

## Sorption Capacity of Mesoporous Metal Oxides for the Removal of MCPA from Polluted Waters

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A study was performed to assess the sorption capacity of the phenoxy acid herbicide, MCPA, on two mesoporous oxides, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, by using a batch equilibrium method. Effects of pH, contact time, initial concentration and sorbent dosage on the sorption of the herbicide were investigated. The collected data evidenced the greater sorption efficiency of Al<sub>2</sub>O<sub>3</sub> with respect to Fe<sub>2</sub>O<sub>3</sub>. These results can be explained by considering the specific mesoporous structure of Al<sub>2</sub>O<sub>3</sub> together with the greater value of surface area. MCPA is assumed to be bound to Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> by a combination of ionic and ion–dipole bonding. Both oxides present as sorbents for a fast and highly efficient removal of MCPA from contaminated waters. For the first time the possible use of mesoporous metal oxides to remove MCPA from contaminated wastewaters identifies these sorbents as suitable filters for the decontamination of point sources.

**KEYWORDS:** Sorption; MCPA; mesoporous metal oxides; decontamination; pollution point sources

### INTRODUCTION

Pesticides play an important role in the success of modern farming and food production; however, their use has been a public concern because of the potential risk to human health and the environment (1). Accidental release, illegal operations and inappropriate disposal of wastes from industries and farms are the main causes of point sources of soil and water pollution by pesticides. The quality of soil and water bodies deserves particular attention for its importance in the survival of the ecosystem as well as in the supply of water for drinking and amenity use; therefore their protection and the development of new methodologies to mitigate the risk deriving from point source pollution is necessary for safeguarding the environment.

Several treatment processes are available for pesticide removal from waters: chemical oxidation, photodegradation, oxidation with ozone, Fenton degradation, biological degradation and adsorption have been investigated with varying success (2).

In particular, for its low maintenance costs, high efficiency, and ease of operation, adsorption has proven to be one of the most attractive and effective techniques successfully applied for removal of heavy metals and organic chemicals from hazardous wastes and has a great environmental significance (3, 4).

Various types of adsorbents have been utilized such as activated carbon, zeolites, fly ash, clays either natural or pillared, organic colloids and metal oxides (5–8). Although activated carbons are among the most effective adsorbents for their high surface area and can be regenerated by thermal desorption or combustion, a substantial fraction of the carbon is lost with each

oxidation cycle. This loss of adsorbent is a major economic consideration in any large scale remediation application.

Clays are widely used as adsorbents due to their high specific surface area. Nevertheless, the anionic character of clay minerals limits their usefulness as adsorbents of acid herbicides when these latter are present in their anionic form.

Some studies have proposed the use of natural organic materials or wastes as biosorbent (9, 10) due to high sorption capacity of organic matter (11, 12). In particular, we reported polymerin, the polymeric organic fraction recovered from olive oil mill wastewater (OMW), to exhibit very interesting sorption capacities for cationic and anionic heavy metals (13, 3), ionic or ionizable pesticides (4), and hydrophobic organic compounds (14). However, its employment as a possible biofilter for the decontamination of wastewaters from pollution point sources revealed some technological and economic limitations.

This has led to an increasing interest for the development of new adsorbents for the efficient removal of organic pollutants from aqueous solutions. Several studies have highlighted that the sorption capacity of a sorbent is definitely determined from its overall surface area, but the pore size distribution is also decisive for an optimal sorption process.

Nanometer-sized pores within mineral particles are thought to contribute to retention of organic pollutants in soils and sediments (15). Studies of hydrophobic organic contaminants (HOCs) indicate that several physical and chemical mechanisms, including increased adsorption energy deriving from compound interaction within pores, may enhance HOC retention in mineral micropores. Although hydrophobic micropores are likely important for HOC adsorption (16, 17), hydrophilic porous surfaces may also be significant, since steric effects, slow diffusion, and tortuosity may inhibit the desorption process.

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Some studies support the likelihood that mineral mesopores may enhance organic compound sorption processes. For example, the structure of water in close proximity to mineral surfaces differs from that in the bulk (18). This may create favorable conditions for contaminant sorption within mesopores, even though the extent of structured water may not permeate throughout a mesopore as it apparently does within a micropore. Previous studies (19) reported that increasing the number of benzene rings in polynuclear aromatic compounds results in more favorable sorbate/sorbate interactions within mesopores, while Zimmerman et al. (20) observed that nitrogenous organic compounds smaller than one-half mesopore diameter exhibited a greater adsorption on mesoporous alumina and silica, relative to nonporous analogues. Therefore, several works have investigated the sorption of HOCs and heavy metals on mesoporous materials (21, 22), but few studies (15) have been carried out on the sorption of ionic organic pollutants.

Among the different pollutants commonly found in soil and waters, 4-chloro-2-methylphenoxyacetic acid (MCPA) deserves a particular interest. MCPA is a postemergence phenoxy acid herbicide extensively used in agriculture to control annual and perennial weeds in cereals, grasslands, trees, and turf. It is very soluble (273.9 mg L<sup>-1</sup> in water at neutral pH), highly mobile, and can leach from soil. This compound has been found in well water in some countries and is classified by the U.S. Environmental Protection Agency (EPA) as a potential groundwater contaminant (23).

