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REMOVAL OF 2,4-MCPA AND 2,4-DP BY ADSORPTION ON ACTIVATED CARBON

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Abstract The adsorption of 2,4-MCPA and 2,4-DP by two activated carbons were studied in aqueous solution. Dynamic modelling of the adsorption showed that the first order reversible Kinetic model was held for the adsorption process. The overall rate constant k', the adsorption rate k_1, the desorption rate constant k_2, and the equilibrium constant K_e for the adsorption process were calculated. Adsorption was influenced by the activated carbon type and solution characteristics (pH and ionic strength). The adsorption was found to decrease with an increasing of pH over the range 1.5-9. The amount of herbicides adsorbed was also found to depend on the ionic strength.

Keywords Herbicides, Adsorption, Activated carbon, Kinetic study

Introduction

Pesticides are chemicals used to remove organisms that are harmful to animal health or to the animal and plant resources needed for food. They include substances of diverse origins (mineral, organic, natural or synthetic) and are increasingly used not only in agriculture but also in the industry for the protection of materials [1].

These waterborne products, in addition to their toxicity to aquatic fauna, humans and animals, have the peculiarity of being able to accumulate particularly in the aquatic ecosystems of which they are among the major pollutants [2].

Several studies have shown that the majority of anionic pesticides are poorly retained by the different soil components [3-4]. As a result, they have a probability of being transported to groundwater. Research by Wauchope [5] and Goodrich [6] has shown the presence of several herbicides, such as 2,4-D, MCPA, MCPB and others, in surface and underground waters.

If the assessment of water quality must take into account the overall content of micropollutants (hydrocarbons, polychlorinated biphenyls, etc.), the pesticide concentration remains one of the main factors of this quality and must be disposed of as completely as possible in drinking water. Thus, in the treatment of natural water for the production of drinking water, the removal of organic micropollutants such as pesticides is carried out by conventional treatments (flocculation, ozonation, etc.) and in particular by adsorption on carbon Active [7].

This adsorption is normally very rapid, and for the concentrations of the pesticides usually found in the waters, small quantities of coal are sufficient [8]. Although other adsorbent media can also be used for this elimination (sand, sediment, etc.), activated carbon remains the most effective and most used [9-10].

However, despite the increasing use of coal as an adsorbent, and despite the importance of physico-chemical studies in the retention of organic pollutants, it is far from having a complete knowledge of all the factors that modify the environment, Effectiveness of activated carbon [11-13].

In this work, we studied the adsorption in static regime of two phenoxyalkanoic pesticides, 2,4-MCPA and 2,4-DP, on two active carbons. After studying the adsorption kinetics of these acids, we examined the influence of NaCl and pH.

Material and Methods

Two types of powdered activated carbon are used for this study. The first (named CH) is a product Merck, the second (named CL) was provided to us by the Moroccan office of the drinking water; Grade 20070D. The particles of the active carbons have a diameter less than or equal to 80 µm. Both activated carbons are washed in a glass column with distilled water until constant pH and conductivity, dried in an oven at 110 °C. overnight and then stored in closed flasks.

The activated carbons are characterized by adsorption of N_2 at 77K. From the data obtained, the specific surfaces calculated by application of the BET equation [14] are 831 and 141 m^2/g respectively for (CH) and (CL). The pH of the zero charge point pH_{PZN} for the two materials is determined according to the method described by Ferro-Garcia et al. [15] and Sontheimer et al. [16]. The values determined are 8.20 ± 0.02 and 1.84 ± 0.05 respectively for (CH) and (CL).

2,4-DPA (2- (2,4-dichlorophenoxy) propanoic acid) are ALDRICH products (greater than 98% purity) Solubility in water at 25 °C of the order of 825 and 700 mg/l respectively. The concentrations of the aqueous solutions are determined by UV spectrophotometry (CECIEL Instruments CE 1021) at a wavelength of 281 and 283 nm respectively for 2,4-MCPA and 2,4-DP. The amounts of the adsorbed herbicides per gram of adsorbent are calculated by measuring the concentrations of the solutions before and after adsorption.

