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2 **Organo-clays and nanosponges for acquifer bioremediation: adsorption and**
3 **degradation of triclopyr.**

4
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16
17 **ABSTRACT**

18
19 To avoid the problem of groundwater contamination, mitigation techniques have been proposed
20 that consist in creating barriers made of suitable materials that can facilitate the adsorption and
21 degradation of the pollutants.

22 The work aims at evaluating the capacity of two organo-clays (Dellite 67 G and Dellite 43 B)
23 and one nanosponge to adsorb the herbicide, triclopyr. Triclopyr was chosen because it is a good
24 example of a moderately mobile, leacheable molecule. The rate of degradation of the molecule in
25 the soil, both with and without the presence of the materials under examination, was also
26 determined.

1 Both the organo-clays adsorbed more than 90% of the herbicide. The nanosponge and the soil
2 adsorbed less than 10% triclopyr. When the soil was added with the two organoclays, adsorption
3 increased to 92%.

4 When added to the soil, the materials accelerated the degradation of triclopyr. The half life in
5 soil was 30 days, whereas in soil with Dellite 67G and Dellite 43B it was 10 and 6 days
6 respectively. The addition of the nanosponge to the soil decreased the half life by 50 %.

7 These results lead us to suggest that they be used in creating reactive barriers for the
8 remediation of soils and aquifers.

9

10 **Keywords:** Triclopyr, organoclays, nanosponges, reactive barriers

11

12 INTRODUCTION

13

14 Considerable importance is now being given to resolving the environmental problems
15 associated with the presence of pesticides in the soil and groundwater.

16 Many compounds are not retained by soil colloids and there is a tendency for infiltrating water
17 to carry them into groundwater. Moreover, the low rate of degradation of the pesticides increases
18 the possibility of water becoming contaminated. ^[1]

19 In order to avoid this problem, mitigation techniques have been proposed that consist in creating
20 barriers made of suitable materials that can favour the adsorption and degradation of pollutants.
21 Reactive barriers are a semi-permeable system placed along the flow path of infiltrating water. As
22 the water passes through the barrier, the pollutant is adsorbed and degraded releasing only a small
23 quantity of non-toxic compounds.

24 Barriers made from a mix of soil and phyllosilicates, such as bentonite, are widely used to limit
25 the migration of mobile pollutants. All kinds of soil can be used and the quantity of bentonite can
26 vary from 6% to 15%. ^[2]

1 Recent studies have suggested that organo-clays have a high water-decontamination potential
2 because they can absorb considerable quantities of organic compounds, both apolar^[3-4] and polar.
3^[5-7] An evaluation on the effects of organoclays on the soil eubacterial community, showed that
4 these materials can both inhibit and stimulate soil microorganisms.^[8]

5 Rodriguez-Cruz et al.^[3] demonstrated the efficiency of intercalating barriers made from a mix
6 of organo-clay and soil in reducing the mobility of linuron, atrazine and metalaxyl by column (3
7 cm i.d. and 20 cm long) testing with 500 mL of water.

8 Witthuhn et al.^[9-10] showed that the association of organo-clays with some soil micro-organisms
9 made it possible to absorb and degrade 2,4-dichlorophenol and chlorobenzene.

10 Cyclodextrins are a class of cyclic oligosaccharides synthesized from starch by enzymatic
11 reaction. They have a characteristic toroidal shape which generates a frusto-conical internal cavity.
12 This cavity measures about 8 Å in depth and 5-9 Å in diameter, according to the number of
13 oligosaccharide rings. Cyclodextrins can include organic compounds inside these cavities. Inclusion
14 is based mainly on an interaction between the guest molecule and the cavity which is particularly
15 hydrophobic. This type of reaction between cyclodextrins and organic molecules can be used as the
16 basis for the adsorption or separation of a number of organic agents. Nevertheless, cyclodextrins
17 are soluble in water and in some organic solvents. Given their solubility in water, cyclodextrins
18 cannot therefore be used directly for retaining organic substances. To overcome these problems of
19 solubility, cyclodextrins have been used as basic building blocks in the preparation of cross-linked
20 insoluble polymers.^[11]

21 These cyclodextrin-based, highly cross-linked polymers are called nanosponges and have a 7-9
22 Å cavity and a lower surface area (1-2 m² / g) than activated carbon (600 m² /g), but their organic
23 molecule loading capacity is similar to that of activated carbon. This implies that the organic
24 molecules are not only adsorbed on the polymer surface but also included within the nanocavity.^[11]

25 Triclopyr is a frequently-used herbicide for post-emergence control of a wide range of annual
26 and perennial broadleaf weeds and woody plant species. It is an auxinic type herbicide that is

1 adsorbed by roots and leaves, is translocated through the plant and accumulates in the meristematic
2 tissues. The auxin-type response in plants is associated with triclopyr interfering with the normal
3 growth processes. ^[12]

4 Symptoms of short-term exposure to triclopyr include lethargy and tremors. Anorexia and
5 diarrhoea have also been observed in animals exposed to triclopyr. ^[13] In a long-term laboratory
6 feeding study, rats fed triclopyr developed kidney damage more often than unexposed rats. In a
7 long-term study using dogs, the animals which were fed triclopyr gained less weight, had less
8 hemoglobin and red blood cells and more microscopic liver damage than did unexposed dogs.
9 These symptoms were observed at doses of 25 mg/kg per day in the rat study and 20 mg/kg per day
10 in the dog study. ^[14]

11 Photolysis is the principal degradation pathway for triclopyr in aqueous solution. Woodburn et
12 al. ^[15] studied the photolysis of triclopyr in both buffered and natural waters under natural and
13 artificial sunlight. Triclopyr in buffered water (pH 7) had an average photolysis half-life of 0.5
14 days, while dissolving the compound in natural water resulted in a half-life of 1.3 days. No
15 degradation or loss of triclopyr was observed in the dark control samples.