Therefore, the objective of the present work was to evaluate (i) the sorption capacity of two commercial nanosized metal oxides (Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) for MCPA removal from polluted waters and (ii) the removal of MCPA from simulated wastewaters by cyclic sorption of the herbicide on the selected sorbents renewed at each cycle.

## MATERIALS AND METHODS

**Materials.** 4-Chloro-2-methylphenoxyacetic acid (MCPA) was purchased from Sigma-Aldrich Chemical Co. (Poole, Dorset, U.K.; 99.0% purity). All solvents were of HPLC grade (Carlo Erba, Milan, Italy) and were used without further purification. All other chemicals were obtained from Sigma-Aldrich unless otherwise specified.

$\gamma$ -Aluminum (Al<sub>2</sub>O<sub>3</sub>) and iron(III) (Fe<sub>2</sub>O<sub>3</sub>) nanosized oxides were purchased from IoliTec Nanomaterials (Denzlingen, Germany; 99.9 and 99.5% purity for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively).

**Physical Analysis of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.** The specific surface area (SSA) of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> was calculated by the Brunauer–Emmett–Teller (BET) method (24). N<sub>2</sub> adsorption–desorption isotherms at 77 K were obtained by a Micromeritics Gemini II 2370 apparatus. Before each measurement the sample was degassed at 250 °C for 2 h under N<sub>2</sub> flow. Pore volumes were determined from the amounts of adsorbed N<sub>2</sub> at  $P/P^{\circ} = 0.98$  (desorption curve), assuming the presence of liquid N<sub>2</sub> (density = 0.807 g cm<sup>-3</sup>) in the pores under these conditions. The average values of pore diameter  $d_p$  were calculated from the relation  $d_p = 4V/A_{BET}$ , where  $V$  is total pore volume.

The Barrett–Joyner–Halenda (BJH) approach (24) was used to calculate pore size distribution of the sample using the desorption data.

**Estimation of the Point of Zero Charge (PZC).** The point of zero charge (PZC) of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> was performed according to the method described by Mustafa et al. (25). Dry samples (100 mg) were dissolved in 40 mL of 0.001 M KCl solution as a background electrolyte and equilibrated for 30 min by means of a magnetic stirrer. Successively, the initial pH of the solution was adjusted to pH 4.0 by the addition of either 0.1 M HCl or 0.1 M KOH. The suspension was equilibrated for another 10 min, and the pH was then measured. The suspension pH was recorded every 2 min as a function of volume of titrant added until the pH 10 was reached. The PZC of two sorbents was determined from the variation of surface charge density as a function of pH.

**Sorption Methodology.** Stock solution of herbicide was prepared by dissolving 100 mg of MCPA in 500 mL of KCl 0.03 M (final concentration

1000  $\mu\text{mol L}^{-1}$ ). This solution was then kept refrigerated. Preliminary sorption experiments were conducted at solid/liquid ratio of 0.5 obtained by adding 10 mg of Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> to a final volume of 20 mL, using a fixed pesticide concentration of 10  $\mu\text{mol L}^{-1}$ , varying the pH from 3.0 to 7.0 and for an incubation time of 24 h. The pH was controlled by addition of 0.01 mmol L<sup>-1</sup> HCl or KOH to the solution. After incubation in a rotatory shaker at 20 °C, the samples were centrifuged at 7000 rpm for 20 min. The amount of MCPA sorbed on the oxides was calculated as the difference between the initial quantity of herbicide added and that present in the equilibrium solution. Blanks of MCPA in KCl 0.03 M were analyzed in order to check pesticide stability and sorption to vials.

**Analytical Determination of MCPA.** MCPA was analyzed with an Agilent 1200 Series HPLC apparatus (Wilmington, DE), equipped with a DAD array and a ChemStation Agilent Software. A Macharey-Nagel Nucleosil 100-5 C18 column (stainless steel 250 × 4 mm) was utilized. The mobile phase, comprising a binary system of 50:50 acetonitrile:phosphate buffer (0.1%, pH 2.0), was pumped at 1 mL min<sup>-1</sup> flow in an isocratic mode. The detector was set at 225 nm, and injection volume was 20  $\mu\text{L}$ . The quantitative determination of MCPA was performed elaborating its corresponding calibration curve between 0.25 and 1000  $\mu\text{mol L}^{-1}$ .

**Effect of Solid/Liquid Ratio.** Experiments were carried out by adding a fixed pesticide concentration of 10  $\mu\text{mol L}^{-1}$  at different solid/liquid ratios. Ratios of 0.1, 0.5, 1.0, and 2.0 were obtained by adding 2.0, 10, 20, and 40 mg, respectively, of Al<sub>2</sub>O<sub>3</sub> or Fe<sub>2</sub>O<sub>3</sub> to a final volume of 20 mL, at 20 °C. The samples were incubated at pH value of 4.0 and 3.5 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively, for 24 h.

**Effect of Time.** Experiments were performed using 10  $\mu\text{mol L}^{-1}$  of MCPA at pH 4.0 for Al<sub>2</sub>O<sub>3</sub> and pH 3.5 for Fe<sub>2</sub>O<sub>3</sub>. The suspensions were stirred for 2.0, 5.0, 20, 40, 60, 90, 120, 320, 960, and 1800 min.