The adsorption tests of the acids studied, alone or in the presence of the salt (NaCl), are carried out in a batch reactor. All the diluted solutions of the solutes examined are prepared with double distilled water. Volumes of 10 ml of solution of determined concentrations (0.1 to 1 mmol/l) are placed in Pyrex tubes in the presence of activated charcoal (1 g/l). The tubes are then stirred with a mechanical rotator (100 rpm) at 25 °C. (± 0.5 °C) for a time corresponding to the equilibration of the adsorption. After a determined stirring time, the two phases are separated by double filtration on millipore filters (Wathman 1.2 µm and 0.45 µm). The filtrate is then analyzed by U.V. absorbance to determine the residual adsorbate concentration. Sodium chloride NaCl (Merck 99%) is used to control the ionic strength. In order to study the effect of the pH of the suspension on the adsorption of the herbicides, the pH is adjusted to the desired values, in the interval 1.5-9, by adding a solution of HCl (1N) or NaOH (1N). All the experiments were carried out in the absence of light in order to avoid possible photodegradation of the adsorbates. However, the change in the molar absorption of the solutions with pH or in the presence of the salt was taken into account. Blank tests (without the addition of activated charcoal) were carried out in order to check any adsorption loss on the filters or the walls of the tubes. All experiments are repeated at least twice, the experimental error does not exceed 4%.

Experimental Results

Adsorption Kinetics

Figures 1 (A) et (B) show the kinetic curves obtained for 2,4-MCPA and 2,4-DP on the two activated charcoals, starting from an initial concentration of 1 mmol/l herbicide.

These results indicate that the kinetics of adsorption of two acids is rapid. The equilibrium times determined for (CH) are 5 and 10 min respectively for 2,4-MCPA and 2,4-DP. These values are 40 and 35 min for (CL). It is noted that about 75% of the amount retained at equilibrium on (CH) or (CL) is adsorbed on the first contact between the solution of the pesticide and the activated carbon. This would correspond to the two adsorption steps. The first rapid, concerning the molecules located in the vicinity of the surface, would be limited by the molecular diffusion in the film of water in contact with the adsorbent particles. The second one is slow, reflecting the molecular diffusion in the adsorbent. The same result has been reported in the literature, for example adsorption of pyrene on activated carbon [17] and pentachlorophenol on various materials [18]. The results also show that 2,4-DP is substantially more adsorbed than 2,4-MCPA. By comparing the adsorption capacities of both activated charcoals with the herbicides studied, the (CH) is more efficient than the (CL). This is probably due to its large surface area.

