the objective of the future implementation of the combined process in the treatment of contaminated waters. Activated carbons with low volume of micropores and high surface areas of mesopores were used. The effect of surface chemistry on the molinate adsorption capacity was evaluated, by modification of a commercial sample by nitric acid oxidation and thermal treatment. The textural and surface chemistry properties of the resulting samples were characterised and their influence on the adsorption/bio-regeneration of the molinate were determined.

2. Materials and methods

2.1. Chemicals and activated carbons

Molinate (*S*-ethyl *N*,*N*-hexamethylene-1-carbamate) of 97% purity was supplied by Herbex, Produtos Químicos (Estoril, Portugal). Some properties of molinate are given in Table 1. Two commercial activated carbons supplied by NORIT (Netherlands) with similar surface characteristics were used: Norit GAC 1240 PLUS (sample ACA) and Norit ROX 0.8 (sample ACB). According to the supplier's specifications, sample ACA has a granular shape with $0.42 < d < 2$ mm and sample ACB has a pellet shape with 0.8 mm diameter and 5 mm length. Both samples have neutral pH and are acid washed activated carbons with a high purity level, with an ash content of about 3%. In addition, an activated carbon sample supplied by Chemviron (France) was also used in the preliminary phase of this work. It has a pellet shape with 3.6 mm diameter and 6.3 mm length.

Table 1
Physical-chemical properties of molinate

Formula	$C_9H_{17}NOS$
Molar mass (g mol^{-1})	187.3
Water solubility (mg l^{-1})	800–912
Koc[a]	186

Data from Mabury et al. [29].
[a] Organic carbon coefficient.

Prior to adsorbent utilization, air was removed using a vacuum pump connected to a filtering flask containing the activated carbon immersed in distilled water. The activated carbon was ground and sieved (0.25 mm), washed several times with distilled water and filtered through a paper filter Whatman 42. The relationship between dry and wet weight for activated carbon ACA, ACB and Chemviron were, respectively, $m_{\text{dry weight}} = 0.4322\ m_{\text{wet weight}}$; $m_{\text{dry weight}} = 0.3832\ m_{\text{wet weight}}$ and $m_{\text{dry weight}} = 0.4878\ m_{\text{wet weight}}$.

2.2. Preparation of modified activated carbons

A Norit GAC 1240 PLUS activated carbon (sample ACA) was selected as the starting material for this study. The treatments were carried out in order to obtain materials with different surface chemistries while maintaining the original textural properties as far as possible.

2.2.1. Treatment with nitric acid

About 9 g of sample ACA were oxidized in a Soxhlet extraction apparatus, with 200 ml of HNO_3 6 M, as described previously [19]. The reflux was interrupted after 3 h; the modified sample was washed with distilled water until neutral pH was reached, dried in an oven at 110 °C for 24 h and stored in a dessicator until later use (sample ACAacid). The relationship between dry and wet weight for ACAacid was $m_{\text{dry weight}} = 0.5136\ m_{\text{wet weight}}$.

2.2.2. Thermal treatment

Papirer et al. [20] reported that thermal treatment with starting materials with high amounts of surface groups produces activated carbons with higher basicity. Thus, about 3 g of sample ACAacid was heated to 700 °C at 5 °C min^{-1} under a flow of H_2 (50 cm^3 min^{-1}) and kept at this temperature for 1 h, in a fused silica tubular reactor. The sample was stored in a dessicator until further use (sample ACAbasic). The relationship between dry and wet weight for ACAacid was $m_{\text{dry weight}} = 0.4546\ m_{\text{wet weight}}$.

2.3. Characterization of the activated carbons

The textural characterization of the activated carbons was based on the N_2 adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. BET surface areas (S_{BET}) were calculated, and the micropore volume (W_{micro}) and mesopore surface area (S_{meso}) determined by the *t*-method [21]. The micropore volume was also calculated with the Dubinin equation. A type IV deviation occurred in all activated carbons conducting to calculation of W_{01} (small micropores volume) and W_{02} (large micropores volume) [22]. The average micropore width was estimated by the Stoekli equation [23], using a value of 0.34 for the affinity coefficient of nitrogen.

The pH_{PZC} (pH value at which the net surface charge is 0) was determined by the pH drift test described previously [24].