16 Cleveland and Holbrook ^[16] studied the hydrolysis of triclopyr in buffered solutions with pH 5,
17 7 and 9. After 1 month, triclopyr constituted 97.2% of the activity remaining in the samples,
18 suggesting that simple hydrolysis is not an important degradation pathway for triclopyr in the
19 environment.

20 Most of the laboratory and field studies carried out indicate that, under most conditions,
21 triclopyr is a relatively mobile herbicide. Values of between 12 and 78 were found for the
22 repartition coefficient K_{oc} of triclopyr in a study performed on 12 soils with different organic
23 carbon content (between 0.081% and 21.7%), indicating that the herbicide is highly mobile under
24 these conditions. ^[17] Another laboratory study on a sandy-loam soil with a low organic matter
25 content (0.62%) observed that, after leaching through a 12 inch column, 75-80% of the triclopyr
26 was recovered 11-15 days after treatment. ^[17]

1 During a field study, a concentration of 3 litres/hectare of Garlon 3A[®] was applied to six plots
2 with different soil textures. Small quantities of triclopyr and its metabolites were found at depths of
3 15-30 cm and 30-45 cm, 28 and 56 days after application, respectively. ^[18]

4 A study performed in Louisiana on the adsorption of 2,4 D, glyphosate and triclopyr to three
5 soils, revealed a low retention of triclopyr (<13%). The adsorption of triclopyr was positively
6 related to the percentage of soil organic matter. The low adsorption of triclopyr to the three soils
7 studied, suggests that this compound has a high surface water contamination potential. ^[19]

8 An analysis of water samples collected from different agricultural and urban sites in the Lower
9 Fraser Valley region of British Columbia, demonstrated that triclopyr was present at varying levels.
10 ^[20]

11 In a study on the occurrence of various pesticides in vernal pools and adjacent streams in
12 different American states, Battaglin et al. ^[21] detected triclopyr at two sites. They suggested that the
13 compound originated from use within the park and was transported to the site by surface runoff or
14 shallow groundwater flow.

15 The aim of this work is to evaluate the capacity of different organo-clays and nanosponges to
16 adsorb triclopyr and also to determine the degradation rate of triclopyr in the soil, with and without
17 these materials.

18 Triclopyr was selected as the model for a mobile, leachable herbicide, which is minimally
19 adsorbed by the soil.

20

21 **MATERIALS AND METHODS**

22

23 **Chemicals**

24

1 The triclopyr (98% purity) was purchased from Sigma-Aldrich (Milan, Italy). All the other
2 chemicals used were analytical reagents or LC grade. The β -cyclodextrin (Kleptose) was a gift
3 from Roquette Freres, Lille, France.

4 The nanosponge was synthesized using a β -cyclodextrin which was left to react with
5 carbonyldiimidazole in dimethylformamide at 90°C for 5 hours. When the reaction was complete,
6 the solid was crushed in a mortar and then treated with ethanol in a Soxhlet extractor to remove the
7 by-products of the reaction. The resulting nanosponge was composed of β -cyclodextrin blocks
8 crosslinked with carbonate bonds. Nanosponges are insoluble in water and organic solvents and
9 have high thermal and chemical stability. Haemolytic and cytotoxic tests demonstrate the low
10 toxicity of the material. ^[22]

11 The Dellite 67 G and Dellite 43 B organo-clays were supplied by Laviosa Mineraria (Livorno,
12 Italy). Dellite 67G is a material deriving from a natural montmorillonite especially purified and
13 modified with a high level of quaternary ammonium salt (di-di (hydrogenated tallow) dimethyl
14 ammonium). Dellite 43B is an organo-clay deriving from a natural montmorillonite especially
15 purified and modified with a quaternary ammonium salt (tallow dimethyl benzyl ammonium).

16

17 **Soil**

18

19 The soil was sampled to a depth of 0.25 cm, dried to a 10% water content (w/w), sieved to
20 obtain a < 2 mm fraction and stored at room temperature in black PVC bags. The soil contained
21 6.2% clay and had an organic carbon content of 0.88%, its pH in water was 7.8 and its Water
22 Holding Capacity (WHC) was 49% (on dry weight).

23

24 **Adsorption and desorption studies**

25

1 Adsorption isotherms were obtained using the batch equilibration method. Duplicate 50 mg
2 samples of the organoclays and the nanosponge were weighed into 15 mL glass centrifuge tubes
3 (with Teflon-lined caps), which were filled with 5 mL 0.01 N CaCl₂ solution of triclopyr with
4 initial concentrations ranging from 10 to 35 µg mL⁻¹.

