



Decontamination of waters polluted with simazine by sorption on mesoporous metal oxides

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ABSTRACT

Two mesoporous metal oxides, Al₂O₃ and Fe₂O₃, were evaluated as regards their ability to remove simazine, a highly persistent herbicide of s-triazines, using a batch equilibrium method. The effect of several experimental parameters such as pH, contact time, initial concentration and sorbent dosage on the sorption of the herbicide was investigated. The maximum sorption of simazine on Al₂O₃ and Fe₂O₃ was observed at pH 6.5 and 3.5, respectively. The different sorption capacities of the two oxides were explained considering a set of factors affecting the sorption process such as the surface area and the porosity.

The kinetics of sorption on both oxides was described using a pseudo second-order model. The sorption of simazine on Fe₂O₃ was faster in comparison to that observed on Al₂O₃.

It was shown that aluminum oxide can be regenerated by incineration, and consequently can be considered for industrial treatment systems designed to mitigate the pesticide pollution in the aquatic environments.

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1. Introduction

Water pollution by pesticides has been recognized in agricultural areas of the world for many years, and considerable evidences suggest that many water resources are contaminated by organic pesticides. Common agricultural practices, accidental spillage or uncontrolled release of contaminated waters due to washing of pesticide containers or industrial effluents in the environment have resulted in the contamination of air, soils, surface and ground waters, as well as of living organisms. Thus, in order to protect the environment and the human health, it is important to develop new remediation technologies.

Currently, sorption is believed to be a simple and effective technique for water and wastewater treatment and its success largely depends on the development of efficient sorbents. Activated carbon [1], clay minerals [2], biomaterials [3], zeolites [4], and some industrial solid wastes [5] have been widely used with varying efficiency. In a wastewater treatment process that utilizes sorption,

the regeneration of the sorbent is crucially important. However, the high costs associated with the regeneration of the sorbents or the necessity of an extraction achieved by acid or alkali solutions represent a serious problem.

New sorbents are required to remove organic pollutants in water decontamination processes. An ideal sorbent should have high surface area (i.e. high density of sorption sites), uniformly accessible pores and physical and/or chemical stability [6]. It is believed that the sorption capacity of a sorbent is largely determined by its surface area, which usually increases with decreasing the particle size, although the pore size distribution is also decisive for an optimal sorption process. Therefore, thanks to the introduction of nano-structured oxide materials, the pollutant removal efficiency can be increased dramatically.

Mesoporous materials, a class of nanoporous materials, have attracted a lot of attention in both the scientific and the industrial communities since the introduction of well-ordered mesoporous silicas which possess large surface areas and uniform and tunable pore sizes (2–50 nm) [7,8]. The great interest of these materials as adsorbents for environmental remediation is due not only to their high surface area but also to their fast contaminant sorption kinetics. Recent works [9–11] have shown that mesoporous materials can have large adsorption capacity, good selectivity and improved recoverability for the removal of toxic compounds from aqueous solutions.

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The encouraging results obtained from these studies prompted us to investigate the sorption of simazine (2-chloro-4,6-bis(ethylamino)-s-triazine), a basic herbicide belonging to s-triazine family, on the mesoporous metal oxides. The s-triazines are selective persistent herbicides, widely investigated due to their still large application in forestry and pre- and post-emergence in agricultural soils [12]. Even though these herbicides are now forbidden in some countries, the recalcitrance of s-triazines against chemical and biological degradation has led to their accumulation in the environment [12]. In Italy, the annex number 5 included in the Legislative Declaration 152/2006 on the environment, states the safe limit of atrazine (s-triazine herbicide) in soil that varies from 0.01 to 1.0 mg kg⁻¹, whereas the limit in waters is 0.3 µg L⁻¹. Simazine is a synthetic s-triazine herbicide used for pre-emergence control of broad-leaf weeds and annual grasses in agricultural and non-crop fields [13,14]. It is the second most commonly detected pesticide in surface and groundwater in the United States, Australia and Europe [15]. Due to the carcinogenic potential of s-triazines, simazine presence in water is of increasing concern [16].

A significant research on the removal of s-triazines by sorption on soils and different organic and inorganic sorbents has been performed [17,18]. Nevertheless, as far as we know, no papers have been published on the sorption capacity of mesoporous oxides towards triazine.