2.4. Adsorption and bio-regeneration experiments

2.4.1. Comparison and selection of adsorbents

The adsorption capacity and the subsequent bio-regeneration of samples ACA and ACB were compared with those of activated carbon Chemviron. Activated carbon samples (approximately 0.3 g wet weight) were immersed in distilled water in 1 l Erlenmyer flasks with caps with Teflon liners. After autoclaving (121 °C, 30 min), each activated carbon was aseptically filtered (porosity: 0.2 μm, diameter: 47 mm) using vacuum, to remove water. Each sample was mixed with 100 ml of mineral medium B (pH 7.2, conductivity 489 mS m^{-1}) [11] with approximately 600 mg l^{-1} molinate. The suspensions were shaken at 120 rpm, and at constant temperature of 30 °C for 48 h, in order to reach the adsorption equilibrium. Subsequently, the equilibrium liquid phase was aseptically removed by filtration under vacuum, and substituted by the same volume of mineral medium B without molinate. The samples of activated carbon, with molinate previously adsorbed, were inoculated with 10% (v/v) of mixed culture DC, pre-grown until exponential phase in mineral medium B with approximately 700 mg l^{-1} molinate, as described before [11]. Cultures were incubated at 30 °C, and 120 rpm. Uninoculated controls (abiotic) were incubated simultaneously. Cell growth at expenses of adsorbed molinate was registered positive for cultures presenting turbidity in the liquid phase after 5 days of incubation.

2.4.2. Adsorption isotherms of molinate on activated carbon

The adsorption isotherms were determined for samples ACA, ACAacid and ACAbasic. Molinate solutions with different concentrations (75–700 mg l^{-1}) were prepared in mineral medium B and mixed with different wet weights of activated carbon (50–150 mg). The assays were performed in batch, using Erlenmeyer flasks with caps with Teflon liners. The suspensions were shaken at 120 rpm, and at constant temperature of 30 °C. Since preliminary kinetics studies showed that equilibrium time was reached after 48 h, samples were collected after that period and centrifuged at 14,000 rpm. Supernatants were stored at −30 °C until analysis of molinate content.

2.4.3. Bio-regeneration of activated carbons

Activated carbon samples (approximately 0.6 g wet weight) were autoclaved, aseptically filtered and mixed with 200 ml of mineral medium B with approximately 650 mg l^{-1} molinate. Adsorption equilibrium, the removal of equilibrium liquid phase, the inoculation with mixed culture DC, and incubation were performed as described above. Three different controls were performed: (1) abiotic control, to confirm sterility and desorption of molinate; (2) without activated carbon to compare the efficiency of mixed culture DC on molinate biodegradation when the herbicide is in free solution; (3) without molinate, to confirm that carbon components were not supporting growth of mixed culture DC, being the adsorbed molinate the only source of carbon, energy and nitrogen.

The same set of assays was conducted without removing the equilibrium liquid phase. In these experiments, activated carbon samples of approximately 100 mg wet weight, and 50 ml of mineral medium B with an initial molinate concentration of 575 mg l^{-1} were used.

2.5. Analytical determinations

Cell growth was monitored spectrophotometrically ($OD_{610\,nm}$) and cells dry weight was determined as described earlier [11]. Concentration of molinate in liquid phase was determined by HPLC-UV, as described previously [11]. The thermogravimetric analysis (TGA) was performed in a Mettler TA4000 apparatus, using about 15 mg of activated carbon, under an air flow of 200 cm^3 min^{-1}, heated at a rate of 5 °C min^{-1} in the temperature range of 25–700 °C. TGA was used to calculate the molinate adsorbed on the activated carbon surface, since it was observed that molinate is completely removed by heat treatment in air flow at temperatures below 400 °C. The amount of molinate adsorbed was obtained as the difference between the weight losses till 400 °C of activated carbon samples with and without molinate. The percentage of bio-regeneration was determined by the difference between the molinate solid phase concentration after the saturation and bio-regeneration step.

3. Results and discussion

3.1. Selection of the activated carbon

In order to compare the molinate adsorption capacity of the different activated carbons and their potential to be bioregenerated using mixed culture DC, preliminary experiments were carried out. After the initial step of adsorption the equilibrium concentration of adsorbed molinate *per* gram of dry weight of activated carbon was 367, 340 and 406 mg g^{-1} for samples ACA, ACB, and activated carbon Chemviron, respectively. As reported by Silva et al. [9], mixed culture DC was unable to grow at expenses of molinate adsorbed onto activated carbon Chemviron. However, this culture grew on molinate adsorbed onto samples ACA and ACB. As there was no relevant difference in the molinate adsorption capacity of these two activated carbons and mixed culture DC grew at expenses of molinate adsorbed onto both carbons, sample ACA was selected for further studies.