**Sorption Isotherms.** Different volumes of a stock solution of herbicide (1000  $\mu\text{mol L}^{-1}$ ) were added to each oxide to give an initial concentration ranging from 0.05 to 200  $\mu\text{mol L}^{-1}$  of MCPA. The pH of each suspension was kept constant at pH 4.0 and 3.5 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively, by the addition of 0.10 or 0.01 mol L<sup>-1</sup> HCl or KOH. The samples were incubated for 20 and 180 min for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively; then after centrifugation, the supernatants were analyzed as described above.

**Cyclic Sorption on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.** Cyclic experiments for sorption of MCPA were carried out at pH 4.0 and 3.5 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. In the first cycle, a predetermined quantity of herbicide stock solution was pipetted into the vials to give 100  $\mu\text{mol L}^{-1}$ .

The samples were treated according to the procedure previously described. After the contact time, the sorbent was separated from the suspension and the filtrate was analyzed to determine the amount of sorbed pesticide. For the second cycle, 20 mL of filtrate was added to fresh sorbent (2 mg). The experiments were repeated until the equilibrium concentrations remained constant.

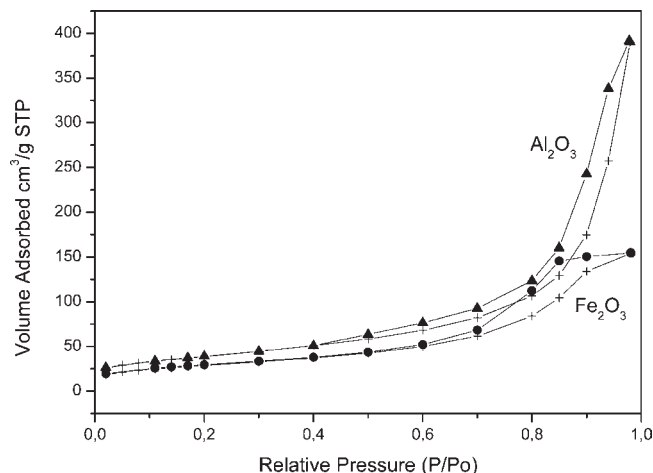
**Data Analysis.** All the experiments were performed in triplicate, and the relative standard deviation was lower than 4%. The kinetic data were analyzed using the Lagergren equation (26),  $\log(q_e - q) = \log q_e - K_a t / 2.303$ , where  $q_e$  and  $q$  are the amount of herbicide sorbed ( $\mu\text{mol kg}^{-1}$ ) at equilibrium and at time  $t$ , respectively,  $K_a$  is the rate constant of sorption ( $\text{min}^{-1}$ ) and  $t$  is the time (min).

The sorption data were analyzed according to the Freundlich equation,  $x = Kc^{1/N}$ , where  $x$  is defined as the amount of pesticide sorbed ( $\mu\text{mol kg}^{-1}$ ),  $c$  is the equilibrium concentration of pesticide ( $\mu\text{mol L}^{-1}$ ), and  $K$  [ $(\mu\text{mol kg}^{-1})/(\mu\text{mol L}^{-1})^{1/N}$ ] and  $N$  (dimensionless) are constants that give estimates of the sorptive capacity and intensity, respectively, according to Giles et al. (27).

The distribution coefficient,  $K_d$  (defined as the ratio of the concentration of pesticide sorbed per unit weight of sorbent to its equilibrium concentration:  $\text{L kg}^{-1}$ ) at saturation was also determined.

## RESULTS AND DISCUSSION

**Characterization of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.** The porosity of the selected matrices was analyzed to get insight into their adsorption capability. N<sub>2</sub> adsorption–desorption isotherms for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are reported in **Figure 1**. The isotherms are of type IV for Al<sub>2</sub>O<sub>3</sub> and of type IIb for Fe<sub>2</sub>O<sub>3</sub> according to the IUPAC classification (28) with large adsorption volumes at  $P/P_0 > 0.4$  and a desorption hysteresis. Although both the isotherms show a



**Figure 1.** N<sub>2</sub> adsorption–desorption isotherm of mesoporous metal oxides, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

**Table 1.** Physical and Chemical Properties of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>

	pore vol (cm <sup>3</sup> g <sup>-1</sup> )	particle size (nm) <sup>a</sup>	ave pore diam (nm)	surf area (m <sup>2</sup> g <sup>-1</sup> )	PZC
Al <sub>2</sub> O <sub>3</sub>	0.723	20	14.8	195	9.1
Fe <sub>2</sub> O <sub>3</sub>	0.239	10–20	9.2	106	10.1

<sup>a</sup> Provided by the supplier.

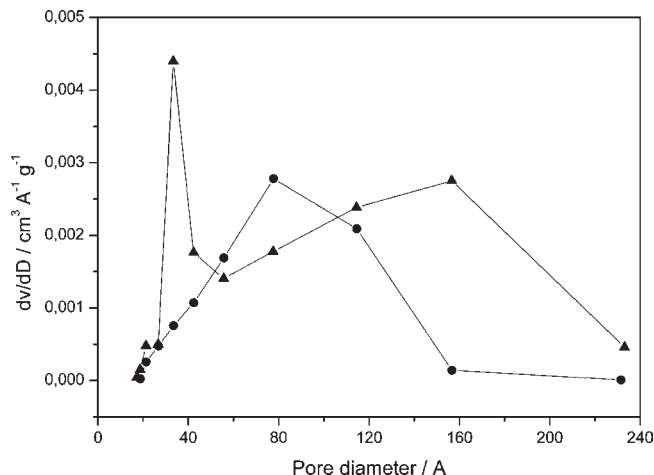
desorption hysteresis, characteristic of mesoporous materials, the type of hysteresis is different for the two samples, indicating a dissimilar mesoporous structure.