Therefore, the objective of this work was to evaluate two commercial metal oxides with mesoporous structure (Al₂O₃ and Fe₂O₃) as regards their ability to remove simazine from aqueous solutions. In view of future applications, the regeneration of these materials is also discussed.

2. Materials and methods

2.1. Materials

2-Chloro-4,6-bis(ethylamino)-1,3,5-triazine (simazine) (Fig. S1 of Supporting Information) was purchased from Sigma–Aldrich Chemical Company (Poole, Dorset, UK; 99.0% purity). All solvents were of HPLC grade (Carlo Erba, Milan, Italy) and were used without further purification. The water used in the preparation of all solutions was obtained from a Millipore Waters Milli-Q water purification system. All other chemicals were obtained from Sigma–Aldrich unless otherwise specified.

γ-Aluminum (Al₂O₃) and iron(III) (Fe₂O₃) oxides were purchased from IoliTec Nanomaterials (Denzlingen, Germany; 99.9 and 99.5% purity for Al₂O₃ and Fe₂O₃, respectively).

2.2. Chemical and physical analysis of Al₂O₃ and Fe₂O₃

The determination of point of zero charge (pzc) of Al₂O₃ and Fe₂O₃ was performed according to the methods described by Addorisio et al. [11].

The specific surface area (SSA) of Al₂O₃ and Fe₂O₃ was calculated by the Brunauer–Emmett–Teller (BET) method [19]. N₂ 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 N₂ flow. Pore volumes were determined from the amounts of adsorbed N₂ at P/P^o = 0.98 (desorption curve), assuming the presence of liquid N₂ (density = 0.807 g cm⁻³) in the pores under these conditions. The average values of the 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 [19] was used to calculate the pore size distribution of the sample using the desorption data.

2.3. Sorption experiments

A stock solution of herbicide was prepared by dissolving 2 mg of simazine in 500 mL of KCl 0.03 M (final concentration 20 µmol L⁻¹). This solution was then kept refrigerated. All sorption experiments were carried out by adding 10 mg of sorbent to 20 mL of simazine solution in glass vials with Teflon caps at a temperature of 20 °C. The samples, after incubation for 24 h in a rotatory shaker (35 rpm), were centrifuged at 7000 rpm for 20 min. The supernatant was analyzed to evaluate the herbicide concentration using high pressure liquid chromatography (HPLC) technique as described below. The amount of simazine sorbed on the oxides was calculated as the difference between the initial quantity of herbicide added and that present at the equilibrium. Blanks of simazine in KCl 0.03 M were analyzed in order to check the pesticide stability and the sorption to vials.

Several experiments were carried out to study the effect of different factors affecting the sorption of simazine on Al₂O₃ and Fe₂O₃, as summarized below:

- Effect of pH:* Experiments were carried out by adding pesticide solutions at fixed concentration (10 µmol L⁻¹) and different pH values from 3.0 to 7.0. The pH was controlled by the addition of a 0.10 or 0.01 mmol L⁻¹ solution of HCl or KOH. The samples were shaken for 24 h and subsequently, after centrifugation, analyzed as described below.
- Effect of sorbent amount:* The experiments were carried out by adding pesticide solutions at two concentrations (5 and 10 µmol 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 Al₂O₃ or Fe₂O₃ to a final volume of 20 mL, at 20 °C. The samples were incubated at pH values of 6.5 (tests with Al₂O₃) and 3.5 (tests with Fe₂O₃), for 24 h.
- Effect of incubation time:* Kinetic studies were performed using 10 µmol L⁻¹ solutions of simazine at pH 6.5 (tests with Al₂O₃) and pH 3.5 (tests with Fe₂O₃). The solutions were stirred for 2.0, 5.0, 20, 40, 60, 90, 120, 320, 960 and 1800 min.
- Sorption isotherm:* Different volumes of a stock solution of herbicide (20 µmol L⁻¹) were added to each oxide to give an initial simazine concentration ranging from 0.50 to 10.69 µmol L⁻¹. The pH of each solution was kept constant at pH 6.5 (tests with Al₂O₃) and 3.5 (tests with Fe₂O₃), by the addition of 0.10 or 0.01 mmol L⁻¹ solutions of HCl or KOH. The samples were incubated for 20 min (tests with Al₂O₃) and 180 min (tests with Fe₂O₃); then, after centrifugation, the supernatants were analyzed as described below.

