

Encapsulation of the glyphosate herbicide in mesoporous and soil-affine sorbents for its prolonged release

Original

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(Article begins on next page)

Chemical Engineering Journal

Encapsulation of the glyphosate herbicide in mesoporous and soil-affine sorbents for its prolonged release --Manuscript Draft--

Manuscript Number:	CEJ-D-21-17253R2
Article Type:	Research Paper
Keywords:	Encapsulation; weed control; Al pillared montmorillonite; herbicide; prolonged release; Glyphosate
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Abstract:	<p>The increase in herbicide consumption, in particularly glyphosate, is causing considerable health and environmental concerns, due to its possible carcinogenic effects. Indeed, its widespread and intensive use promotes its diffusion in the surrounding environment. Additionally, the operator's exposure to the herbicide is not negligible.</p> <p>In this work the encapsulation of glyphosate into three selected, eco-friendly silica- and clay- based supports, namely SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT) to promote both a punctual application and a prolonged release of glyphosate is innovatively presented.</p> <p>Preliminary, substrates were characterized pre and post encapsulation through XRD and nitrogen adsorption measurements, to assess the incorporation of the herbicide. Release studies were performed in aqueous matrices of different composition, namely ultrapure water, 0.02M oxalic pH 3 (simulating acid rains) and 0.01M CaCl₂ solution (simulating soil salinity). Within all these media, Al-MMT exhibited a slow-releasing mechanism, with about 10-20% of glyphosate still retained on the support after 7 days, ascribed to complexation and electrostatic interactions.</p> <p>Three different kinetic models usually applied within controlled-releasing processes, i.e. zero order, pseudo-first order and Korsmeyer–Peppas models, were used to describe glyphosate release from Al-MMT in CaCl₂ solutions, with Korsmeyer–Peppas model providing the best fit to experimental data ($R^2 > 0.990$). Finally, a water/soil bench-scaled system was efficiently tested, confirming the successfully applicability of Al-MMT in the prolonged release of glyphosate in real systems.</p>
Suggested Reviewers:	Francesca Baldassarre francesca.baldassarre@unisalento.it Isabel Diaz idiaz@icp.csic.es Mattia Biesuz mattia.biesuz@unitn.it Flaviano Testa f.testa@unical.it

	<p>Myroslav Sprynskyy mspryn@chem.umk.pl</p>
<p>Response to Reviewers:</p>	<p>Dear Prof. Bingcai Pan,</p> <p>We are writing you with reference to your evaluation of the Manuscript CEJ-D-21-17253R1 (sent by e-mail on December 10th) in which you encouraged us to submit a revised version of the manuscript after considering the minor revisions proposed by independent reviewers.</p> <p>The issue raised up by Reviewer #1 was carefully replied, improving the quality of manuscript.</p> <p>In details:</p> <p>Reviewer #1: Most questions are addressed in the revised manuscript. However, I don't think morphology study should be removed. Also, the particle size should be required, as Reviewer 3 mentioned. The observation by SEM or TEM is a basic and necessary method to characterization analysis for the proposed materials. I cannot believe the successful preparation of SBA-15, MMT and Al-MMT pre- and post-impregnation without any SEM or TEM image.</p> <p>AUTHORS: Thank you for your comment. We apology for having removed the FESEM characterization from the first revision of the manuscript. Following your suggestion, we introduced a new paragraph in the "Physicochemical characterization" section (§3.1), discussing morphology and particle size of all pristine supports. Accordingly, figures S1 to S3 (FESEM images) of the revised supplementary material were added and all the other figures were consequently renumbered. The new paragraph is as follows: "Particle size and morphology of SBA-15, MMT and Al-MMT were evaluated by FESEM analysis (Figs. S1, S2 and S3 in the Supplementary Material, respectively). MMT and Al-MMT are characterized by irregular and heterogenous particles (with size ranging roughly from about 40 nm to 200 nm). Conversely, SBA-15 showed its typical hexagonal, elongated particle shape, with length from sub-micron size up to a few μm" FESEM analysis on impregnated supports have not been carried out because the occurrence of new phases was excluded by XRD analysis for all samples. Moreover, previous results on incipient wetness impregnation of silicas with other molecules (specifically a drug, such as piroxicam) did not shown any modification of particles morphology [Gallo, M., Serpella, L., Leone, F., Manna, L., Banchemo, M., Ronchetti, S., & Onida, B. (2021). Piroxicam Loading onto Mesoporous Silicas by Supercritical CO₂ Impregnation. <i>Molecules</i>, 26(9), 2500]</p> <p>According to the above-mentioned considerations, we would like now to propose to your kind attention this revised form of manuscript CEJ-D-21-17253R1 for the publication into the Chemical Engineering Journal.</p> <p>Kind regards L. Rivoira and M.C. Bruzzoniti</p>



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Torino, December 13rd, 2021

Dear Prof. Bingcai Pan,

We are writing you with reference to your evaluation of the Manuscript CEJ-D-21-17253R1 (sent by e-mail on December 10th) in which you encouraged us to submit a revised version of the manuscript after considering the minor revisions proposed by independent reviewers.

The issue raised up by Reviewer #1 was carefully replied, improving the quality of manuscript.

As required, a new paragraph fully discussing morphology and particle size of all pristine supports was implemented in “Physicochemical characterization” section (§3.1). Consequently, FESEM images of all supports were added in the Supplementary Material.

According to the above-mentioned considerations, we would like now to propose to your kind attention this revised form of manuscript CEJ-D-21-17253R1 for the publication into the Chemical Engineering Journal.

Briefly, we report scopes and originality remarks of the research.

The aim of our work is presenting for the first time a proof of concept of the encapsulation of glyphosate inside three eco-friendly silica- and clay- based supports for the punctual application and prolonged release of glyphosate directly in soil. SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT) were considered because of their low cost and of their chemical structure affine to the composition of the soil.

After the **determination of the main physicochemical characteristics of the supports pre- and post-impregnation**, prolonged release studies were performed in aqueous matrices simulating different environmental conditions, like acid rain or soil leaching effect. **The kinetics tests demonstrated that after 7 days of application, the supports are still able to release glyphosate** which amount depends on the physicochemical properties of the support. For the best performing support, Al pillared montmorillonite (Al-MMT), this amount is about 20% after 7 days.

Kinetic models applied to the release data (i.e. zero order, pseudo-first order and Korsmeyer–Peppas models) **were used to in-depth describe glyphosate release**, allowing the elucidation of the interaction (electrostatic and complexation) mechanisms occurring between glyphosate and Al-MMT support.