The isotherm of Al<sub>2</sub>O<sub>3</sub> does not exhibit any limiting adsorption at high  $P/P_0$ , revealing a type H3 hysteresis according to the IUPAC classification (28). This behavior is observed with non-rigid aggregates of platelike particles giving rise to slit-shaped pores. Because of the delayed capillary condensation, multilayer adsorption is able to proceed on the particle surface until a high value of  $P/P_0$  is reached.

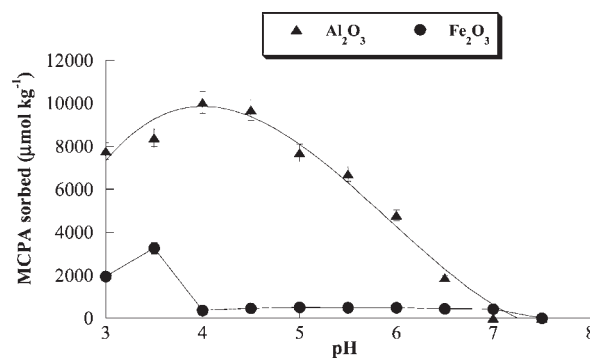
The isotherm of Fe<sub>2</sub>O<sub>3</sub> shows a plateau at a high value of  $P/P_0$ , and a type H2 loop can be detected. This situation is often associated with disordered materials where the distribution of pore size and shape is not well-defined. The pore structures in these materials are complex, and often they are made up of interconnected networks of pores of different size and shape.

The adsorption isotherms were elaborated using the BET method, and the corresponding surface areas are reported in **Table 1** together with the total pore volume and the estimated average pore diameter. It can be observed that the surface area of aluminum oxide (195 m<sup>2</sup> g<sup>-1</sup>) is much greater than that of iron oxide (106 m<sup>2</sup> g<sup>-1</sup>), meanwhile the aluminum oxide possesses a porous structure with a total pore volume much higher than that of iron oxide.

The average values of pore diameter, in both the selected supports, are further evidence that most of the porosity is due to quite large cavities, with size far from that of MCPA (~7–9 Å) (29). It is worth underlining the greater porosity of the aluminum oxide with respect to the iron oxide, as indicated by the total pore volume together with the higher average values of pore diameter (**Table 1**). To obtain the pore size distribution of these materials, the desorption data were elaborated by the BJH method and reported in **Figure 2**. The iron oxide shows a unimodal distribution, and most of the N<sub>2</sub> volume is adsorbed in the pore range of 6–10 nm. For Al<sub>2</sub>O<sub>3</sub> the distribution appears to be bimodal characterized by two maxima, the former at about 3 nm and the latter at about 15 nm. The peak in the range



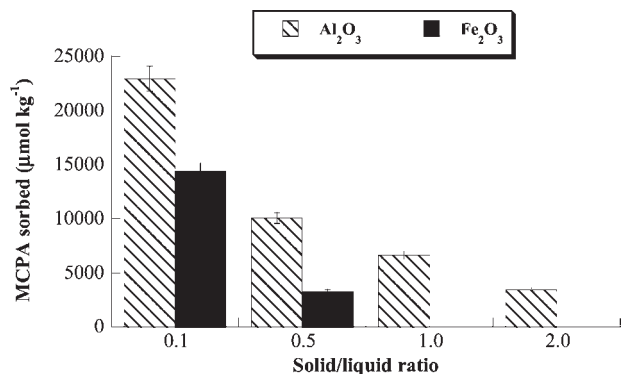
**Figure 2.** Pore size distribution of mesoporous metal oxides: Al<sub>2</sub>O<sub>3</sub> (▲) and Fe<sub>2</sub>O<sub>3</sub> (●).



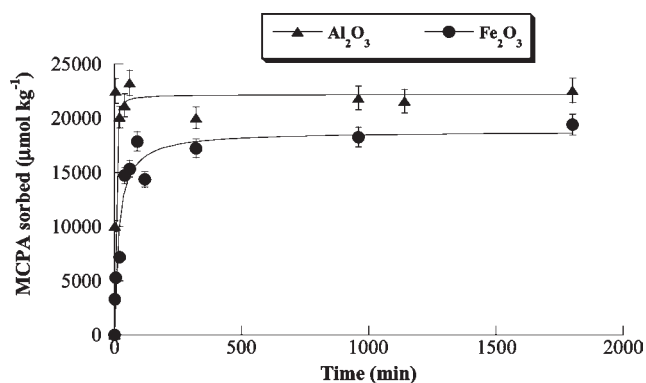
**Figure 3.** Effect of pH on the sorption of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at a solid/liquid ratio of 0.5.

20–40 Å is a tricky point because it could be caused by the forced closure of the H3 hysteresis loop.