2.4. Analytical determination

Simazine was analyzed with an Agilent 1200 Series HPLC apparatus (Wilmington, U.S.A.), equipped with a DAD array and a ChemStation Agilent Software. The procedure of analysis is described in detail in Supporting Information.

2.5. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis

The procedure of sample preparation for DRIFTS determinations is reported in detail in Supporting Information.

2.6. Scanning Electron Microscopy (SEM) analysis

The SEM analysis of Al₂O₃ samples at pH 4.0 and 6.5 was carried out by a FEI Quanta 200 ESEM.

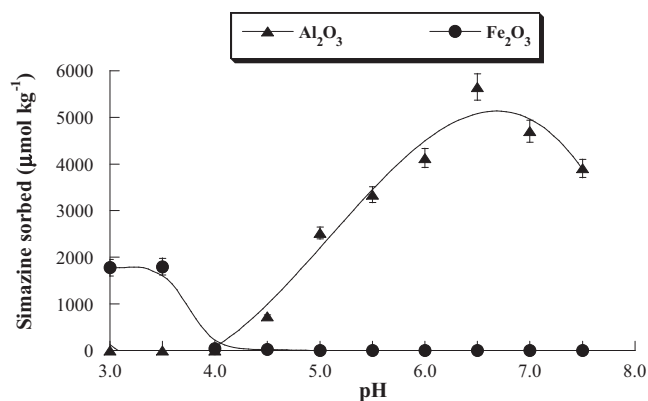


Fig. 1. Effect of pH on the sorption of simazine by Al₂O₃ and Fe₂O₃ at solid/liquid ratio of 0.5.

2.7. Analysis of the data

All the experiments were performed in triplicate and the relative standard deviation was in all cases lower than 3%.

3. Results and discussion

3.1. Effect of pH

In order to evaluate the optimum pH to be used in the subsequent experiments, sorption tests were carried out to study the effect of pH at a 0.5 solid/liquid ratio, preliminarily found as the optimal value for sorption. The results reported in Fig. 1 show that the greatest sorbed amount of simazine was observed at pH 6.5 when using Al₂O₃, and at pH 3.5 in the tests with Fe₂O₃.

In aqueous solution, triazines such as simazine exist in either neutral or protonated form, depending on the pK_a of the compound (the pK_a of simazine is 1.70) and on the pH of the system. The ring nitrogen atom, located in the 3-position between the electron-rich alkyl-side chains, is the most basic and hence the most likely site of protonation. At low pH values (e.g. 3.0–3.5) the surfaces of Fe-oxide and of soluble species are strongly protonated [20], so that the most basic triazinic nitrogen (N-3) could easily form coordination bonds with Fe₂O₃ deriving from the overlap of nitrogen lone pair electrons and partially filled metal d-orbitals on iron, being this latter a transition metal (d-block element).

The adsorption of simazine onto Al₂O₃ as a function of pH is quite different. A possible explanation of our findings is that the key role in the sorption of the herbicide is played by the aggregation state of the oxide, which is greatly influenced by the pH of the medium. In particular, as reported in Fig. 2, large aggregates and small particles were observed at pH 4.0 and pH 6.5, respectively. Consequently, the textural properties of Al₂O₃ are expected to be modified by the pH. To support the latter hypothesis, a physical analysis on Al₂O₃ sample at pH 4.0 and pH 6.5 was performed through the analysis of the relative N₂ adsorption–desorption isotherms.

As shown in Table 1, the surface area of Al₂O₃ sample at pH 4.0 (157 m² g⁻¹) results comparable to that at pH 6.5 (150 m² g⁻¹).

Table 1
Physical properties of Al₂O₃ at pH 4.0 and pH 6.5.

Sample	A _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average d _p (nm)
Al ₂ O ₃ (pH 4.0)	157	0.352	8.9
Al ₂ O ₃ (pH 6.5)	150	0.643	17.3