5 In addition, adsorption isotherms were determined on the soil (5 g) and on the soil (5 g) added
6 with organo-clays (0.1 g of Dellite 67G or Dellite 43B) and 25 ml of 0.01 N CaCl₂ solution of
7 triclopyr at different concentrations (0.5 to 5 µg mL⁻¹).

8 The suspensions were shaken mechanically at 30° ± 2°C for 16 hours. Previous kinetic studies
9 showed that 16 h were enough to reach adsorption equilibrium. After equilibration, the suspensions
10 were centrifuged at 3000 rpm for 30 min. Solutions shaken in tubes without adsorbent served as
11 control and showed no loss of triclopyr.

12 The amount of pesticide adsorbed was considered to be the difference between that initially
13 present in the solution and that remaining after equilibrium with the adsorbent.

14 The adsorption data were modelled using the Freundlich equation:

15
$$x/m = KfCe^{1/n}$$

16 where Kf and 1/n are Freundlich parameters, characteristic of the sorbate-adsorbent system, x/m is
17 the amount of triclopyr adsorbed and Ce is the triclopyr equilibrium concentration.

18 Desorption experiments were conducted immediately after adsorption from the highest point of
19 the adsorption isotherms by batch successive dilution method. Four mL of supernatant were
20 removed for the adsorption analysis and were then replaced with 4 mL of 0.01 N CaCl₂ solution.
21 After shaking at 30°C for 2 h, the suspensions were centrifuged and 4 mL supernatant removed for
22 analysis. The desorption cycle was repeated three times for the desorption isotherm.

23

24 **Degradation tests**

25

1 In order to evaluate the effect of the organo-clays and nanosponges on the persistence of
2 triclopyr in the soil, the degradation kinetics were measured. 40.0 mg of the materials under
3 examination were added to 20 g of dry soil and 1 mL of triclopyr in aqueous solution (100 µg mL⁻¹).
4 After thorough mixing, the correct quantity of distilled water was added to bring the soil
5 humidity level to 50% of the WHC.

6 The samples were then placed in a thermostated cell to incubate at 25° C for 56 days. During
7 the incubation period, the aerobic conditions of the samples was assured by the partial closure of the
8 screw-top on the container. At prefixed time intervals (0, 3, 7, 14, 28 and 56 days) the
9 concentration of triclopyr remaining was determined by means of liquid chromatography. The
10 active ingredient was extracted by adding 50 ml of ethyl acetate to the soil and shaking the mixture
11 for 30 minutes. After centrifugation (3000 rpm for 30 min) the supernatant was collected in a
12 vacuum flask. This operation was repeated twice using 25 ml of solvent and halving the shaking
13 times. The three extracts were combined, filtered through anhydrous sodium sulfate, dried in a
14 rotary evaporator and then hydrated with 10 ml of acetonitrile.

15

16 **Chromatography analyses**

17

18 The concentration of triclopyr was determined by means of liquid chromatography, using a
19 Shimadzu LC10 ADvp instrument, fitted with a UV/vis set at 230 nm and a Supelcosil-LC ABZ
20 column (15cm x 4.6cm x 5µm). The mobile phase was water acidified to pH 3 with phosphoric
21 acid (30%) and acetonitrile (70%).

22

23 **RESULTS AND DISCUSSION**

24

25 **Adsorption studies**

1 Before determining the adsorption isotherms, a single concentration of the active ingredient was
2 used to verify the extent of the interaction between triclopyr and the adsorbent. The results of this
3 preliminary test are shown in Fig. 1.

4 The herbicide appeared to have little affinity either with the soil or the nanosponge while it
5 interacted intensively with the two pure organo-clays and the soil-organo-clay mix.

6 Obenshain et al. ^[19] evaluated the adsorption of various pesticides including triclopyr on a soil
7 with a 3.4% organic carbon content. The authors found that only 1.2% of the herbicide was
8 adsorbed on the surface layer and 3.5% on the deeper layer. The same experiment showed that the
9 small quantity of the product adsorbed was totally released during the 24 hours following
10 adsorption. These results confirm the poor affinity of triclopyr with the solid soil phase, in
11 particular, with the large quantity of organic matter content in the tested soil.

12 The lack of interaction between the triclopyr and the nanosponge was unexpected, given that
13 cyclodextrin based nanosponges are known to have a high solubilizing power when forming
14 inclusion complexes with numerous active molecules, such as camptothecin ^[23], paclitaxel ^[24] and
15 1-methylcyclopropene ^[25] to name only a few. In this case, it is probable that the structure of the
16 triclopyr kept it from penetrating the crosslinked carbonate bonds to a significant extent.

17 A recent study by Singh et al. ^[26], presents the results of an experiment regarding the adsorption
18 and desorption of carbofuran on different soils, with and without β -cyclodextrin. In all the soils
19 studied, the adsorption capacity of carbofuran was lower when β -cyclodextrin was present than
20 when only water was present. According to the authors, this decrease could be due to the formation
21 of inclusion complexes between the β -cyclodextrin and the carbofuran, characterized by a higher
22 hydrosolubility than pure carbofuran. This condition leads to a reduced adsorption of the molecule
23 to the soil. Using a β -cyclodextrin solution there was a more pronounced desorption of carbofuran
24 than when it was treated with distilled water, indicating the formation of inclusion complexes that
25 reduced the number of molecules interacting with the soil colloid surfaces.