**Sorption Studies.** Preliminary experiments were conducted to select the experimental conditions most suitable for the sorption of MCPA on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. In a previous study (4) we reported that among 2.5, 1.25, and 0.5 the best solid/liquid ratio for sorption of 2,4-D and paraquat was 0.5. For this reason, we utilized 10 mg of oxide in 20 mL of final solution. In order to evaluate the optimum pH to be used later in all the experiments, sorption experiments were carried out as a function of pH at 0.5 solid/liquid ratio and are reported in **Figure 3**. The results obtained showed the greatest sorbed amount of MCPA at acidic pH, with an optimum pH of 4.0 and 3.5 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. This behavior could be explained considering the pK<sub>a</sub> value (3.07) of MCPA and the PZC of two oxides, 9.1 and 10.1 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively (**Table 1**). Indeed, at sorption optimum pH (4.0 and 3.5 for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively) both the oxides have the completely positive surface by OH<sub>2</sub><sup>+</sup> groups because of PZC value (**Table 1**), whereas the proportions of un-ionized and ionized herbicide carboxylic group were roughly estimated as 40:60% and 50:50% for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. This means that the ionized carboxylic group (–COO<sup>–</sup>) of MCPA formed ionic bonding with the positive surface of both the sorbents. The hydrogen bonded to the protonated hydroxyl group presents a very high mobility due to positive charge on O atom. In these conditions and considering the aqueous medium where the adsorption occurs, it can be supposed that the formation of hydrogen bonds contributes to stabilize the interaction between the anionic form of MCPA and



**Figure 4.** Effect of solid/liquid ratio on the sorption of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at pH 4.0 and 3.5, respectively.



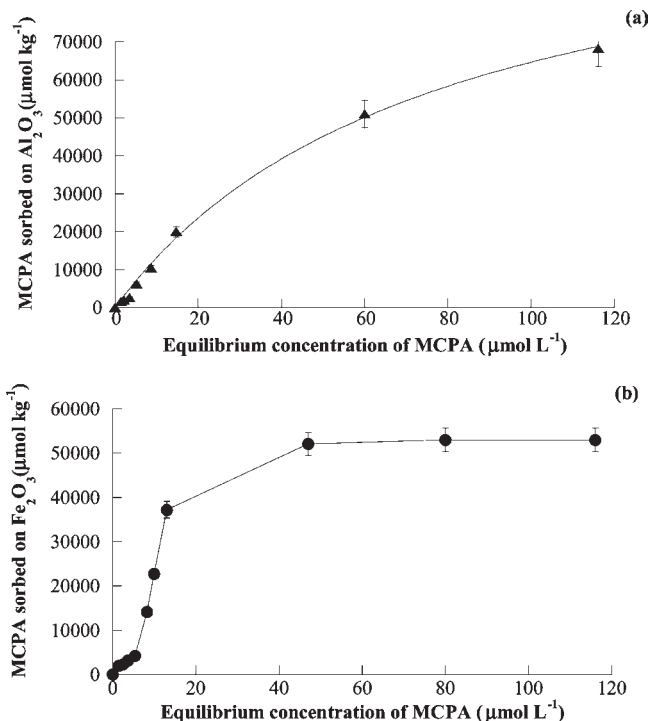
**Figure 5.** Effect of time on the sorption of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

the positively charged surface of the matrices, attenuating very likely the ionic character of the bond. The amount of sorbed MCPA on Fe<sub>2</sub>O<sub>3</sub> was much lower than that detected on Al<sub>2</sub>O<sub>3</sub> due very probably to (i) the lower proportion of ionized herbicide thus available for ionic bonding with the matrix and (ii) the lower surface area and the lack of secondary small pores with respect to Al<sub>2</sub>O<sub>3</sub>.

Previous studies confirmed that metal oxides exhibited a strong sorption of ionic and ionizable pesticides at low pH and a decreasing sorption as pH increased (30). Cho et al. (31) investigated the sorption ability of MCPA on activated carbon and demonstrated a higher sorption of the herbicide at pH 3.5 and a decrease with increasing the pH of the solution.

Sorption studies of MCPA were carried out at pH 4.0 and pH 3.5 on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively, and varying the amount of sorbent. The results obtained and reported in Figure 4 showed for both of the oxides a higher sorption at the lowest solid/liquid ratio (0.1). In fact, the amount of sorbed herbicide on Al<sub>2</sub>O<sub>3</sub> significantly decreased by increasing the amount of oxide, but a drastic reduction with a negligible amount of herbicide was found on Fe<sub>2</sub>O<sub>3</sub> at 1.0 and 2.0 solid/liquid ratio. This behavior could be explained by considering the mass transfer resistance involved in the sorption process. The sorption on a solid surface takes place in several steps, such as external diffusion, internal diffusion, and actual sorption. Intraparticle diffusion has been generally considered as the rate controlling step in liquid-phase sorption. Evidently, the greater the amount of oxide, the greater the resistance to the diffusion inside the particle, and the result is a lower sorption of the herbicide.