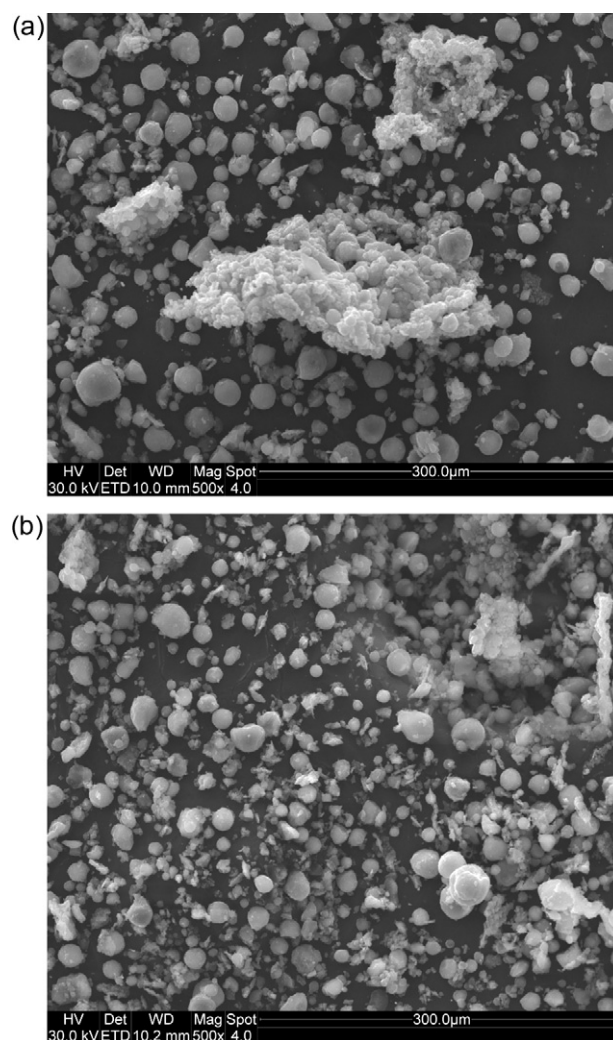


Fig. 2. SEM image of Al₂O₃ at 500× magnification at pH 4.0 (a) and at pH 6.5 (b), respectively.

However, more interesting indications can be obtained from a comparison between the pore size distributions (Table 1), obtained by the elaboration of the desorption data by the BJH method. Clearly, the contact with solutions at different pH strongly affects the intrinsic organization of Al₂O₃ particles, generating a porosity made of smaller cavities in the case of Al₂O₃ sample at pH 4.0. Moreover, the pore volume of the samples at pH 6.5 is much greater than that observed at pH 4.0 (Table 1). These observations are confirmed by the SEM analysis (Fig. 2).

Finally, at pH 6.5, the herbicide could give an acid–base reaction with Al₂O₃, that at this pH is present as Al[(H₂O)₆]³⁺. Alternatively, being simazine more nucleophilic than water molecules, it can replace some water molecules in the hexacoordinate complex.

Chappell et al. [21] showed the interaction of atrazine with smectite surfaces through hydrogen bonding, and at the same time demonstrated that alkyl tails of the herbicide may interact with hydrophobic nanosites on the smectite basal surfaces.

Other studies demonstrated that noncovalent binding forces, cation–π, may occur between s-triazine and metallic cation [22]. In the literature, the information about the binding mechanism of triazine herbicides on the oxides is very scarce. Consequently, the explanation of the observed behaviour reported above deserves a close attention.

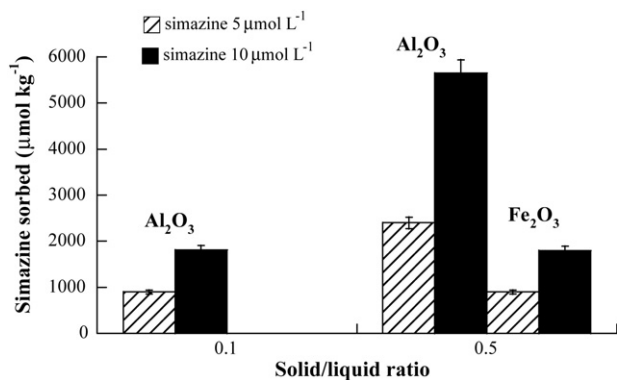


Fig. 3. Effect of solid/liquid ratio on the sorption of two different concentrations of simazine by Al_2O_3 and Fe_2O_3 at pH 3.5 and 6.5, respectively.