The results confirmed the prolonged release of glyphosate from Al-MMT in a water/soil bench-scaled system.

The manuscript includes Supplementary Material.



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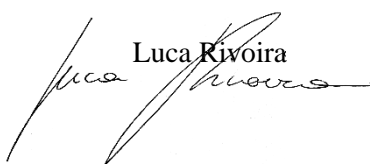
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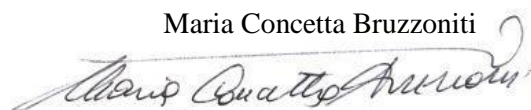
The manuscript is original; it has not been published previously by any of the authors and is not under consideration for publication in another journal.

For the aforementioned reasons, we hope that in this form the manuscript is now appropriate for Chemical Engineering Journal.

We would like to thank you in advance for your cooperation.

Best regards

Luca Rivoira


Maria Concetta Bruzzoniti


List of suggested reviewers:

- a. Dr. Francesca Baldassarre, Biological and Environmental Sciences Department, University of Salento. francesca.baldassarre@unisalento.it
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Ms. Ref. No.: CEJ-D-21-17253R1

Title: Encapsulation of the glyphosate herbicide in mesoporous and soil-affine sorbents for its prolonged release

Chemical Engineering Journal

Dear Dr. Rivoira,

Reviewers have now commented on your paper. For your guidance, reviewers' comments are appended below. As you can see, reviewers have a favorable opinion of your work and minor corrections are suggested.

Please send your revised manuscript, together with an itemized letter answering all the comments made and describing all changes made in response, or the reason why no change should be made. In order to facilitate assessment of the revised manuscript, please copy-paste the comments received and then answer them one by one indicating clearly where and what changes have been made to the manuscript in response to the comments.

In addition to your revised manuscript, please upload one version of your revised manuscript with changes marked-up, either using highlights or a different font color, so that the revisions can easily be identified, make sure to incorporate the essence of your response to the reviewers into the revised manuscript for the benefit of all readers.

I would appreciate if you could submit your revised paper by 23 Dec 2021.

Yours sincerely,

Professor Bingcai Pan
Associate Editor
Chemical Engineering Journal

AUTHORS: Dear Professor Bingcai Pan, we would like to thank you and all the Reviewers for your favourable impression about our revised manuscript. Hereafter we carefully reply to the issue raised up by the Reviewer #1. We hope you will positively welcome our text in this improved form.

Kind regards

L. Rivoira and M.C. Bruzzoniti

Reviewers' comments:

Reviewer #1: Most questions are addressed in the revised manuscript. However, I don't think morphology study should be removed. Also, the particle size should be required, as Reviewer 3 mentioned. The observation by SEM or TEM is a basic and necessary method to characterization analysis for the proposed materials. I cannot believe the successful preparation of SBA-15, MMT and Al-MMT pre- and post-impregnation without any SEM or TEM image.

AUTHORS: Thank you for your comment. We apology for having removed the FESEM characterization from the first revision of the manuscript. Following your suggestion, we introduced a new paragraph in the "Physicochemical characterization" section (§3.1), discussing morphology and particle size of all pristine supports. Accordingly, figures S1 to S3 (FESEM images) of the revised supplementary material were added

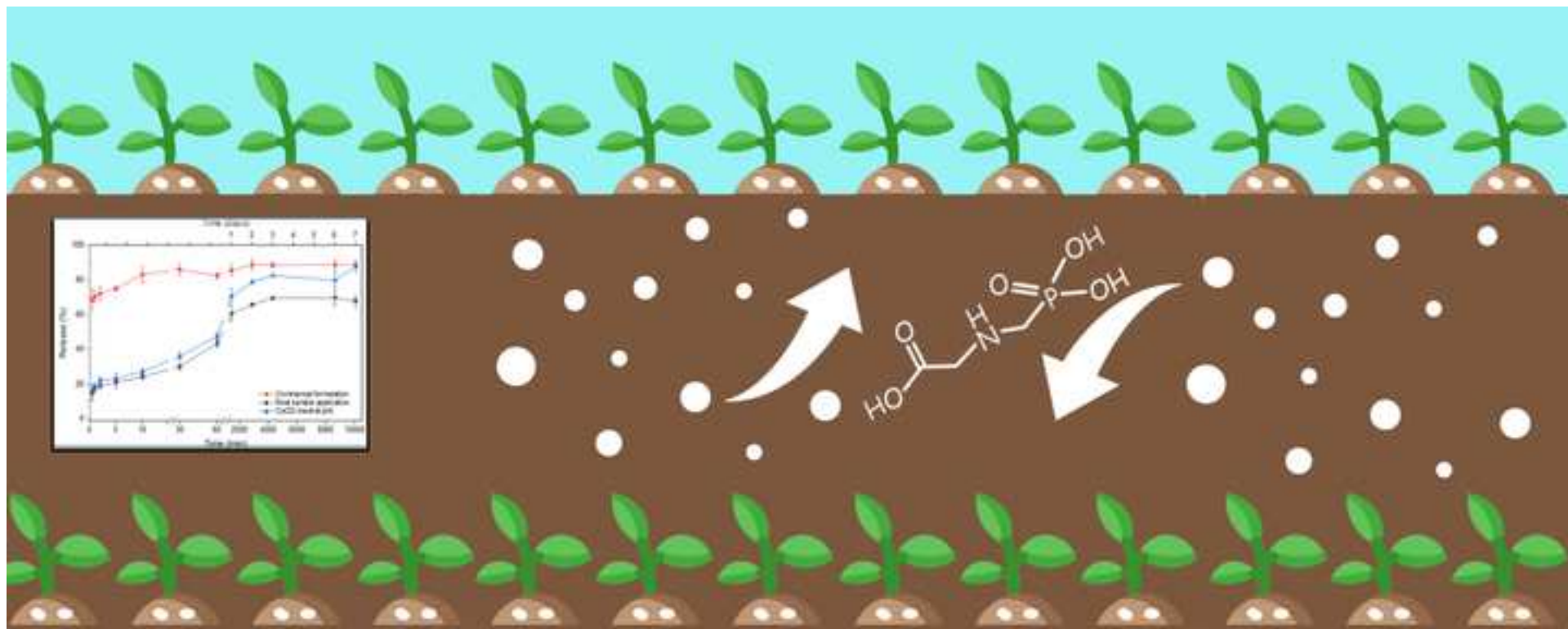
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FESEM analysis on impregnated supports have not been carried out because the occurrence of new phases was excluded by XRD analysis for all samples. Moreover, previous results on incipient wetness impregnation of silicas with other molecules (specifically a drug, such as piroxicam) did not shown any modification of particles morphology [Gallo, M., Serpella, L., Leone, F., Manna, L., Banchemo, M., Ronchetti, S., & Onida, B. (2021). Piroxicam Loading onto Mesoporous Silicas by Supercritical CO₂ Impregnation. *Molecules*, 26(9), 2500]

We thank you for your valuable revision and we hope you will favourably welcome the manuscript in this new form.