Table 2
Activated carbon textural characterisation

Adsorbent	S_{BET} ($m^2\,g^{-1}$)	W_{micro} ($ml\,g^{-1}$)	S_{meso} ($m^2\,g^{-1}$)	W_{01} ($ml\,g^{-1}$)	W_{02} ($ml\,g^{-1}$)	L_1 (nm)	pH_{pzc}
ACA	972	0.367	125	0.312	0.058	1.1	9.7
ACAacid	909	0.353	91	0.303	0.048	1.1	2.7
ACAbasic	972	0.375	103	0.318	0.058	1.2	10.8
ACB	1035	0.382	138	0.350	0.038	1.0	10.4
Activated carbon Chemviron[a]	1485	0.636	53	0.514	0.124	0.9	6.6

[a] Data from Pinto [30].

3.2. Characterization of the activated carbons

Surface parameters, in terms of micropore volume, mesopore surface area and pH_{pzc} value of samples ACA and ACB were similar (Table 2), which explain the similar molinate adsorption capacities referred above. These activated carbons have about half of the volume of micropores and the double of mesopores specific surface area when compared with activated carbon Chemviron. Therefore, the adsorption capacity of samples ACA and ACB was lower, and probably, also the adsorption energy is lower, when compared with activated carbon Chemviron. Thus, it is expectable molinate can be easily desorbed from activated carbons ACA and ACB, in comparison to activated carbon Chemviron where, probably, molinate adsorbs almost irreversibly, avoiding its bio-regeneration. Activated carbon ACA was modified through two physicochemical different methodologies in order to evaluate the possibility of improving the molinate adsorption capacity by changing its surface chemical characteristics. As expected, none of the treatments produced relevant differences in micropore volume and mesopore surface area of samples ACAacid and ACAbasic relatively to sample ACA. In fact, similar results were obtained by other authors for activated carbons modified by liquid phase oxidation and thermal treatments [18].

In another study [24], these materials were characterised by temperature programmed desorption (TPD). It was shown that sample ACAacid presents a large amount of acid surface groups, mainly carboxylic acid, anhydrides, lactone and phenol groups, which agrees with the pH_{pzc} value of 2.7 obtained for this sample. Sample ACAbasic was heat treated under H_2 flow in order to produce very stable basic activated carbon [19], and it was shown by TPD that the oxygen-containing surface groups were almost completely removed. The high basicity of this sample, with a pH_{pzc} of 10.8, is explained by the few basic oxygen surface groups that remained at the surface after the heat treatment and mainly by the electron rich oxygen-free sites located on the carbon basal planes [25]. The original activated carbon (sample ACA) presents, in addition to the mentioned basic groups, few acid oxygen-containing surface groups, which slightly decrease the pH_{pzc} when compared with sample ACAbasic.

3.3. Adsorption isotherms

One of the goals of this study was to understand how different surface chemical groups influence the sorption of molinate on the selected activated carbon. Adsorption isotherms were obtained at 30 °C, and the experimental data fitted by a Langmuir isotherm:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$$

where C_e and q_e are the adsorbate equilibrium concentrations in the liquid and solid phases, q_m the maximum adsorption capacity and K_L is a constant. The calculated parameters are shown in Table 3 and the adsorption isotherms in Fig. 1.

Table 3
Parameters of the Langmuir model

Sample	q_m ($mg\,g_{AC}^{-1}$)	K_L ($l\,mg^{-1}$)	r^2
ACA	370	1.59	0.999
ACAacid	309	0.17	0.991
ACAbasic	459	0.34	0.998

The differences obtained for the maximum adsorption capacity can be explained in terms of the surface chemistry of the activated carbon samples. It is known that the oxygen surface complexes affect the surface hydrophobicity [17]. In general, an increase in the oxygen-containing surface groups of activated carbon brings about a decrease in its hydrophobicity. The molinate adsorption is expected to be controlled by hydrophobic interactions, as a result of the attraction between molinate (apolar molecule) and hydrophobic carbon surfaces. As discussed above, sample ACAacid has the highest and sample ACAbasic the lowest amount of oxygen surface groups, and it is expected that surface hydrophobicity can be ranked as