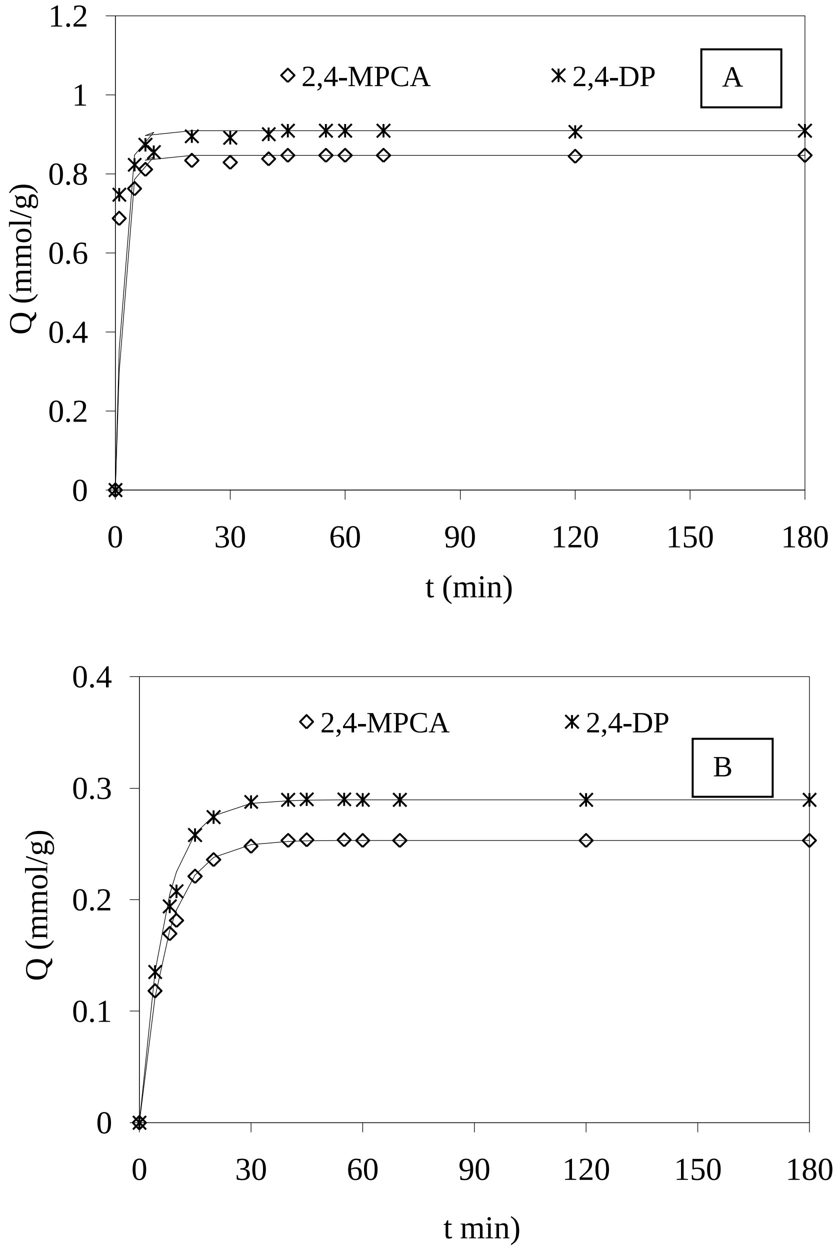

Figure 1 : Kinteic of adsorption of 2,4-MCPA et 2,4-DP on activated carbon CH (A) and CL (B) at 25°C.

The adsorption of the molecules studied from the liquid phase to the solid phase can be considered as a reversible reaction with establishment of the equilibrium between the two phases. Therefore, the first order kinetic law can be used to model this reaction [19].

The equation of the first-order kinetic model is of the form: ln (1-U (t)) = -k't

With K' being the kinetic constant.

In addition, k '= k_1 (1+ (1 / k_e)) = k_1 + k_2

Where k_e is the equilibrium constant; K_1 and k_2 are the adsorption and desorption constants respectively.

K_e = C_a / C_e and U (t) = (Co-C_t) / (Co-Ce)

C_0, C_t, C_e and C_a (all in mmol/l) are the initial herbicide concentrations, at a time t, at equilibrium and in the adsorbed phase, respectively.

The plot of ln (1-U (t)) as a function of time for the different couples examined is generally linear. This indicates that the adsorption of the two solutes on (CH) and (CL) can be expressed by the first order reversible kinetic law. The set of calculated kinetic parameters is summarized in Table 1.

On reading this table, it is observed that the values of k 'and k_1 for 2,4-DP, on the two activated charcoals, are appreciably greater than those of 2,4-MCPA. It is also noted that for coal with low adsorption capacity, (CL), the values of k_2 are larger than those of k_1. The high k1 value observed for 2,4-DP may indicate that the interaction between the molecules of this herbicide and the activated carbon particles is stronger than in the case of 2,4-MCPA.

Table 1: Calculated Kinetic parameters for the adsorption of 2,4-MCPA et 2,4-DP on Activated carbon (CH) and (CL)

			(CH)	
	K_e	**K' (min^{-1})**	**k_1 (min^{-1})**	**k_2 (min^{-1})**
2,4-MCPA	1.987	0.550	0.366	0.184
2,4-DP	2.416	0.551	0.389	0.161
			(CL)	
	K_e	**K' (min^{-1})**	**k_1 (min^{-1})**	**k_2 (min^{-1})**
2,4-MCPA	0.321	0.140	0.034	0.106
2,4-DP	0.369	0.151	0.040	0.109

Adsorption isotherms

The adsorption isotherm is studied for a ratio R of 1 g/l and 6 hours of stirring. Figure 2 (A) and (B) show the adsorption isotherms of the acids studied on (CH) and (CL) respectively.

According to the classification of GILLS [20], the isotherms are of type L. This type indicates that the more the adsorbent sites are occupied, the more difficult it is for the adsorbate molecules to find vacant sites available. It also indicates that the molecules are preferentially adsorbed flat or at low competition with the solvent.

The modeling of the adsorption isotherms was carried out by applying the classical Freundlich model whose equation is of the form:

$$Q = KC^n_e.$$

Where Q is the amount of adsorbed solute per gram of adsorbent (mmol / g). This is the solute concentration in the equilibrium solution (mmol / l), and K and n are the Freundlich constants respectively, to the capacity and the intensity of adsorption.

Table 2 summarizes the Freundlich constants, computed by logarithmic transform of the equation, for the different systems studied. Based on the correlation coefficients of the linear regression, the Langmuir model also adequately describes the adsorption isotherms. In this study, both models fairly describe the adsorption of the two solutes, and therefore only the Freundlich parameters are given in Table 2.

FIGS. 3 and 4 also show that the adsorption of 2,4-DP is substantially greater than that of 2,4-MCPA. Although 2,4-DP is less soluble than 2,4-MCPA, and according to the rule of Leuindeuse, [21] it will be strongly adsorbed, only this slight difference is noted. This is probably due to differences in the alkyl chains of the two compounds. In fact, 2,4-DP is a phenoxyproponoic acid, whereas 2,4-MCPA is a phenoxyacetic acid.