1 Even only small proportions of organoclays added to the soil appeared to be very efficient in
2 extracting triclopyr from water.

3 The poor adsorption of triclopyr to the soil and the nanosponge meant that it was not possible to
4 determine the relative isotherms.

5 As regards the pure organoclays, the adsorption isotherms are well-described by the Freundlich
6 equation ($r^2 = 0.98$ and 0.99 for the Dellite 67 G and 43 B respectively). In both cases, the $1/n$
7 coefficient was higher than 1 placing the isotherms as type S in the Giles et al. Classification. [27]
8 The K_f value was seen to be higher for the Dellite 43 B than for the Dellite 67 G, indicating that the
9 former has a greater aptitude to retain the active ingredient (Figs. 2 and 3).

10 During the first phase, desorption from the surface was about 15%, reducing thereafter. In the
11 case of the Dellite 43 B a larger quantity of the herbicide was desorbed than with the Dellite 67 G.
12 It is possible that the organic cation in the latter creates more stable interactions with the molecule.

13 The $1/n$ coefficient was also higher than 1 for the soil-organoclay mix. As regards the soil-
14 Dellite 67 G mix, the value was calculated at 2.56; this indicates a great increase in adsorption as
15 the concentration of the herbicide increases. This behaviour determined a high level of K_f , which
16 indicates the entity of adsorption when the pesticide concentration is equal to 1.

17 The $1/n$ value of the soil-Dellite 43 B mix was 1.81 and indicates the same behaviour as
18 observed for the other organoclay but with a different response to increased concentrations. The K_f
19 value is, in fact, lower (Figs. 4 and 5).

20 Triclopyr was released in small quantities by the two mixtures.

21

22 **Degradation kinetics**

23

24 The degradation kinetics were all first order kinetics ($r^2 > 0.94$). In the soil, the active ingredient
25 had a half-life time of 30 days while in the soil mixed with Dellite 67 G and 43 B half-life times of
26 10 and 6 days respectively were found (Fig. 6).

1 The literature reports relative values of half-life times for triclopyr as varying from 8 to 69 days
2 according to the type of soil. Under anaerobic conditions the rate of degradation appears very low
3 (half-life = 1300 days). This data indicates that the aerobic microbial population affects the
4 degradation process. Biodegradation is the main path for the dissipation of triclopyr in the soil.
5 Under aerobic conditions, the main metabolite is 3,5,6-trichloropyridinol (TCP), which undergoes a
6 further transformation in carbon dioxide, water and organic acids. TCP is more stable than triclopyr.
7 [28]

8 The increase in the rate of degradation obtained in the presence of the two organo-clays could be
9 ascribed to a catalytic reaction by the inorganic fraction with which the triclopyr has interacted.
10 The catalytic activity of clay minerals in the degradation of pesticides is well documented.

11 Yaron et al. [29] studied the interaction of different phosphorated pesticides and three mineral
12 clays (montmorillonite, kaolinite and attapulgite). The pesticides adsorbed by the clay degraded by
13 means of hydrolysis to become nitrophenol and phosphate ions. The rate of hydrolysis was
14 influenced by the type of clay, the type of exchangeable cation and the state of hydration. Kaolinite
15 was the most efficient, determining a 93% decrease in parathion in 40 days.

16 An experiment on the chemical hydrolysis of atrazine showed the formation of formamide near
17 the surface of a Na-montmorillonite. Infrared analyses showed that the formamide, which formed
18 as a consequence of the interaction between the herbicide and the Na-montmorillonite, was
19 collocated in the crystal interspace. [30]

20 Nevertheless, the degradation process can also have been influenced by the organic cation in the
21 organo-clay.

22 Groisman et al. [31] proposed using bifunctional organoclays as adsorbents and as detoxifying
23 agents for pesticides. Their experiment involved a Na-montmorillonite intercalated with
24 decyldimethyl-2-aminoethyl ammonium and the pesticides used were methyl parathion and
25 tetrachlovinphos. The aminoethyl functional group exercised a detoxifying effect by catalyzing the
26 hydrolysis of the adsorbed compounds. When bifunctional organoclays were present, the products

1 under examination hydrolyzed at a rate 12 times higher than when there was a spontaneous reaction.
2 It was hypothesized that the catalytic effect can be attributed to a nucleophilic attack on the
3 organophosphate ester by the unprotonated ethylamino group in the organic cation.

4 In a later work, Rav-Acha et al. ^[32] demonstrated that the methyl parathion was degraded on the
5 surface of a clay modified with a bifunctional organic cation containing an alkylamino group. They
6 identified three possible catalytic paths: a) a nucleophilic attack on the centre of reaction of the
7 phosphate ester by the organic cation amino group; b) a similar mechanism mediated by water
8 molecules; c) a methylation of the amino group followed by a catalytic attack on the
9 organophosphorous compound.