Reviewer #3: The authors have well solved the problems

AUTHORS: We warmly thank you for your positive comment and for your effort in improving the quality of our manuscript



- Minimize glyphosate adverse impact in the environment and operator's exposure
- Encapsulation of glyphosate into supports for a punctual and prolonged release
- Preliminary characterization (pre-post encapsulation) to assess its incorporation
- Release/kinetic studies in aqueous matrices to simulate acid rains or soil salinity
- Successful bench-scaled application in a water/soil dispersion to simulate real use

Encapsulation of the glyphosate herbicide in mesoporous and soil-affine sorbents for its prolonged release

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Keywords: encapsulation; weed control; Al pillared montmorillonite; herbicide; prolonged release, glyphosate

Abstract

The increase in herbicide consumption, in particularly glyphosate, is causing considerable health and environmental concerns, due to its possible carcinogenic effects. Indeed, its widespread and intensive use promotes its diffusion in the surrounding environment. Additionally, the operator's exposure to the herbicide is not negligible.

In this work the encapsulation of glyphosate into three selected, eco-friendly silica- and clay- based supports, namely SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT) to promote both a punctual application and a prolonged release of glyphosate is innovatively presented.

Field Code Changed

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Preliminary, substrates were characterized pre and post encapsulation through XRD and nitrogen adsorption measurements, to assess the incorporation of the herbicide. Release studies were performed in aqueous matrices of different composition, namely ultrapure water, 0.02M oxalic pH 3 (simulating acid rains) and 0.01M CaCl₂ solution (simulating soil salinity). Within all these media, Al-MMT exhibited a slow-releasing mechanism, with about 10-20% of glyphosate still retained on the support after 7 days, ascribed to complexation and electrostatic interactions.

Three different kinetic models usually applied within controlled-releasing processes, i.e. zero order, pseudo-first order and Korsmeyer–Peppas models, were used to describe glyphosate release from Al-MMT in CaCl₂ solutions, with Korsmeyer–Peppas model providing the best fit to experimental data ($R^2 > 0.990$). Finally, a water/soil bench-scaled system was efficiently tested, confirming the successfully applicability of Al-MMT in the prolonged release of glyphosate in real systems.

1. Introduction

Weed control is the botanical component of pest control that is used to prevent weeds from reaching a matured crop which is ready for cultivation [1]. Both physical and chemical methods are exploited to reduce weeds that are harmful to agricultural plants and fodder. Among them, herbicides are the dominant tool used for weed control in modern agriculture.

Nowadays, it is recognized that, to ensure the effectiveness of crop production, herbicides are often applied at exceeding dosages [2] and that current formulations generally release the compound into the environment practically instantaneously [3].

In the light of the information described above, a wide use of herbicides is evident, thus leading all the countries of the world to face different problems, such as the rapid evolution of herbicide-resistant weeds [4, 5], the environmental impact of these compounds, [6], and the impact on human health, with particular attention to worker exposure [7, 8], with 170,000 workers worldwide employed in the agricultural died every year. On these incidences, a correlation between deaths and exposure to toxic pesticides through spray, drift and direct contact cannot be excluded [9].

In order to prevent the above-mentioned issues and given the public pressure to reduce the overall pesticide use, new integrated weed management strategies are now strongly encouraged [10, 11]. Among these, an important part is devoted to the development of new methods for the application of herbicides on soils.

Among the several herbicide formulations that are applied, glyphosate is probably the most used in the world (about 720k tons production in 2012) [12]. Glyphosate (N-(phosphonomethyl)glycine) is a broadspectrum post-emergence herbicide used both in agriculture and for the conservation of green spaces, such as parks and gardens [13]. The more common methods of glyphosate use include broadcast, aerial, spot, and directed spray applications [14]. It should be remarked that despite glyphosate is typically spread on leaves, its absorption through roots has been clearly assessed [15] and application to soils are also reported, i.e. for fungicidal aims [16].

Despite its huge consumption, glyphosate has been the subject of controversial discussions over its impact on the environment and human health in recent years, with IARC (International Agency for Research on Cancer) classifying glyphosate as *a probable human carcinogen compound* (class 2A), oppositely to EFSA (European Food Safety Authority) stating that this herbicide *is unlikely to pose a carcinogenic hazard to humans*.

Despite this still-open discussion, on December 12, 2019 European Union renewed the licence for the sale of glyphosate for five years [17], even if some countries (for example Italy) has already introduced some restrictions on the use of this herbicide [18].

The impact of glyphosate on the environment has been extensively studied, as traces of glyphosate and its metabolites could be found both in water basins, in soils and even in the atmosphere [19]. Therefore, selected approaches are nowadays exploited to face the emergency caused by the use of glyphosate. Most of them are post-use remedies, and are mainly based on the development of new technologies for the removal of the herbicide from the environmental compartments [20, 21]. However, it is also appropriate to evaluate some approaches defined "a priori" which, on the contrary, are based on the reduction of the quantity of glyphosate released into the environment.

The incorporation of active formulations inside specific carriers to obtain a controlled release in the environment has been extensively explored for agricultural applications, in order to set-up the concentration of the active principle within a range spanning from the minimum effective concentration to the maximum concentration safe for the operator [22]. Applications reporting the encapsulation of fungicides [23], herbicides [24], insecticides [25], acaricides [26], as well as of compounds intended for the stimulation of plant growth and productivity [27] are frequently presented in the scientific literature. Conversely, research concerning glyphosate is under-investigated and light controlled [28] and supramolecular [29] systems are the only solutions proposed.

Mesoporous silica and clay based materials exhibit adsorption properties that were exploited for the preparation of sorptive substrates [30, 31] and in water remediation technologies [32, 33]. In

particular, the removal of herbicides using both types of supports through selective bonds between silica or clay supports with the active compounds is demonstrated [34].