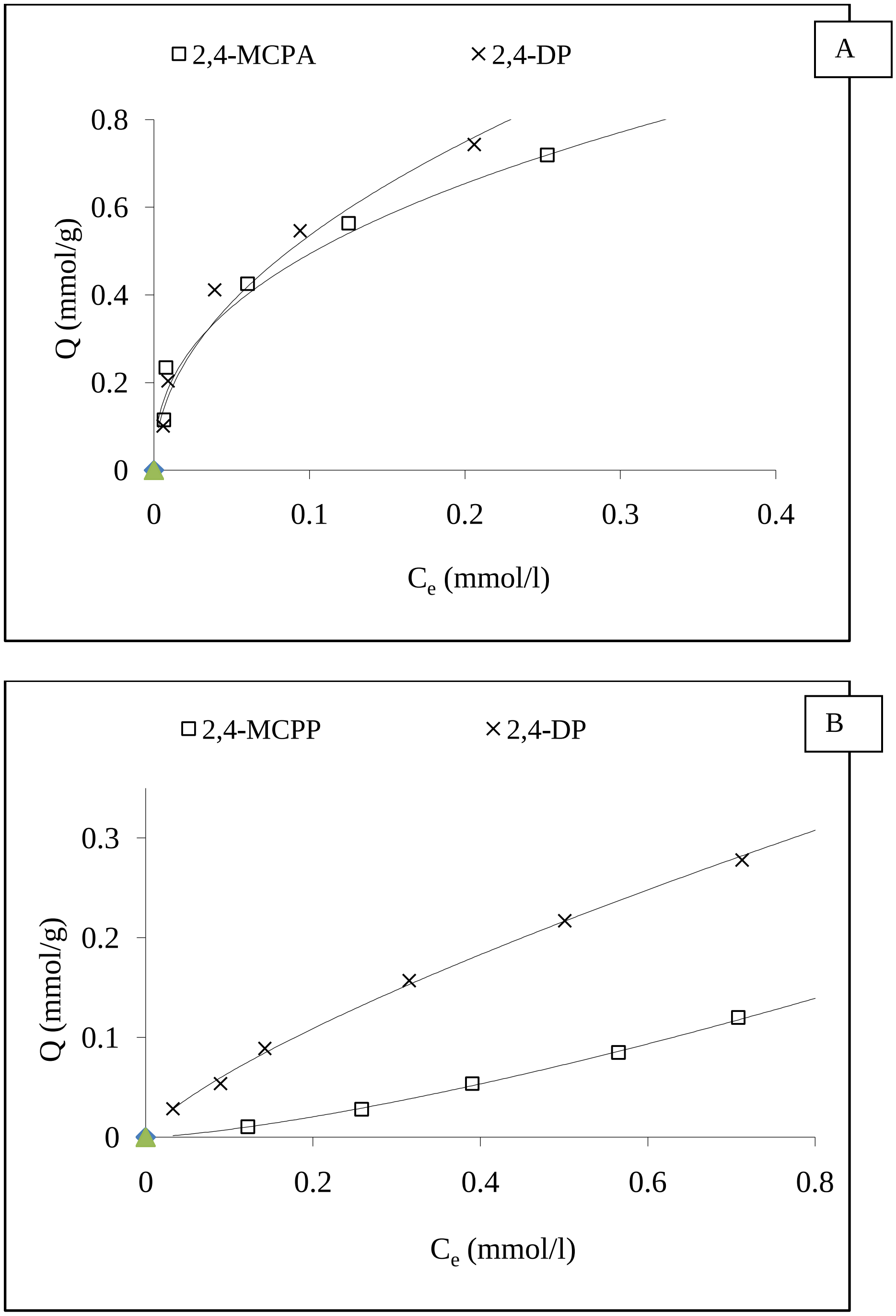

Figure 2: adsorption isotherms for 2,4-MCPA et 2,4-DP on activated carbon (CH) and (CL) at 25°C.

Table 2: Freundich parameter's for adsorption of 2,4-MCP and 2,4-DP on activated carbon

	(CH)		(CL)	
	K	**n**	**K**	**n**
2,4-MCPA	1.2840	0.4097	0.3542	0.9297
2,4-MCPP	1.4284	0.4606	0.3353	0.7777

Conclusion

This study shows that the adsorption of 2,4-MCPA and 2,4-DP is rapid and follows the first order kinetic law. The time needed to reach equilibrium is shorter with the activated carbon with a large specific surface. The results also show that the adsorption of 2,4-DP is substantially greater than that of 2,4-MCPA due to its low solubility. Adsorption is also influenced by the characteristics of adsorbates such as solubility and molecular structure.

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