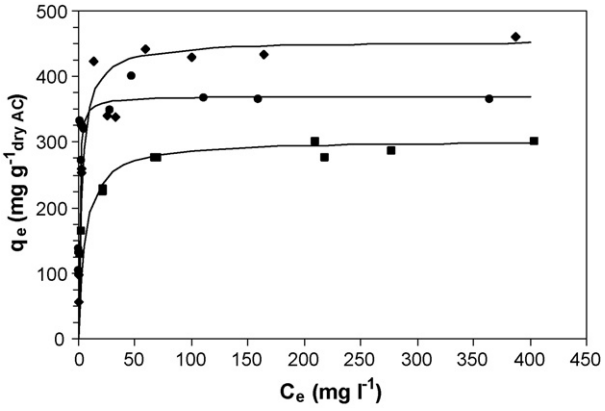

Fig. 1. Adsorption equilibrium isotherms (30 °C) of molinate onto samples ACA (●), ACAacid (■) and ACAbasic (♦). The solid curves correspond to the Langmuir model.

ACAbasic > ACA > ACAacid, which has the same trend of the maximum adsorption capacity (Table 3 and Fig. 1).

3.4. Bio-regeneration of activated carbons

The influence of surface chemical properties on the bio-regeneration of the activated carbons was evaluated through the ability of mixed culture DC to grow at expenses of adsorbed molinate onto the original and modified samples. With this purpose, after an initial adsorption step, the equilibrium liquid phase was removed, substituted by mineral medium without any organic compound and inoculated with mixed culture DC. Running in parallel, for each activated carbon sample, a non-inoculated control permitted to follow molinate desorption.

After the initial adsorption step, when equilibrium was reached, the experimental values of molinate solid phase concentration of control samples ACA, ACAacid and ACAbasic were, respectively, 364, 306 and 425 mg *per* gram of dry activated carbon. Molinate desorption was fast, as was evidenced by the new adsorption equilibrium, reached after 3 h (Fig. 2), with liquid phase concentrations of approximately 37 mg l^{-1} for sample ACA and 40 mg l^{-1} for sample ACAacid, corresponding to solid phase concentrations of approximately 336 and 280 mg g^{-1}, respectively. Due to its higher affinity for molinate, sample ACAbasic desorbed slightly less molinate; the new equilibrium was established at liquid and solid concentrations of about 34 and 400 mg g^{-1}, respectively. The percentages of activated carbon regeneration after desorption were low: approximately 6%, 8% and 9% for samples ACAbasic, ACA and ACAacid, respectively.

During the first 6 h of incubation of mixed culture DC on molinate adsorbed onto the different activated carbons, the molinate concentration in the liquid phase also increased, probably due to molinate desorption. However, because of molinate utilization for cell growth, molinate concentration in free solution dropped to values below the detection limit of the HPLC (0.9 mg l^{-1}), after 26 h of incubation (Fig. 3). The comparison of growth curves of mixed culture DC grown with molinate in free solution (biotic control) (Fig. 4) and with previously adsorbed molinate (Fig. 3), show that growth rate obtained for the culture grown on free molinate was much higher (0.071 h^{-1}) than

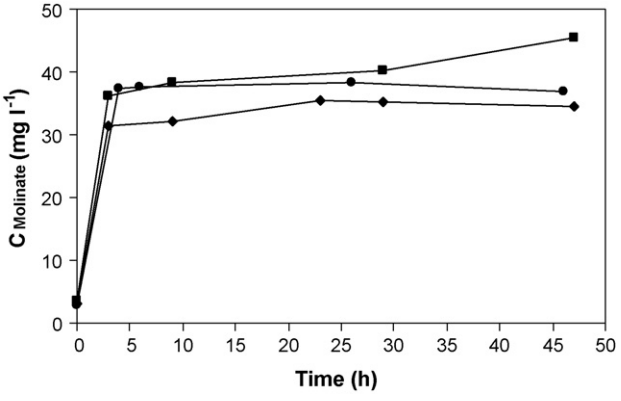

Fig. 2. Experimental desorption values obtained at 30 °C. (●) Sample ACA; (■) sample ACAacid; (♦) sample ACAbasic.

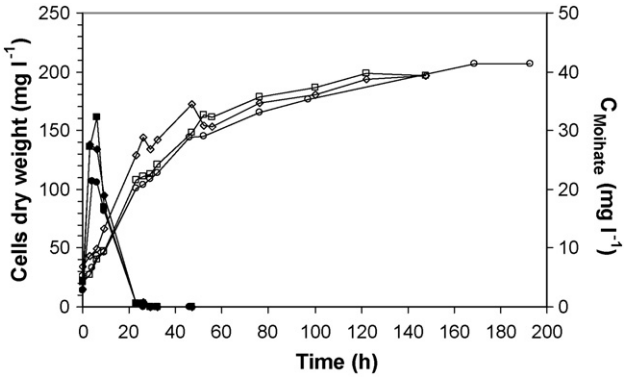

Fig. 3. Growth and free molinate depletion by mixed culture DC grown on previously adsorbed molinate onto AC samples. Biomass (open symbols) and free molinate concentration (filled symbols) for culture on samples ACA (◯, ●), ACAacid (□, ■), and ACAbasic (◊, ♦).