3.2. Effect of solid/liquid ratio

Sorption studies of simazine were carried out using Al_2O_3 (at pH 6.5) and Fe_2O_3 (at pH 3.5), varying the amount of sorbent and adding two different concentrations of herbicide. The results reported in Fig. 3 show, for both the oxides and regardless of the herbicide concentration, a higher sorption at solid/liquid ratio 0.5. In particular, the amount of sorbed herbicide on Al_2O_3 was already significant at the lowest solid/liquid ratio (0.1) and was greatly increased by increasing the amount of oxide. However, in the presence of 20 and 40 mg of oxide, no sorption of simazine was observed. Evidently, the greater the amount of oxide, the greater the resistance to the diffusion in the mesoporous structure, which results in a lower sorption of the herbicide.

3.3. Effect of incubation time

The kinetic data were analyzed adopting a pseudo first-order kinetic equation [23]:

$$\frac{dq}{dt} = k_1 \cdot (q_e - q) \quad (\text{E1})$$

where q_e and q are the amounts of herbicide sorbed ($\mu\text{mol kg}^{-1}$) at equilibrium and at time t , respectively, k_1 is the rate constant of sorption (min^{-1}) and t is the time (min). Integrating with the boundary condition $q|_{t=0} = 0$ Eq. (E1), the following expression is obtained:

$$\log(q_e - q) = \log q_e - \frac{K_d t}{2.303} \quad (\text{E2})$$

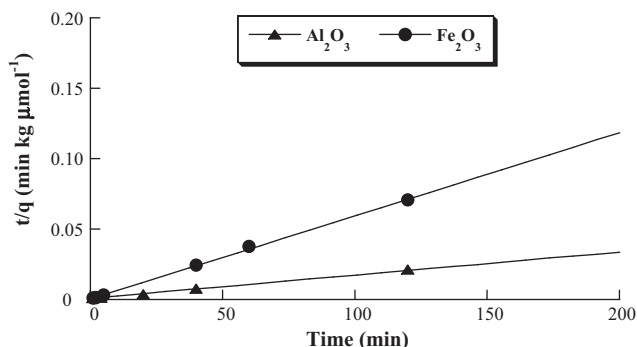


Fig. 4. Effect of time on the sorption of simazine by Al_2O_3 and Fe_2O_3 .

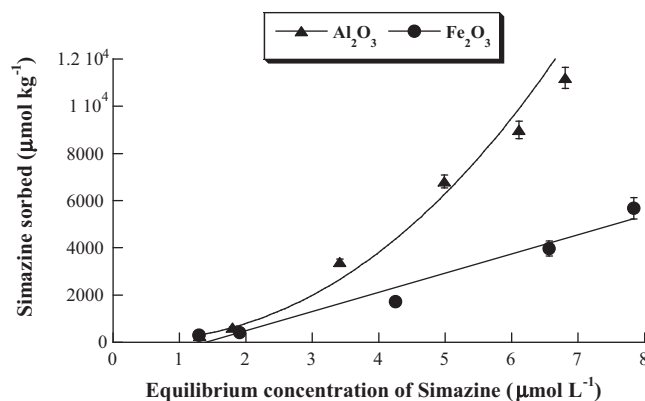


Fig. 5. Sorption isotherm of simazine by Al_2O_3 and Fe_2O_3 .

Alternatively, the sorption kinetic curves were analyzed adopting the pseudo second-order kinetic model:

$$\frac{dq}{dt} = k_2 \cdot (q_e - q)^2 \quad (\text{E3})$$

where k_2 is the rate constant of sorption ($\text{kg } \mu\text{mol}^{-1} \text{ min}^{-1}$). Upon integration with the boundary condition $q|_{t=0} = 0$, Eq. (E3) yields the following expression:

$$\frac{t}{q} = \frac{1}{k_2 \cdot q_e^2} - \frac{t}{q_e} \quad (\text{E4})$$

The best model to describe the sorption kinetics data was the pseudo second-order model (i.e. Eq. (E3)), as shown by the linear behaviour of the (t/q) versus time plot (Fig. 4).

The corresponding model parameters (q_e and k_2) were estimated with reference to the simazine sorption on Al_2O_3 ($q_e = 6098 \mu\text{mol kg}^{-1}$, $k_2 = 2.85 \times 10^{-5} \text{ kg } \mu\text{mol}^{-1} \text{ min}^{-1}$, $r^2 = 0.99$), and on Fe_2O_3 ($q_e = 1695 \mu\text{mol kg}^{-1}$, $k_2 = 9.03 \times 10^{-4} \text{ kg } \mu\text{mol}^{-1} \text{ min}^{-1}$, $r^2 = 0.99$). The sorption on Fe_2O_3 , reaching the equilibrium after 5 min, was faster in comparison to that pertaining Al_2O_3 , showing an equilibrium time of 120 min. Therefore, all the equilibrium determinations were carried out adopting an incubation period of 20 min for Fe_2O_3 and 180 min for Al_2O_3 .