Hence, this work aimed at the innovative encapsulation of glyphosate into selected silica- and clay- based supports. The encapsulation of the herbicide allows the application of the loaded support, promoting both a punctual application and the controlled release of glyphosate, thus limiting human exposure to glyphosate, during application. To the best of our knowledge, this manuscript represents the first study specifically devoted to the encapsulation of glyphosate into mesoporous sorbents, which indeed have a structure affine to the composition of the soil.

For this study, three different types of environmental-friendly mesoporous silica and clay-based supports were selected, namely: SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT). MMT and Al-MMT can be also considered low cost and then their use appears feasible in the proposed application. After physicochemical characterization of the pre- and post-impregnated supports, tests on the release of glyphosate were performed simulating different environmental conditions, such as acid rains or soil leaching. Data obtained within release tests were fitted to kinetics models typically used to describe desorption of active principles from mesoporous supports. Finally, the sorbent showing the best releasing performances was chosen for a real sample application, in a water/soil bench-scaled system.

2. Experimental

2.1 Materials and reagents

A highly stable mesoporous silica sieve (Santa Barbara Amorphous, hereafter called SBA-15), montmorillonite K-10 (MMT) and Al pillared montmorillonite (Al-MMT) were purchased from Sigma-Aldrich (Darmstadt, Germany).

Glyphosate, sodium hydroxide solution (grade >98%), ethanol, hydrochloride acid (40%), oxalic acid (98%) and calcium chloride were from Sigma-Aldrich (Darmstadt, Germany).

High purity water (18.2 M Ω cm resistivity at 25 °C), produced by an Elix Milli Q Academic system (Millipore, Vimodrone, MI, Italy) was used for standard and eluent preparation.

2.2 Instrumental setup and calibration

The release profiles of glyphosate from the tested substrates were evaluated by means of suppressed ion chromatography as recently optimized by our research group [20]. A DX-100 ion chromatograph (25- μ L injection loop) from Dionex, Thermo Scientific, (Sunnyvale, CA, USA) equipped with a conductivity detector was used. An IonPac AG16 (50 \times 4 mm) and IonPac AS16 (250 \times 4 mm) were used as guard and analytical columns, respectively. Mobile phase was 35 mM NaOH at a flow rate of 1.0 mL/min. Detection was performed by electrochemical suppressed conductivity (100mA current set-up) using a 4-mm ESRS-300 membrane suppressor. Chromatographic data were collected by PeakNet 2.8 software.

For calibration curve, a 100 mg/L glyphosate stock solution was used to prepare standard solutions (six levels, from 0.5 to 15 mg/L). Each level was injected in triplicate and a new calibration curve was run, weekly. Limits of detection and limits of quantifications of the chromatographic method were calculated according to Shrivastava and Gupta and were 0.1 mg/L and 0.3 mg/L, respectively [35].

2.3 Impregnation of the supports with glyphosate

The impregnation of supports with glyphosate was achieved using water as solvent through the incipient wetness impregnation technique [36], by which a volume of a solution containing the active ingredient to be incorporated is put in contact with the support itself. Consequently, the solution is forced to spread by capillary within the available pores, by means of a manual or a

mechanical mixing. Finally, the impregnated material is dried as to evaporate the excess of solvent and to allow the deposition of the desired molecules inside the support.

In detail, a saturated solution of glyphosate was prepared by dissolving 0.4 g of glyphosate in 33 mL of water (solubility=12 g/L, at room temperature [37]). Subsequently, 1 mL of such solution was added dropwise to 0.6 g of each support, thus obtaining a homogenous slurry, which was finally oven dried at 60°C for 24 hours. The impregnation procedure was performed at room temperature and was repeated until the glyphosate saturated solution was totally consumed. The procedure allowed to obtain 40% glyphosate impregnation in respect to the total weight of the support.

2.4 Physicochemical characterization of the supports pre- and post-impregnation

X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert Powder (Cu K α radiation) diffractometer. The measurements were performed by means of a circular sample holder with diameter of 30 mm and thickness of 2 mm. [Field Emission Scanning Microscopy \(FESEM\) images were recorded with a Merlin instrument \(Zeiss, Germany\).](#) Nitrogen adsorption isotherms were measured using a Quantachrome (FL, USA) AUTOSORB-1 instrument. Prior to nitrogen adsorption, samples were outgassed (393 K, 5 h). BET specific surface areas (SSA) were calculated in the relative pressure range 0.04–0.1.

2.5 Release of glyphosate from supports in aqueous solutions

The release of encapsulated glyphosate from the different tested supports in aqueous solutions, was evaluated simulating different environmental conditions. In detail, 0.25 g of each impregnated material was put in contact with 15 mL of the following aqueous solutions: i) ultrapure water, pH 6.5; ii) 0.02 M oxalic acid (pH 3), to simulate acid rains; iii) 0.01 M CaCl₂ solution, to simulate soil salinity (experiments were performed both at neutral and acidic pH). The suspension was stirred in an orbital shaker up to 7 days at room temperature, withdrawing 100 μ L-aliquots from each solution at scheduled times, namely: 0 and 30 seconds, 1, 2, 5, 10, 30, 60, 1140 (1 day), 2880 (2 days), 4320 (3

days), 8640 (6 days) and 10080 minutes (7 days). The cumulative sampled volume was less than 5% of the initial volume (15 mL), thus it can be assumed that the influence of the volume change on the release pattern is negligible. Release tests were performed separately for each support, in order to avoid any competitive equilibrium, and were repeated in triplicates.

Each sampled solution was then diluted 1:1000 with ultrapure water prior to IC analysis. The concentration of the glyphosate released (C_r) was derived through the calibration curve previously commented. The percentage of glyphosate released (*Release %*) was calculated according to the following equation:

$$Release\% = \left(\frac{1000 \cdot C_r}{C_{max}} \right) * 100.$$

Where C_{max} is the maximum concentration that could be released from each support, according to the encapsulation procedure and the nominal glyphosate content (i.e. 40 % w/w), namely 6400 mg/L. This concentration was chosen to match the content of glyphosate in commercial formulations (e.g. 64-66% for granular RoundUp product) in consideration of the amount of commercial product to be applied in real applications (about 10 g of granules per liter, according to the manufacturer indications).

2.6 Mathematical modelling of glyphosate release

The profiles of glyphosate release from the studied supports were mathematically modelled to better understand the dissolution profile. Within this work, several models were evaluated, as hereafter listed. Even if all models were originally developed for drug delivery from polymeric and non-polymeric supports, they are commonly applied for the release of herbicides [38, 39] as well.