those found for cultures on molinate adsorbed onto samples ACA, ACAacid and ACAbasic (0.016, 0.014 and 0.012 h^{-1}, respectively). When molinate was in free solution, its decrease to undetectable values led, almost immediately, to the stationary phase of growth (Fig. 4). By the opposite, when the herbicide was adsorbed onto the different activated carbons, growth slowly continued for several days until stationary phase was reached (Fig. 3). These results indicate that mixed culture DC was able to use molinate present in liquid phase as the sole nutrient and suggest that the reduction of the adsorbate concentration in solution promotes a continuous desorption of molinate, that despite of being undetectable by HPLC, was able to support bacterial growth. Similar results were obtained when mixed culture DC was grown with molinate previously adsorbed onto resin Amberbile XAD-4 [9]. In fact, a commonly accepted model for bio-regeneration processes is the desorption of the adsorbate molecules followed by molecular diffusion to the bulk liquid where biodegradation may occur [4,7,8].

To quantify the molinate irreversibly adsorbed onto the activated carbons, TGA analysis were performed by the end of the growths, using saturated and uninoculated activated carbons (after the desorption step), as controls. This method permits, by the weight lost corresponding to the adsorbed molinate, to quantify the amount of adsorbed herbicide onto the activated carbon and thus, to determine the bio-regeneration percentage of

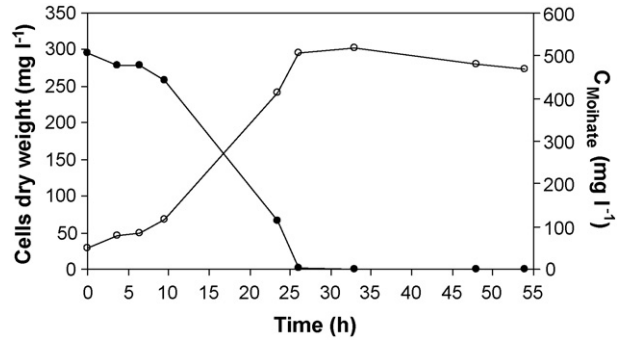

Fig. 4. Growth and free molinate depletion by mixed culture DC grown on molinate at 555 mg l^{-1} in free solution; (◯) biomass and (●) free molinate concentration.

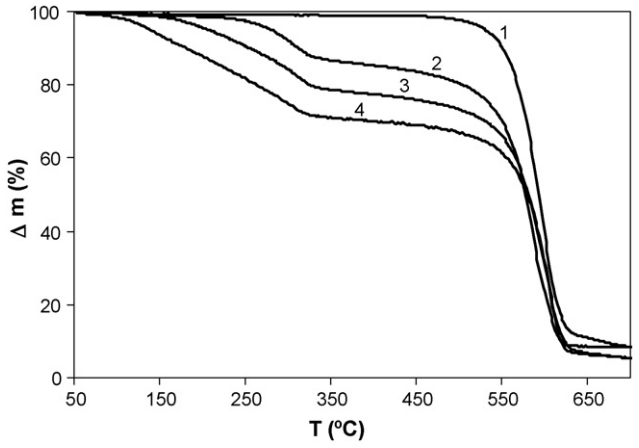

Fig. 5. Thermogravimetric analysis of sample ACA. (1) Original, (2) bio-regenerated, (3) after desorption and (4) saturated.

the different activated carbons. As an example, Fig. 5 shows the TGA profiles of sample ACA in a dry basis. It can be observed that the amount of molinate adsorbed (curve 4) decreased after the desorption step (curve 3) and was further reduced by the activity of mixed culture DC (curve 2). In addition, the onset temperature of molinate removal increases from curve 4 to curve 2, meaning that the adsorption energy of molinate after the bio-regeneration is high. Probably, molinate adsorbed on the macro and mesopores can be easily removed by bio-regeneration, in opposition to the molinate strongly adsorbed on the micropores.