Kinetic studies on the sorption of MCPA on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were carried out at pH 4.0 and pH 3.5, respectively (Figure 5). The results obtained by the Lagergren equation showed that the



**Figure 6.** Sorption isotherm of MCPA by (a) Al<sub>2</sub>O<sub>3</sub> and (b) Fe<sub>2</sub>O<sub>3</sub>.

sorption of the herbicide on each mesoporous oxide fitted a first-order mechanism ( $r^2 > 0.90$ ). This process was very fast on Al<sub>2</sub>O<sub>3</sub>, reaching the sorption equilibrium after 5 min, but was much slower on Fe<sub>2</sub>O<sub>3</sub>, it being observed within 90 min. In correspondence, the rate constants determined from the slopes of the plots of  $\log(q_e - q)$  versus  $t$  were 0.908 and 0.230 min<sup>-1</sup>, for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. Therefore, an incubation period of 20 min for Al<sub>2</sub>O<sub>3</sub> and 180 min for Fe<sub>2</sub>O<sub>3</sub> was utilized.

Previous studies (15) showed similar results in the sorption process of 2,4-D on three Al<sub>2</sub>O<sub>3</sub> adsorbents with varying degrees of mesoporosity (pore diameter 2–50 nm). In another investigation conducted by Wang et al. (22), the adsorption kinetics of Cr(VI) on mesoporous Fe<sub>2</sub>O<sub>3</sub> was shown to be very fast.

The rapid sorption of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> further suggests that the sorption mechanism is mainly due to electrostatic attraction, and it also implies that the mesopores are not a limiting factor for the herbicide diffusion into the interior of the mesoporous oxides.

The sorption isotherms of MCPA on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, shown in Figure 6a,b, were well-fitted by the linearized form of Freundlich equation ( $r^2 > 0.99$ ) (Table 2). According to Giles classification (27) the experimental sorption isotherms were of L-type for Al<sub>2</sub>O<sub>3</sub> and S-type for Fe<sub>2</sub>O<sub>3</sub>.

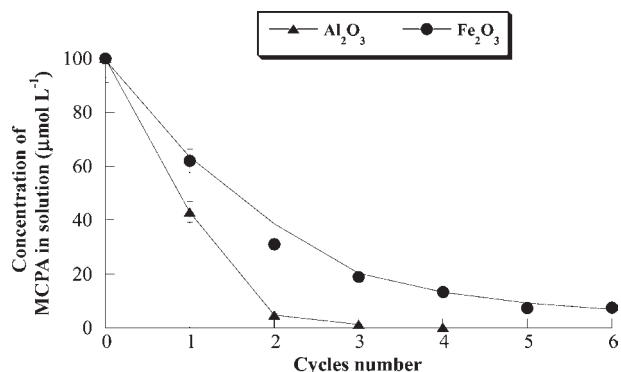
In particular, at low equilibrium concentrations the sorbed amount of MCPA on Fe<sub>2</sub>O<sub>3</sub> was slightly higher than that detected on Al<sub>2</sub>O<sub>3</sub>, but at higher concentrations there was a marked difference in the behavior of the two mesoporous oxides. Actually, at a 100 μmol L<sup>-1</sup> equilibrium concentration of MCPA, the amount of sorbed herbicide significantly increased from 59000 on Fe<sub>2</sub>O<sub>3</sub> to ~68000 μmol kg<sup>-1</sup> on Al<sub>2</sub>O<sub>3</sub>. This trend was confirmed analyzing both the Freundlich constants ( $K$  and  $N$ ) and also  $K_d$  values (Table 2), showing that Al<sub>2</sub>O<sub>3</sub> sorbed the herbicide with both the greatest binding energy and sorptive intensity.

The isotherm of MCPA observed with Fe<sub>2</sub>O<sub>3</sub> resembles S-type isotherm but tends to L-type. A change from S to L within the same isotherm was detected in the sorption of MCPA by MgAl-layered double hydroxides. This behavior was associated with a change in the sorption process from outside to inside of the pores,

**Table 2.** Freundlich Parameters for the Sorption of MCPA on Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>

	Freundlich parameters			
	$K$ ( $\mu\text{mol kg}^{-1}$ )( $\mu\text{mol L}^{-1}$ ) <sup>1/N</sup>	$N$ (dimensionless)	$r^2$ <sup>a</sup>	$K_d$ <sup>b</sup> (L kg <sup>-1</sup> )
Al <sub>2</sub> O <sub>3</sub>	1317.35	1.10	0.99	588
Fe <sub>2</sub> O <sub>3</sub>	804.45	1.01	0.99	456

<sup>a</sup> Correlation coefficient. <sup>b</sup> Distribution coefficient.

**Figure 7.** Cyclic removal of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> from simulated wastewaters (the sorbent was renewed in each cycle).

and the process occurred by anion exchange in two steps, an external exchange followed by an interlayer exchange (32). As far as Fe<sub>2</sub>O<sub>3</sub> is concerned, the textural analysis data would suggest that the interconnected networks of pores of different size and shape are accountable for two different sorption processes.

The highest sorption observed with Al<sub>2</sub>O<sub>3</sub> can be explainable probably by considering the presence of secondary small pores at boundary of micropore region in Al<sub>2</sub>O<sub>3</sub> (Figures 1 and 2) that have a positive influence in the uptake of small organic molecules (i.e., organic molecules having sizes in the range of 6–8 Å). It is likely that the sorption energy increases in those pores whose dimensions approach to the herbicide dimensions (0.7–0.9 nm).

On the contrary, nonlinear sorption isotherms for MCPA and similar acidic pesticides are frequently reported (33, 34). This might be explained by an increased difficulty to access the active sorption sites when pesticide concentrations in solution are elevated. Nonlinear sorption of organic compounds to natural organic matters is due to sorbent heterogeneity and limited sorption site abundance (35).