Zero-order model (*Release % vs. time*) [40]

The release rate is supposed to be independent from the concentration of herbicide, And the same amount of compound is expected to be released per unit of time, according to eq. 1.

$$C_t = C_0 + K_0t \quad (1)$$

where C_t is the amount of herbicide (mg/L) dissolved at the time t (expressed in hours), C_0 is the initial amount of the herbicide dissolved in the solution and K_0 is the zero-order release constant, expressed as mg/L/h.

Pseudo first-order model (log of Release % vs. time) [41]

Differently to the zero-order model, in the first-order kinetic, the release rate depends on the concentration. The linearized model is expressed by eq. 2:

$$\log C_t = \log C_0 - Kt/2.303 \quad (2)$$

where C_t is the concentration of herbicide (mg/L) released at t time (expressed in hours), C_0 (mg/L) is the initial dissolved concentration of herbicide in the media and K is first order constant (1/hour).

Korsmeyer and Peppas model (log of Release % vs. log of time) [42]

The Korsmeyer-Peppas model (eq. 4) can be used to discriminate between Fickian diffusion or non-Fickian (anomalous) diffusion [43]. The linear relation is expressed by eq. 3

$$\log C_t = \log K + n \log t \quad (3)$$

where C_t is the concentration of drug released at time t (mg/L), K (hour^{-n}) is the release rate constant and n is the diffusional exponent (adimensional). This kinetic equation is claimed valid only for the first 60% of the released active principle [42].

For a dispersed, non-swellaable system, the value of n gives an indication of the release mechanism, as hereafter listed [44]: i) $n < 0.5$, quasi-Fickian diffusion, ii) $n = 0.5$, Fickian diffusion mechanism, iii) $0.5 < n < 1$, non-Fickian diffusion, iv) $n = 1$, case II transport (zero-order release), v) $n > 1$, super case II transport.

It should be noted that for $n=0.5$, a Fickian diffusion is present. Accordingly, eq. 3 simplifies into the Higuchi's equation (eq.4):

$$C_t = K_H t^{0.5} \quad (4)$$

where C_t is the amount of drug released (mg/L) at time t (expressed in hours) and K_H is the release rate constant of H ($\text{hour}^{-1/2}$).

2.7 Water/soil bench-scaled system

The release of glyphosate from the most promising support among the four tested (Al-MMT) was evaluated in a real soil/water system and compared in parallel with the release of glyphosate from a commercial formulation. Soil was collected from a public garden in the town of Torino (Valentino Park) and was chosen to have the representative composition of typical soils intended for horticulture uses [45], where glyphosate is mostly employed. In detail, 0.25 g of each formulation was added to 15 g soil/15 ml tap water dispersion in a glass bottle. pH of the suspension was measured and was equal to 6.8. At selected times after herbicide application (from 0 min to 7 days, as for the water release studies), the bottles were hand-shaken, the contents were allowed to settle, and 100 μ L of the supernatant solution were filtered and analysed by IC to determine the glyphosate concentration released. The periodic sampling of such a small amount of supernatant was assumed not to have any influence on the release pattern. Release kinetics were evaluated in triplicate.

3. Results and Discussions

3.1 Physicochemical characterization

The Incipient Wetness Impregnation technique is a protocol frequently exploited for the encapsulation of active principles in supporting materials, since it does not require specific reagents or procedures, and since it guarantees quantitative impregnation of the supports [6].

To investigate how glyphosate was encapsulated in the tested materials, physicochemical characterization of SBA-15, MMT and Al-MMT was performed.

Particle size and morphology of SBA-15, MMT and Al-MMT were evaluated by FESEM analysis (Figs. S1, S2 and S3 in the Supplementary Material, respectively). MMT and Al-MMT are characterized by irregular and heterogenous particles (with size ranging roughly from about 40 nm to 200 nm). Conversely, SBA-15 showed its typical hexagonal, elongated particle shape, with length from sub-micron size up to a few μ m.

Specific surface area (SSA_{BET}) and pore volume of each substrate, obtained by nitrogen sorption analysis before and after impregnation (Figure S44, S25 and S36 in the Supplementary Material) are reported in Table 1.

Table 1. Specific surface area (SSA) and pore volume of the four tested materials, before and after the encapsulation of glyphosate. Brunauer–Emmett–Teller (BET) model was used for calculations.

	SSA_{BET} (m^2/g)	Pore volume (m^3/g)
SBA-15	701	0.99
SBA-15 impregnated	492	0.74
MMT	279	0.42
MMT impregnated	83	0.15
Al-MMT	250	0.26
Al-MMT impregnated	6	0.017

The three sorbents cover a wide range of porosity (from 0.26 to 0.99 m^3/g pore volume and from 250 to 700 m^2/g SSA).

The impregnation with glyphosate resulted, for all the supports, in a significant modification of nitrogen adsorption-desorption isotherms (Figure S44, S25 and S36 in the Supplementary Material) and a reduction of SSA and pore volume (Table 1). These results indicate the location of glyphosate molecules inside the mesopores of the materials. This evidence is dramatic for Al-MMT (around 98% and 96% reduction of SSA and pore volume, respectively), suggesting that in this case the original mesoporous structure has been fully occupied by the herbicide. Indeed, the adsorption-desorption isotherms of N_2 on Al-MMT (Figure S44) reveal that the hysteresis loop, typical of

disordered mesoporous materials, almost disappeared after the inclusion of glyphosate (red-triangled line).

The almost complete filling of pore volume for Al-MMT by glyphosate, at variance with SBA-15 and MMT, is in agreement with the lowest pore volume measured for Al-MMT ($0.26 \text{ m}^3/\text{g}$) when compared to those of SBA-15 ($0.99 \text{ m}^3/\text{g}$) and MMT ($0.42 \text{ m}^3/\text{g}$), considering that the same amount of glyphosate (0.40 g) per gram of support is present in the three impregnated materials.

In order to characterize the glyphosate in SBA-15, MMT and Al-MMT, XRD measurements were also performed (Figure 1).