10 Studies are available in the literature demonstrating that the desorption of pollutants is not a pre-
11 requisite for degradation and that the phase adsorbed by the substrate can be degraded. Park et al.
12 ^[33] developed an experimental mathematical approach to evaluate whether desorption and
13 degradation are strictly sequential or independent processes. In their experiment, adsorption was
14 effected using 2,4 -D and sepiolite, while *Flavobacterium* sp. was the degrading microorganism. It
15 was shown that the degradation of 2,4-D was not a sequential process that depended exclusively on
16 the concentration in the liquid phase. In fact, in all the experiments, degradation occurred more
17 quickly than would be expected considering a single concentration in liquid phase.

18 A work by Sigh et al. ^[34] shows that fenamiphos adsorbed by an organo-clay can be degraded by
19 *Brevibacterium* sp in quantities 77% higher than can be desorbed under abiotic conditions.

20 Neither is it possible to eliminate the hypothesis that the development of soil bacteria
21 populations can stimulate an acceleration in degradation. An experiment carried out to verify the
22 effect of Dellite 67 G and 43 B on soil microorganisms showed that some microbial populations in
23 the soil increase when the two organoclays are present. This information was obtained by analyzing
24 DNA extracted from a soil with and without the materials under examination. The results, that do
25 not form part of this paper, have not yet been published.

1 This hypothesis may also be supported by the knowledge that soil micro-organisms play an
2 important role in the degradation of triclopyr. Newton et al. ^[35] maintain that hot, humid climate
3 conditions and high levels of organic matter factors that favour the development of soil micro-
4 organisms, generally determine an increase in the rate at which the pesticide disappears.

5 This hypothesis must be confirmed by further experimentation including a molecular analysis of
6 microbial populations treated with the materials under examination.

7 The rate of degradation of the active ingredient also increased when nanosponges were present
8 (half-life = 15 days) (Fig. 6). There is no proof that nanosponges can catalyse degradation
9 phenomena but information is available in the literature regarding the capacity of cyclodextrins to
10 favour the degradation process of organic compounds.

11 Fava and Ciccotosto ^[36] studied the biodegradation of polychlorinated biphenyls (PCBs) in the
12 soil in the presence of methylated – β – cyclodextrins (RAMEB). They found that the presence of
13 RAMEB led to an increase in the biodegradation of the PCBs because water-soluble inclusion
14 complexes formed which supported the co-metabolic processes of the microorganisms in the soil.
15 Similar results were obtained by Wang et al. ^[37] who evaluated the efficiency of hydroxypropil- β -
16 cyclodextrin in the solubilisation and biodegradation of phenantrene.

17 On the basis of the undeniable fact that nanosponges are insoluble in water and have a limited
18 capacity to include the triclopyr molecule, their strong influence on degradation kinetics is probably
19 due to their great capacity to adhere to the cell membranes, as has been widely shown and reported
20 in the literature regarding a number of anti-cancer drugs.^[38] Similar behaviour could lead the
21 nanosponges to adhere to the walls of the micro-organisms thus facilitating the degradation process.

22 The results of this work suggest that it is possible to use the Dellite 67 G and 43 B organo-clays
23 to create barriers that limit the contamination of deep and surface water bodies.

24 Nanosponges also appear to be suitable for use in limiting the risks of water pollution as they
25 favour the degradation process of the molecule in the contaminated soil.

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4 **FIGURE CAPTIONS**

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6 Figure 1. Percentage of triclopyr adsorption to the materials examined. Means of four replications.