**Cyclic Removal of MCPA by Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> from Simulated Wastewaters.** Experiments on cyclic sorption investigated the potential to remove MCPA from simulated wastewaters. Figure 7 shows that a total removal of MCPA on Al<sub>2</sub>O<sub>3</sub> was performed after four sorption cycles, whereas decontamination was still incomplete on Fe<sub>2</sub>O<sub>3</sub> even after five cycles, leaving a constant residue of 7.5  $\mu\text{mol L}^{-1}$ . The behavior of two oxides toward MCPA showed the different sorption capacities as seen previously, with an herbicide removal of 100 and 92.0% for Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, respectively. These data indicate that a threshold concentration value of 7.5  $\mu\text{mol L}^{-1}$  existed at which no sorption occurred, and this value was independent of cycle number. This suggests that at the concentration of 7.5  $\mu\text{mol L}^{-1}$  the acid–base equilibrium of the herbicide was strongly in competition with the sorption equilibrium between the undissociated form of MCPA and Fe<sub>2</sub>O<sub>3</sub>. Therefore, Al<sub>2</sub>O<sub>3</sub> was shown to be the most efficient sorbent for the removal of MCPA from contaminated waters. Previous experiments of cyclic sorption carried out by using other sorbents, such as polymerin or ferrihydrite–polymerin complex, and phenoxy acid herbicides such as 2,4-D or cyhalofop acid,

showed the presence of herbicide concentrations higher than those detected after five cycles and reported in this work.

In conclusion, the present research work has highlighted the capability of the selected oxides to work as sorbents for a fast and highly efficient removal of MCPA from contaminated waters. Moreover, the authors evidenced the influence of both chemical composition and mesoporous structure on the sorption capability toward a widely used phenoxy acid herbicide (MCPA).

A further relevant result of this study is the identification of these sorbents as suitable filters for the decontamination of point sources. Indeed, they can be regenerated by incineration, and could be considered for small-scale treatment systems and industrial scale. In particular, Al<sub>2</sub>O<sub>3</sub> turned out to allow the total removal of the herbicide from contamination waters by four sorption cycles, by using the usual procedure of centrifugation for the separation of purified waters. This observation recognizes Al<sub>2</sub>O<sub>3</sub> as a potential filter for the control of wastewater contamination with MCPA in point sources.

## LITERATURE CITED

- (1) De Wilde, T.; Spanoghe, P.; Debaer, C.; Ryckeboer, J.; Springael, D.; Jaeken, P. Overview of on-farm bioremediation systems to reduce the occurrence of point source contamination. *Pest Manage. Sci.* **2007**, *63*, 111–128.
- (2) Ignatowicz, K. Selection of sorbent for removing pesticides during water treatment. *J. Hazard. Mater.* **2009**, *169*, 953–957.
- (3) Sannino, F.; De Martino, A.; Pigna, M.; Violante, A.; Di Leo, P.; Mesto, E.; Capasso, R. Sorption of arsenate and dichromate on polymerin, Fe(OH)<sub>x</sub>-polymerin complex and ferrihydrite. *J. Hazard. Mater.* **2009**, *166*, 1174–1179.
- (4) Sannino, F.; Iorio, M.; De Martino, A.; Pucci, M.; Brown, C. D.; Capasso, R. Remediation of waters contaminated with ionic herbicides by sorption on polymerin. *Water Res.* **2008**, *42*, 643–652.
- (5) Konstantinou, I. K.; Albanis, T. A.; Petrakis, D. E.; Pomonis, P. J. Removal of herbicides from aqueous solutions by adsorption on Al-pillared clays, Fe-Al pillared clays and mesoporous alumina aluminum phosphates. *Water Res.* **2000**, *34*, 3123–3136.
- (6) Cruz-Guzman, M.; Celis, R.; Hermosin, M. C.; Koskinen, W. C.; Cornejo, J. Adsorption of pesticides from water by functionalized organobentonites. *J. Agric. Food Chem.* **2005**, *53*, 7502–7511.
- (7) Sheng, G.; Johnston, C. T.; Teppen, B. J. Potential contributions of smectite clays and organic matter to pesticide retention in soils. *J. Agric. Food Chem.* **2001**, *49*, 2899–2907.
- (8) van Beinum, W.; Beulke, S.; Brown, C. D. Pesticide sorption and diffusion in natural clay loam aggregates. *J. Agric. Food Chem.* **2005**, *53*, 9146–9154.
- (9) Rodriguez-Cruz, S.; Andrades, M. S.; Sanchez-Camazano, M.; Sanchez-Martin, M. J. Relationship between the adsorption capacity of pesticides by wood residues and properties of wood and pesticides. *Environ. Sci. Technol.* **2007**, *41*, 3613–3619.
- (10) Wang, X.; Yang, K.; Tao, S.; Xing, B. Sorption of aromatic organic contaminants by biopolymers: effect of pH, copper (II) complexation and cellulose coating. *Environ. Sci. Technol.* **2007**, *41*, 185–191.
- (11) Kang, S.; Xing, B. Phenanthrene sorption to sequentially extracted soil humic acid and humans. *Environ. Sci. Technol.* **2005**, *39*, 134–140.
- (12) Gunasekara, A.; Xing, B. Sorption and desorption of naphthalene by soil organic matter: importance of aromatic and aliphatic components. *J. Environ. Qual.* **2003**, *32*, 240–246.
- (13) Capasso, R.; Pigna, M.; De Martino, A.; Pucci, M.; Sannino, F.; Violante, A. Potential remediation of waters contaminated with Cr (III), Cu, and Zn by sorption on the organic polymeric fraction of olive mill wastewater (polymerin) and its derivatives. *Environ. Sci. Technol.* **2004**, *38*, 5170–5176.
- (14) Iorio, M.; Pan, B.; Capasso, R.; Xing, B. Sorption of phenanthrene by dissolved organic matter and its complex with aluminum oxide nanoparticles. *Environ. Pollut.* **2008**, *156*, 1021–1029.
- (15) Goyne, K. W.; Chrover, J.; Zimmerman, A. R.; Komarneni, S.; Brantley, S. L. Influence of mesoporosity on the sorption of