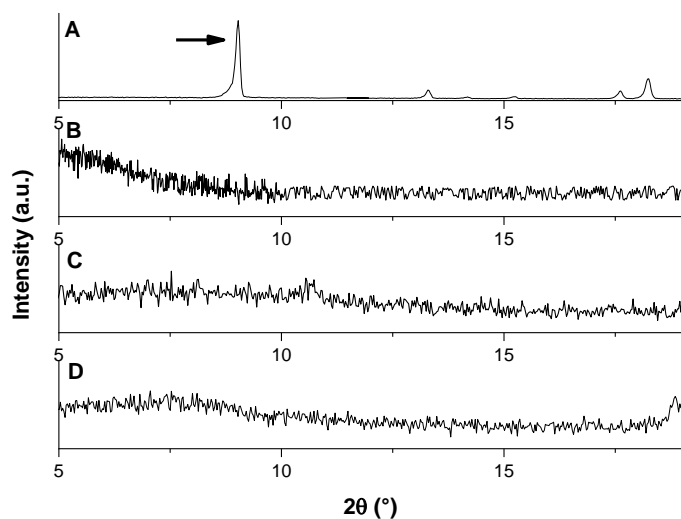


Figure 1. XRD patterns of glyphosate (A) and post-impregnated support: B - SBA-15, C - MMT, D - Al-MT. Black arrow points the main peak of crystalline glyphosate ($2\theta = 8.9^\circ$)

Results showed that the main peak of crystalline glyphosate ($2\theta = 8.9^\circ$, Fig.1A) is absent for all sorbents (1B, 1C, 1D). The lack of crystalline glyphosate signal is indicative for a complete amorphization of glyphosate. This is ascribed to the location of molecules inside materials mesopores, preventing crystallization [46] , and to their interaction with the surface sorbents.

The location of glyphosate molecules inside mesopores was confirmed by small angle XRD patterns (see Supplementary Material). In details, to what concern SBA-15 a decrease of the intensity of the peak (100) is observed (Figure S74), being indicative of the pore filling, in agreement with the decrease of the scattering contrast between the pores and the walls [47]. As far as MMT (Figure S58) and Al-MMT (Figure S96) are concerned, the location of glyphosate molecules in the interlayer spacing of the clays is evidenced by the vanishing of the typical basal peak (related to d001), indicating that the interlayer has expanded due to the inclusion of glyphosate [46].

3.2 Desorption tests in ultrapure water

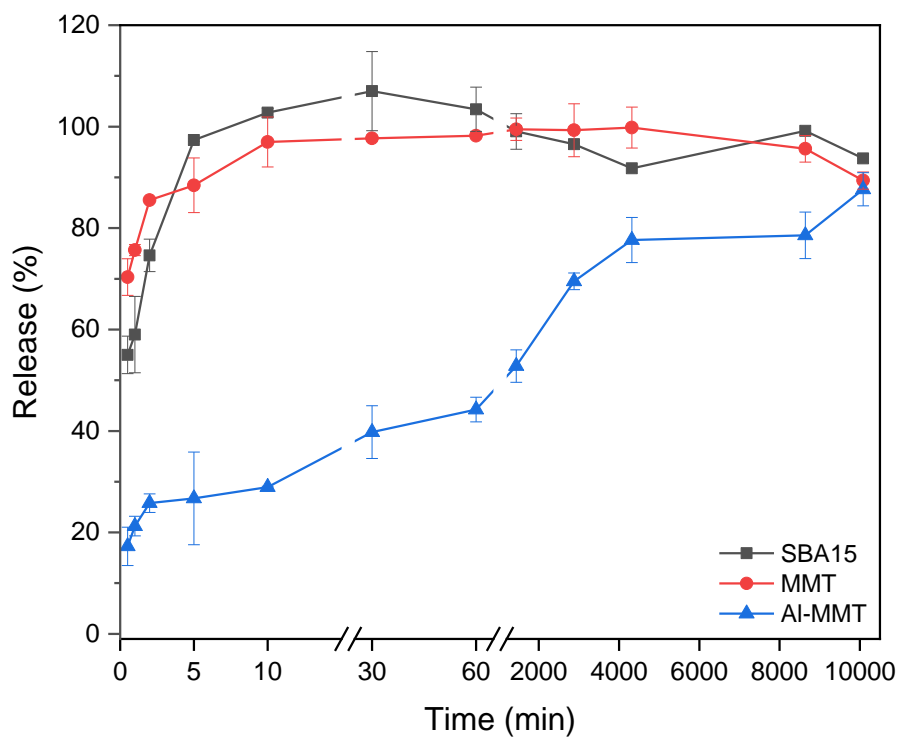


Figure 2. Desorption kinetics of glyphosate in ultrapure water from impregnated supports SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Ultrapure water (pH 6.5) was chosen as the first aqueous medium to be tested in order to avoid any competition of external species which could affect the release of glyphosate from supports.

The dissolution profiles of glyphosate in ultrapure water from SBA-15, MMT and Al-MMT are shown in Figure 2. The values on the left y-axis are given as percentages of the total amounts of glyphosate present in the dissolution vessel and, for all release curves, a 100% release corresponds to 6400 mg/L glyphosate concentration (for more details, see Experimental Section, §2).

When focusing on the short sampling times, it is observed that more than 50% of the glyphosate is released from both SBA-15 and MMT after only 30 seconds, reaching a quantitative release after 10 minutes. Hence, no prolonged release of the herbicide was observed for such sorbents. For SBA-15, less than 10% of the herbicide is still retained after 5 minutes and a complete release is observed after 10 minutes of contact with water, suggesting that weak interactions occur between glyphosate molecules and SBA-15 surface. This behaviour is in agreement with adsorption results previously obtained [20], showing negligible interactions between glyphosate and SBA-15 at neutral pH, whereas partial adsorption was observed only at acidic pH (see next paragraph).

A similar behaviour was observed also for MMT (96.9% release after 10 minutes). Despite several works report that selective interactions between glyphosate and MMT can occur, in particular at acidic pH (< 4) [48, 49], desorption tests here presented are performed at a neutral pH, which is higher than the point of zero charge (PZC) of MMT (about 3.4). In such conditions, the clay mineral surface is negative [48] and the negatively charged glyphosate [20] could hardly be retained by the negatively charged surface adsorption sites due to electrostatic repulsion. Such behavior is responsible for the fast and quantitative release rate of glyphosate within the short sampling time.

Differently to what previously discussed for MMT and SBA-15, the trend of Al-MMT indicate a slower kinetic release. Indeed, after 2 minutes only 28% (of impregnated glyphosate was released in the solution from Al-MMT, suggesting that the interactions between the herbicide and the support are stronger than those occurring in SBA-15 and MMT. To explain this behavior, it should be mentioned that Al-MMT is characterized by the presence of Al³⁺ ions that could be complexed with glyphosate, mainly through phosphate-Al interaction [50], forming monomeric and dimeric complexes [51]. This interaction is, therefore, proposed to be responsible for the slower release of the herbicide from Al-MMT. As regards the releasing mechanism, it should be mentioned that the complexation constants of Al-glyphosate are lower than Al-H₂O constants [51]. Hence, a competition of water molecules, interacting with aluminium, could occur.