7 SD < 10%

8 Figure 2. Triclopyr adsorption and desorption isotherms obtained with Dellite 67 G. Means of four

9 replications. SD < 10%

10 Figure 3. Triclopyr adsorption and desorption isotherms obtained with Dellite 43 B. Means of four

11 replications. SD < 10%

12 Figure 4. Adsorption and desorption isotherms obtained with the soil-Dellite 67 G mix. Means of

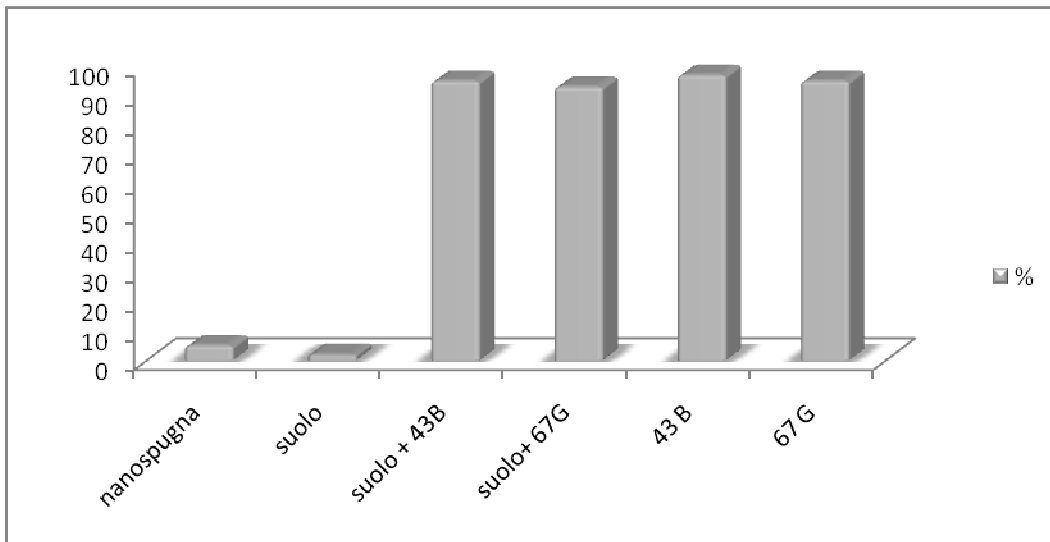
13 four replications. SD < 10%

14 Figure 5. Adsorption and desorption isotherms obtained with the soil-Dellite 43 B mix. Means of

15 four replications. SD < 10%

16 Figure 6. Triclopyr degradation kinetics in the soil, the soil-Dellite 67 G mix, the soil Dellite 43

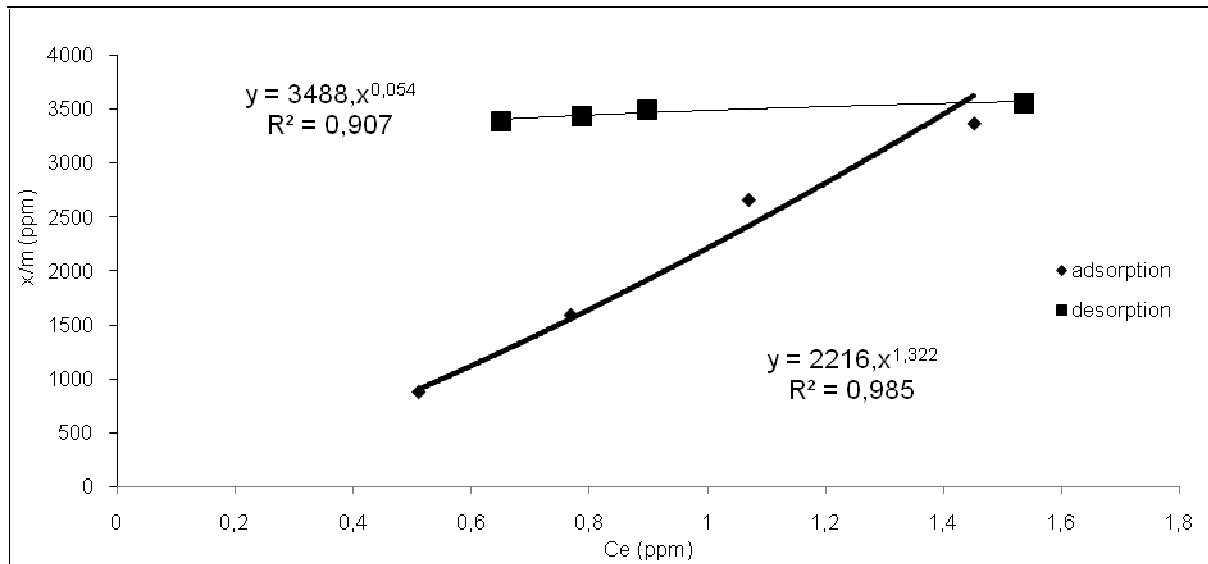
17 mix, and the soil-nanosponge mix. Means of six replications. SD < 10%



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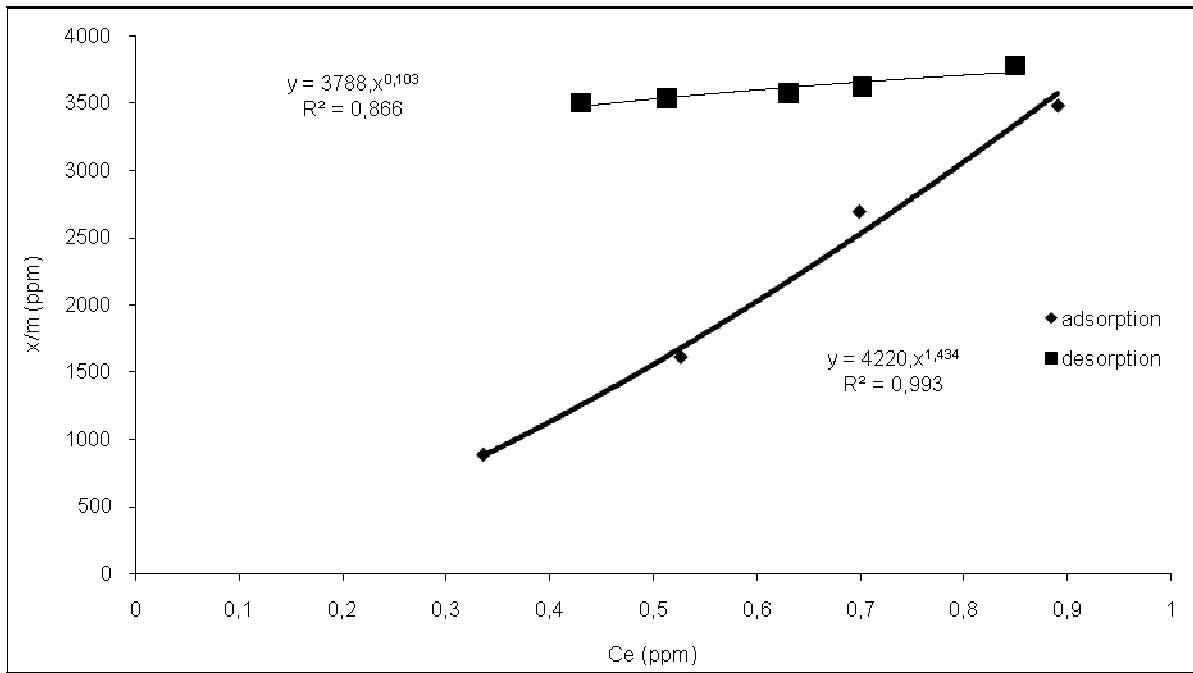
3 Fig.1.