3.4. Sorption isotherm

The sorption isotherms of simazine on Al_2O_3 and Fe_2O_3 are displayed in Fig. 5. The obtained data were analyzed according to the Freundlich equation:

$$x = Kc^{1/N} \quad (\text{E5})$$

where x is the amount of pesticide sorbed ($\mu\text{mol kg}^{-1}$), c is the equilibrium concentration of pesticide ($\mu\text{mol L}^{-1}$), 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. [24].

The sorption isotherms of simazine on Al_2O_3 and Fe_2O_3 , shown in Fig. 5, were well-fitted by the linearized form of Freundlich equation ($r^2 > 0.99$) (Table 2). According to the classification of Giles et al.

Table 2
Freundlich parameters for the sorption of simazine on Al_2O_3 and Fe_2O_3 .

	Freundlich parameters		
	K ($\mu\text{mol kg}^{-1})/(\mu\text{mol L}^{-1})^{1/N}$	N (dimensionless)	r^2 ^a
Al_2O_3	168.11	0.44	0.99
Fe_2O_3	156	0.56	0.99

^a Correlation coefficient.

Table 3
Comparison of surface area, pore volume and average pore diameter of Al₂O₃ and Fe₂O₃ samples.

Sample	A _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average d _p (nm)
Al ₂ O ₃	195	0.723	14.8
Al ₂ O ₃ 500	200	0.770	14.7
Fe ₂ O ₃	106	0.239	9.2
Fe ₂ O ₃ 500	33	0.0650	7.9

[24], the experimental sorption isotherms were of S-type for Al₂O₃ and C-type for Fe₂O₃.

In particular, at low equilibrium concentrations the sorbed amount of simazine on Fe₂O₃ was similar to that detected on Al₂O₃, whereas at concentrations greater than 3 μmol L⁻¹ there was a marked difference in the behaviour of the two mesoporous oxides. As a matter of facts, at a 6.0 μmol L⁻¹ equilibrium concentration of simazine, the amount of herbicide sorbed on Fe₂O₃ was 4000 μmol kg⁻¹, whereas that sorbed on Al₂O₃ was ~8000 μmol kg⁻¹.

The S-type isotherm of simazine on Al₂O₃ indicates that the presence of molecules of herbicide already sorbed on the surface favours the sorption process by a cooperative effect. This effect can be explained assuming that the molecules already sorbed modify the affinity of the sorption sites towards the molecules present in solution.

On the contrary, the C-type isotherm of simazine on Fe₂O₃ was characterized by a straight line trend, indicative of a constant partition of the herbicide between solution and sorbent until reaching saturation.

The Freundlich constants (*K* and *N*) (Table 2) showed that Al₂O₃ sorbed the herbicide with a higher sorptive capacity and a lower affinity in comparison to Fe₂O₃.

The presence of secondary small pores at the boundary of micropores region in Al₂O₃ may affect positively the sorption of small organic molecules such as simazine (0.784 nm), as it is possible that the sorption energy increases in those pores whose dimensions approach the herbicide dimensions (0.7–0.9 nm). In fact, as reported in Fig. S2 of Supporting Information, the pore size distribution of Al₂O₃ appears to be bimodal, characterized by two maxima at about 3 nm and at about 15 nm. On the contrary, Fe₂O₃ shows a unimodal distribution and most of the N₂ volume is adsorbed in the pore size range 6–10 nm [11].

A combination of factors such as the surface area and the porosity concurs significantly to influence the highest sorption capacity of Al₂O₃ than Fe₂O₃ (see Table 3).

Finally, DRIFT analyses were carried out on each metal oxide after the sorption of the herbicide. The DRIFT spectra of Al₂O₃- and Fe₂O₃-simazine complexes were recorded and compared with those of simazine and untreated oxides (Fig. S3 of Supporting Information). In particular, in Fig. S3a, the characteristic sorption bands of simazine corresponding to NH stretching (3260 cm⁻¹) and C=N stretching (1637, 1565 and 1406 cm⁻¹) were observed [27].