Al-MMT system exhibits a prolonged release of glyphosate which appears appealing for the proposed application. The slow release observed for Al-MMT is ascribed to strong interactions between glyphosate molecules and internal surface of the support. Moreover, the diffusion of glyphosate molecules from the internal pore structure may at same extent control the release. The location of glyphosate molecules in the interlayer spacing of the pillared clay is evidenced by the XRD pattern at small angles (Figure S6 in the Supplementary Material), as previously discussed. The release of glyphosate by Al-MMT is in agreement with the work of Siepmann and co-workers, in which the drug release was shown to be kinetically longer for supports in which the active principle was encapsulated in the material core [52].

The performances of Al-MMT (20% of the herbicide still inside the support after 7 days) were compared with those reported in the only two literature papers on the release of glyphosate. Data show that Al-MMT exhibits better or at least similar prolonged release performances (i.e. slower dissolution profiles) than biochar-attapulgitite (quantitative glyphosate release of glyphosate after 2 hours) [28], and supramolecular organic guest intercalated layered double hydroxides (40% release after 24 hours) [29] systems, respectively.

3.3 Desorption tests in simulated acid rain solution

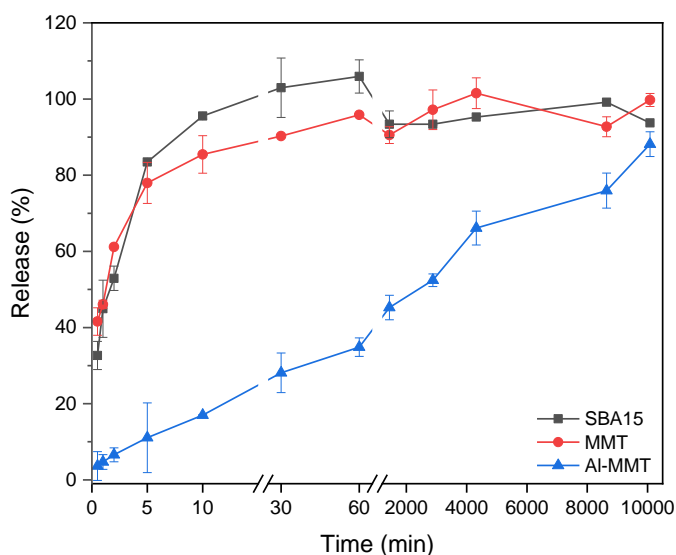


Figure 3. Desorption kinetics of glyphosate in 0.02M oxalic acid (pH=3) from SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Once assessed the desorption behaviours in ultrapure water, the same tests were replicated at pH 3, simulating worst conditions of rain acidity [53] (Figure 3).

The dissolution profiles of Figure 3 showed that, also at acidic conditions, Al-MMT was the only support characterized by a prolonged release of glyphosate (about 13% still retained after 7 days), with a partial slowdown of the kinetic in comparison to the one obtained in ultrapure water (Table 2, column A vs B). A slowdown was also observed for pure MMT (Table 2, column C vs D), despite this support quantitatively release glyphosate after 60 minutes.

Table 2. Comparison of glyphosate release up to 3 days between ultrapure water medium (UP) and 0.02M oxalic acid, pH3 (pH3). Gray cells show sampling times in which quantitative release of glyphosate is reached.

	Glyphosate release (%)			
	Al-MMT		MMT	
	pH3 (A)	UP (B)	pH3 (C)	UP (D)
0.5 min	3.6	17.3	41.6	70.3
1 min	4.7	21.2	46.1	75.7
2min	6.6	25.8	61.2	85.5
5min	11.1	26.7	78.0	88.4
10min	17.0	28.9	85.4	97.0
30min	28.1	39.8	90.3	97.7
60 min	34.9	44.2	95.9	98.2
1 day	45.3	52.8	90.5	99.5
2 days	52.4	69.5	97.2	99.3
3 gg	66.1	77.6	101.5	99.8

To explain the slowdown of Al-MMT and MMT kinetics, both acid-base equilibrium of glyphosate and surface properties of montmorillonite should be considered. Indeed, at pH 3 glyphosate is present with a protonated carboxylic, and a monovalent phosphonic group (Figure 4A).

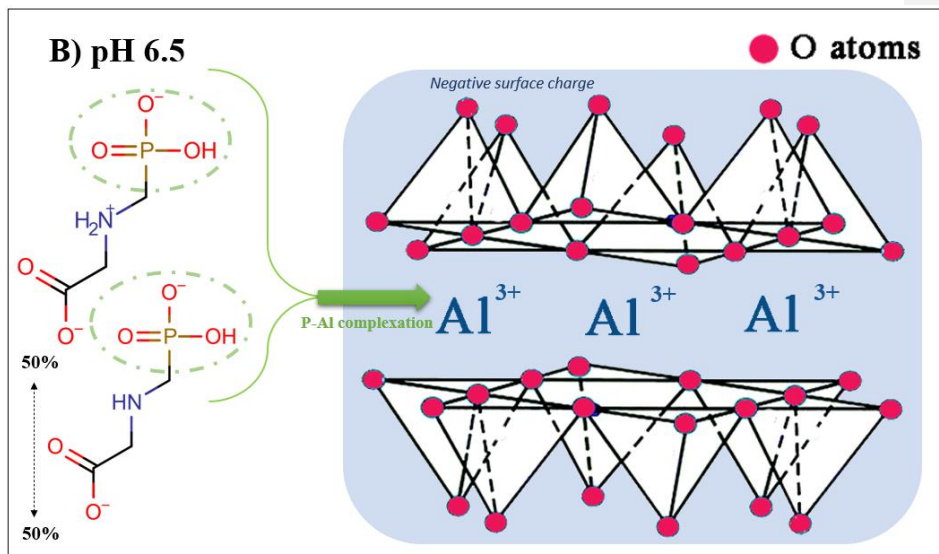
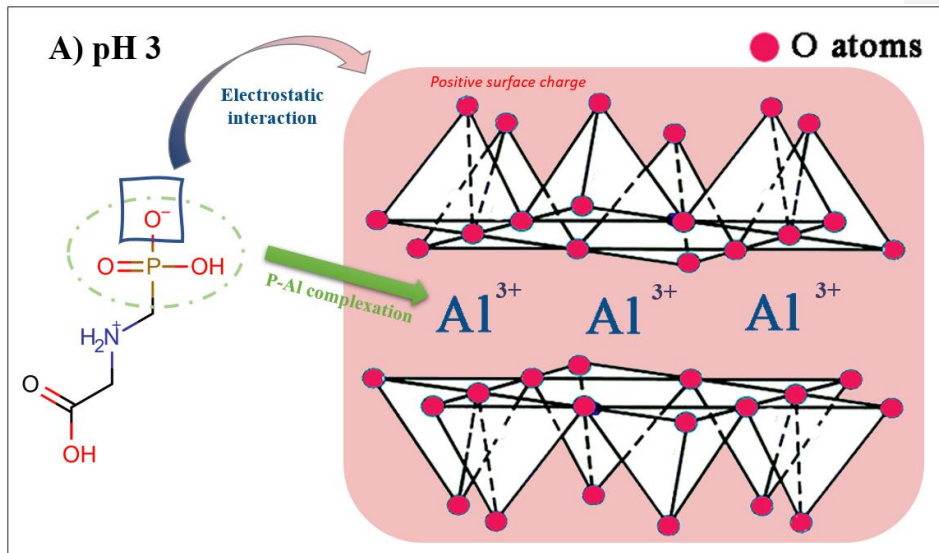