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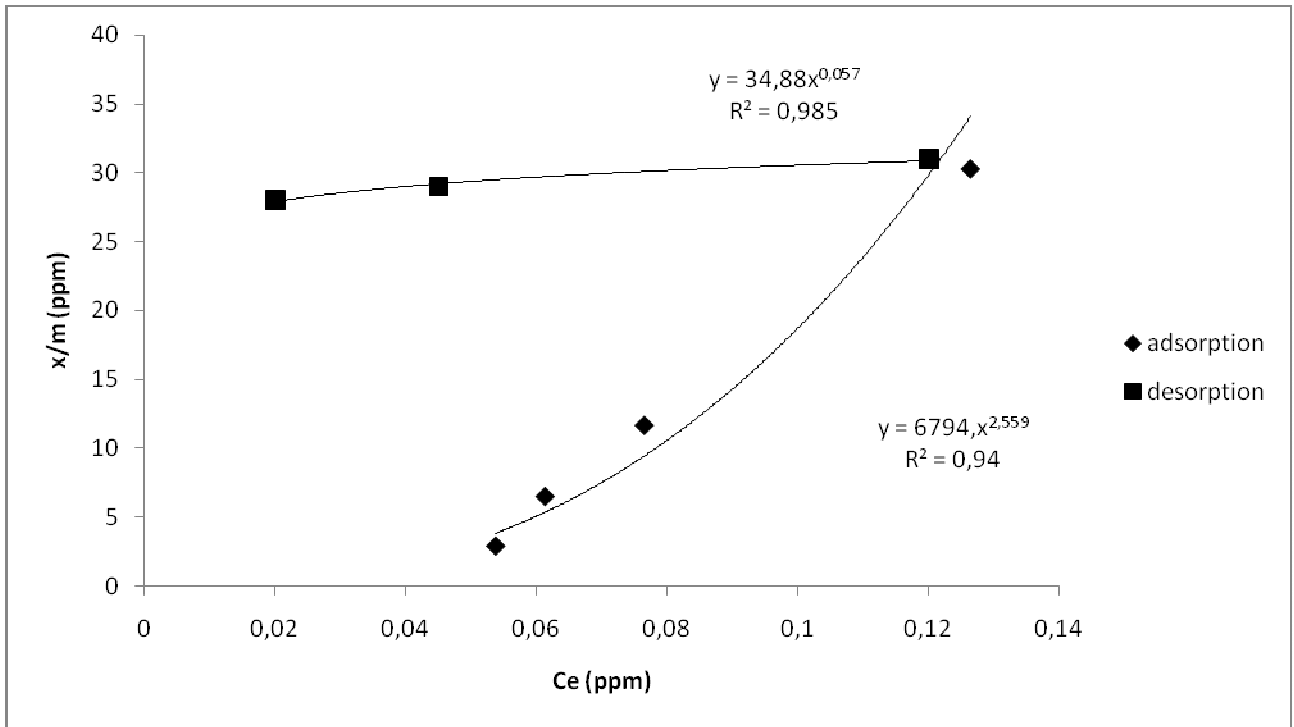
3 Fig.2.