Fig. S3b and c shows that, after the sorption of the herbicide, the sorption band at 3440 cm⁻¹, corresponding to –OH stretching of each oxide, was reduced more or less strongly due to a possible coordination interactions simazine–Fe₂O₃ and acid–base reactions or replacement of the herbicide with water molecules in the acid hexacoordinate complex [Al(H₂O)₆]³⁺, respectively.

In a sorption–desorption study of atrazine and simazine by model soil colloidal components, Celis et al. [25] demonstrated that ferrihydrite does not adsorb triazine herbicides. Enhanced sorption of these herbicides on montmorillonite was measured after increasing the surface acidity of the clay. On the contrary, a carbon-rich product (biochar) generated from biomass through pyrolysis sorbed an amount of simazine of ~2480 μmol kg⁻¹ [26].

3.5. Regeneration of Al₂O₃ and Fe₂O₃

In a wastewater treatment involving a sorption process, the regeneration of the sorbent is crucially important. Nowadays, in many applications, the reuse of the sorbent through regeneration of its sorption properties is an economic necessity. Desorption agents (e.g. sodium hydroxide solution) are commonly used to recover sorbents such as Fe- and Al-based supports [28]. However, the utilization of a desorption agent has some disadvantages because it increases the operating cost, and the waste solution containing NaOH discarded from the regeneration of the sorbent causes environmental pollution.

The incineration method could be considered as an alternative way for the regeneration of the sorbents, as it avoids the use of hazardous desorption agents. To assess the feasibility of this option, Al₂O₃ and Fe₂O₃ were annealed at 500 °C for 1 h; subsequently, to ascertain whether the textural properties were retained, a physical characterization on heat treated oxides was performed through the analysis of the relative N₂ adsorption–desorption isotherms.

The porosities of Al₂O₃ and Fe₂O₃ have been previously analyzed by the authors [11]; herein we report a comparison with the physical properties of the heat treated samples.

The notation used for the samples is referred to the chemical formula followed by a number indicating the temperature of the heat treatment, i.e. Al₂O₃500 and Fe₂O₃500; the samples before the heat treatment are simply denoted with the chemical formula, as in the text.

The perfect correspondence between the isotherms obtained with Al₂O₃500 and Al₂O₃ [11], indicated that the mesoporous structure was not damaged by the annealing. The adsorption isotherms were elaborated using the BET method, to obtain the corresponding surface areas reported in Table 3 together with the total pore volume and the estimated average pore diameter. As clearly shown by the data in Table 3, all the textural properties of Al₂O₃ are well preserved after the heat treatment. These results drive us to consider the incineration method as an effective option for the regeneration of aluminum oxide.

On the contrary, the thermal stability of Fe₂O₃ was not comparable to that of Al₂O₃ as regards the pore structure. As a matter of facts, the heat treatment strongly altered the textural properties of the sample and a drastic collapse of the surface area was observed (Table 3). To observe to which extent the pore size distribution of iron oxide was modified by the annealing procedure, the desorption data were elaborated by the BJH method. The comparison between the pore size distributions of Fe₂O₃ and Fe₂O₃500 samples (Fig. S4 of Supporting Information) indicates beyond doubt that the mesoporous structure was completely destroyed by the heat treatment at 500 °C, making the iron oxide not recoverable by incineration.

4. Conclusions

In this study, two metal oxides with mesoporous structure, Al₂O₃ and Fe₂O₃, showed different capacities to adsorb simazine, a highly persistent herbicide. In particular, the optimum pH for sorption was found to be 6.5 for Al₂O₃ and 3.5 for Fe₂O₃. The different sorption capacities of the two oxides were explained by considering a set of factors significantly concurring to influence the sorption process, such as the surface area and the porosity.

The kinetics of sorption was described by a pseudo second-order model, demonstrating that Fe₂O₃ adsorbs simazine faster than Al₂O₃. Finally, we demonstrated that Al₂O₃ can be regenerated by incineration and could be considered for industrial treatment systems, to remove effectively simazine from the aquatic environments and eventually to mitigate the pesticide pollution.

Supplementary data

The chemical formula of simazine and its analytical determination, the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) analysis, the pore size distribution of Al_2O_3 and Fe_2O_3 , and the pore size distribution of Fe_2O_3 at 500 °C are reported.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.022.

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