The solid phase molinate concentrations after the initial adsorption step were approximately 340, 310 and 430 mg g^{-1}, while after the bio-regeneration step were of approximately 127, 103 and 161 mg g^{-1} for samples ACA, ACAacid and ACAbasic, respectively, corresponding to percentages of bio-regeneration of about 63% for samples ACA and ACAbasic, and 67% for sample ACAacid. The slightly higher percentage of bio-regeneration obtained for this last sample suggests that in the presence of oxygen-containing surface groups molinate is weakly adsorbed and thus easily desorbed, favouring the bio-regeneration, when compared with the other activated carbons.

In order to evaluate the effect of the biomass content on the bio-regeneration of these activated carbons, a similar set of assays was conducted without removing the molinate liquid equilibrium solution after the initial adsorption step. At the beginning of the growth the free molinate concentrations were of 186, 214 and 164 mg l^{-1}, corresponding to solid phase concentrations of approximately 427, 339 and 433 mg g^{-1}, for samples ACA, ACAacid and ACAbasic, respectively. Due to the high initial molinate concentrations in the liquid phase, mixed culture DC presented growth rates (0.06, 0.07 and 0.06 h^{-1} for samples ACA, ACAacid and ACAbasic, respectively) closer to that obtained for the biotic control grown on free molinate (0.07 h^{-1}). Despite of the higher biomass content obtained in these cultures, TGA analysis revealed that, by the end of the growth, the molinate solid phase concentrations (155, 69 and 151 mg g^{-1} for samples ACA, ACAacid and ACAbasic, respectively) were similar to those found for cultures grown exclusively at expenses of adsorbed molinate, as described above (127, 103 and 161 mg g^{-1} for samples ACA, ACAacid and ACAbasic, respectively). Thus, the increase on the biomass content had little impact on the percentage of bio-regeneration, as reported by Vinitnantharat et al. [26].

Altogether, these results suggest that growth rate of mixed culture DC is eventually controlled by molinate desorption and diffusion to the bulk liquid, where it is further degraded, regenerating the adsorbent. Continuous desorption of molinate would occur until the equilibrium concentration become below the bio-availability. Using concentration values of free molinate predicted by the isotherm equations, the limit of molinate bio-availability would be between 0.4 and 0.5 mg l^{-1}, independently of the biomass concentration used. However, Castro et al. [27] reported that mixed culture DC is able to treat rice paddies waters, reducing molinate concentrations ranging from 0.5 to 0.01 mg l^{-1} to values within the legally recommended limits (<2 μg l^{-1}) [28]. At least part of the amount of molinate remaining adsorbed onto the activated carbons may occupy the micropores, becoming unavailable for desorption and, thus, biodegradation, as described by Klimenko et al. [5] for other adsorbents. In fact, activated carbon Chemviron, which was unable to be bio-regenerated by mixed culture DC [9, present work], has almost the double of the micropores volume and less than half of the mesopores specific surface area of the activated carbons Norit, meaning that the most interesting activated carbons for this application are those with larger pores, consisting mainly of meso and macropores.

Comparatively to the present study, in a similar study using resin Amberlite XAD-4 as adsorbent it was possible to achieve, after the biological treatment, lower molinate solid phase concentrations (60–70 mg g^{-1}) [9]. Nevertheless, considering that resin Amberlite XAD-4 is an expensive material, the future implementation of activated carbon-based systems to treat molinate contaminated waters may be a good alternative. In this respect, the selection of the activated carbon should take into account surface chemistry and porosity characteristics.

4. Conclusions

1. Original, nitric acid treated and thermal treated Norit GAC 1240 PLUS were observed to be good adsorbents for the apolar herbicide molinate and the adsorption isotherms were well described by the Langmuir equation.
2. The maximum adsorption capacity of the activated carbons could be explained by their surface properties. Lowest and highest adsorption capacities were observed for, respectively, nitric acid treated activated carbon and thermal treated activated carbon, expected to contain the highest and lowest amount of oxygen surface groups. Due to lowest surface hydrophobicity, molinate desorption occurred at a slightly higher extent with nitric acid treated activated carbon.
3. Mixed culture DC consumption of molinate present in the liquid phase displaced the equilibrium towards the activated carbons partial regeneration. Bio-regeneration of the nitric acid treated acid activated carbon was slightly more extensive (∼67%) than that obtained for original and thermal treated

activated carbon (∼63%), indicating that hydrophobicity of the surface favour the irreversible adsorption of molinate.

4. The future implementation of a combined adsorption/bioregeneration treatment process using activated carbon seems feasible. However, adsorbent characteristics are a matter of concern since parameters as microporosity and concentration of oxygen-containing surface groups influence the bioregeneration extent.

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