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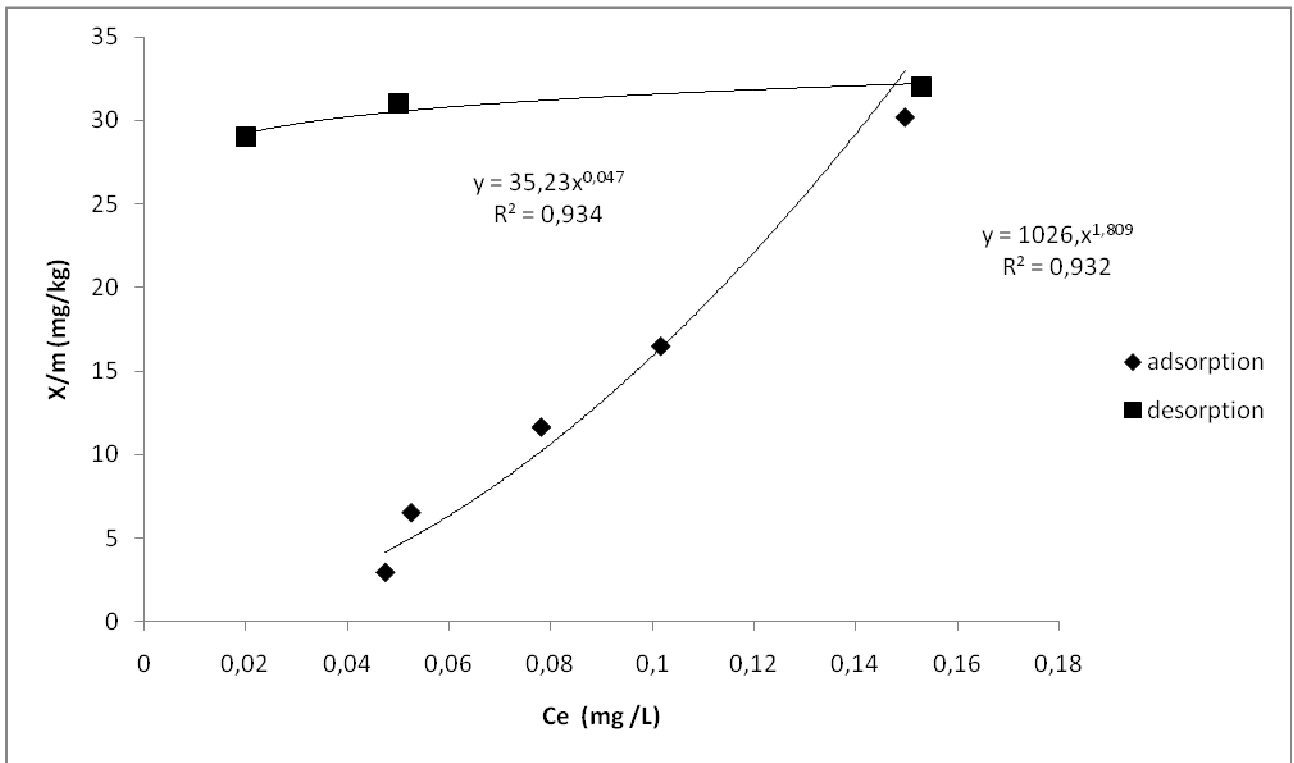
3 Fig.3.



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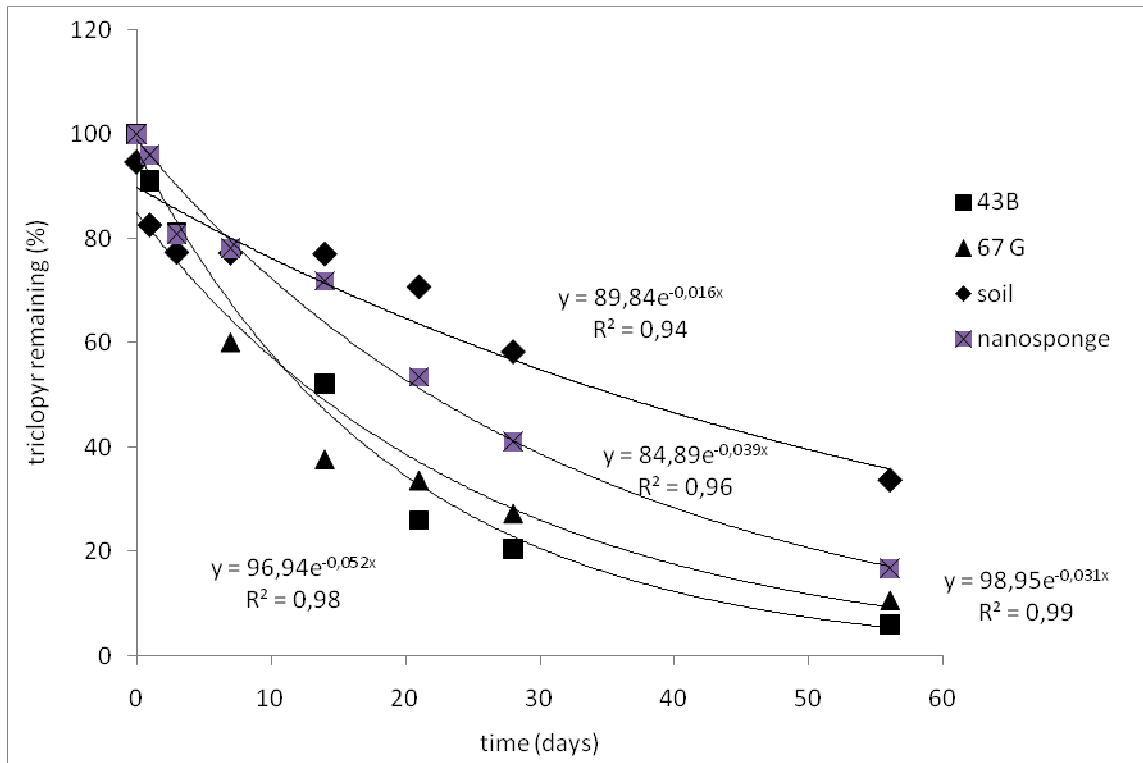
3 Fig.4.



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3 Fig. 5.



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3 Fig. 6.