- 2,4-dichlorophenoxyacetic acid onto alumina and silica. *J. Colloid Interface Sci.* **2004**, *272*, 10–20.
- (16) Werth, C.; Reinhard, M. Temperature on trichloroethylene desorption from silica gel and natural sediments. I. Isotherms. *Environ. Sci. Technol.* **1997**, *31*, 689–696.
- (17) Li, J.; Werth, C. Evaluating competitive sorption mechanisms of volatile organic compounds in soils and sediments using polymers and zeolites. *Environ. Sci. Technol.* **2001**, *35*, 568–574.
- (18) Pignatello, J. The measurement and interpretation of sorption and desorption rates for organic compounds in soil media. *Adv. Agron.* **1999**, *69*, 1–73.
- (19) Mastral, A. M.; García, T.; Callén, M. S.; Navarro, M. V.; Galbán, J. Removal of naphthalene, phenanthrene, and pyrene by sorbents from hot gas. *Environ. Sci. Technol.* **2001**, *35*, 2395–2400.
- (20) Zimmerman, A. R.; Goynes, K. W.; Chorover, J.; Komarneni, S.; Susan, L. Mineral mesopore effects on nitrogenous organic matter adsorption. *Org. Geochem.* **2004**, *35*, 355–375.
- (21) Farrell, J.; Reinhard, M. Desorption of halogenated organics from model solids, sediments, and soil under unsaturated conditions. I. Isotherms. *Environ. Sci. Technol.* **1994**, *28*, 53–62.
- (22) Wang, P.; Lo, I. M. C. Synthesis of mesoporous magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and its application to Cr(VI) removal from contaminated water. *Water Res.* **2009**, *43*, 3727–3734.
- (23) Walker, M.; Lawrence, H. *EPA's Pesticide Fact Sheet Database*; Lewis Publishers Inc.: Chelsea, MI, 1992.
- (24) Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by powders and porous solids: principles, methodology and application*; Academic Press: London, 1999.
- (25) Mustafa, S.; Tasleem, S.; Naeem, A. Surface charge properties of Fe<sub>2</sub>O<sub>3</sub> in aqueous and alcoholic mixed solvents. *J. Colloid Interface Sci.* **2004**, *275*, 523–529.
- (26) Namasivayam, C.; Yamuna, R. T. Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry. *Chemosphere* **1995**, *30*, 561–578.
- (27) Giles, C. H.; Smith, D.; Huitson, A. A general treatment and classification of the solute adsorption isotherms. I. Theoretical. *J. Colloid Interface Sci.* **1974**, *47*, 755–765.
- (28) IUPAC Recommendations. *Pure Appl. Chem.* **1985**, *57*, 603–619.
- (29) Gimeno, O.; Plucinski, P.; Kolaczowski, S. T.; Rivas, F. J.; Alvarez, P. M. Removal of the herbicide MCPA by commercial activated carbons: equilibrium, kinetics, and reversibility. *Ind. Eng. Chem. Res.* **2003**, *42*, 1076–1086.
- (30) Clausen, L.; Fabricious, I. Atrazine, isoproturon, mecoprop, 2,4-D, and bentazone adsorption onto iron oxides. *J. Environ. Qual.* **2001**, *3*, 858–869.
- (31) Cho, S. Y.; Park, S. S.; Kim, S. J.; Kim, T. Y. Adsorption and desorption characteristics of 2-methyl-4-chlorophenoxyacetic acid onto activated carbon. *Korean J. Chem. Eng.* **2006**, *23*, 638–644.
- (32) Inacio, J.; Taviot-Gueho, C.; Forano, C.; Besse, J. P. Adsorption of MCPA pesticide by MgAl-layered double hydroxides. *Appl. Clay Sci.* **2001**, *18*, 255–264.
- (33) Thorstensen, C. W.; Lode, O.; Eklo, O. M.; Christiansen, A. Sorption of bentazone, dichlorprop, MCPA, and propiconazole in reference soil from Norway. *J. Environ. Qual.* **2001**, *30*, 2046–2052.
- (34) Socias-Viciana, M.; Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E.; Flores-Cespedes, F. Sorption and leaching of atrazine and MCPA in natural and peat-amended calcareous soil from Spain. *J. Agric. Food Chem.* **1999**, *47*, 1236–1241.
- (35) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley-Interscience: Hoboken, NJ, 2003.

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