Figure 4. Surface charge of Al-MMT and chemical dissociation of glyphosate at pH 3 (A) and pH 6.5 (B). Main interaction occurring at both pH values are also highlighted.

Since pH conditions are lower than Al-MMT PZC (about 4.3 [54]), the surface of montmorillonite has to be considered positively charged (Figure 4A). Conversely, in ultrapure water (pH around 6.5) glyphosate is present with the same monovalent phosphonic group but with the deprotonated carboxylic, (Figure 4B) and the surface of montmorillonite has to be considered negatively charged, being above its PZC. Therefore, electrostatic repulsions occur in ultrapure water, which instead are not present at pH 3.

Summarizing, for Al-MMT at pH values close to neutrality, the effect of both P-Al interactions and electrostatic repulsion influence the release of glyphosate, thus justifying the lower retention of glyphosate, and hence the faster kinetic release, observed in respect to acidic pH conditions where only P-Al interactions occur. Moreover, despite the zwitterionic form of glyphosate at pH3, electrostatic attractive interactions between the negative phosphonic group and the positive surface of Al-MMT may give a further contribution to the retention, besides the complexation of Al^{3+} ions by glyphosate.

A fast release was observed for SBA-15 since more than 85% of glyphosate is released after 5 minutes. However, after 30 seconds about 35% release was observed at pH 3, against 55% in ultrapure water, thus supporting the role of surface charge also in the interaction between SBA-15 and negatively charged glyphosate. Indeed, pH 3 may be considered below the PZC of SBA-15 PZC (5.2), whereas at pH around 6.5 the surface of SBA-15 has to be considered mainly negatively charged [55].

3.4 Desorption tests in simulated soil conditions

Previous tests were performed without considering any competing species. However, the presence of the soil matrix can affect the release of glyphosate from encapsulating support. Competitive interactions between surface moieties and soil salts, such as calcium chloride [56], can be established, with charged species potentially promoting a faster release of the herbicide.

Experiments were performed on Al-MMT only, since MMT and SBA-15 were shown to exhibit a fast release, not compatible with prolonged applications. Glyphosate desorption from Al-MMT in 0.01M CaCl₂ solution was studied, roughly simulating the ionic strength of soil solutions [56].

Dissolution profiles obtained in 0.01M CaCl₂ at pH conditions acidic (pH=3) and close to neutrality (pH=6.7) are reported in Figure 5 (triangled blue- and squared black- lines, respectively), together with desorption profiles obtained in ultrapure water and oxalic acid solution (starred green- and pointed red- lines, respectively) for a better comparison.

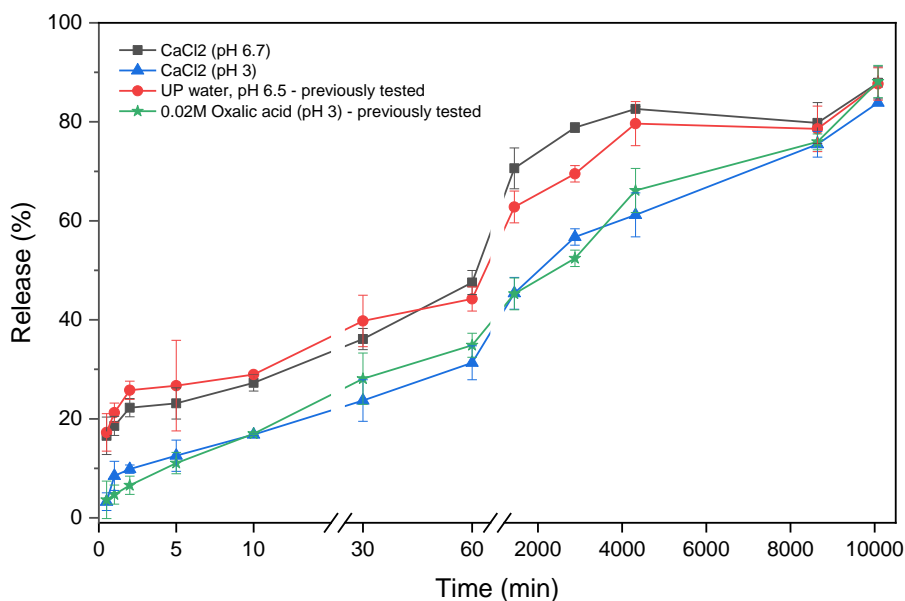


Figure 5. Desorption profiles of glyphosate 0.01M CaCl₂ solution, at acidic (pH 3) and almost neutral (pH 6.7) conditions. Release percentage in ultrapure water (UP water) and 0.02 oxalic acid solution are overlaid. For an easier comprehension, sampling time is expressed both as minutes and

hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Results confirmed that, within the standard deviation of the measurements, glyphosate release is not affected by CaCl₂, thus suggesting the absence of significant competitive interactions between Al-MMT and CaCl₂. It is important to highlight that after 7 days, about 10-15% of the herbicide is still adsorbed on the support and that the prolonged release of Al-MMT is confirmed also when simulating soil salinity conditions. Furthermore, the slower kinetic in acidic conditions (as discussed in the “Desorption tests in simulated acid rain solution” paragraph) is still confirmed in CaCl₂ solution (green and blue lines -obtained in 0.02M oxalic acid solution and in CaCl₂, pH3 respectively- have a similar trend and are well separated from red and black ones -obtained at neutral conditions-).

3.5 Computational treatment of release data through kinetic models

The release data of glyphosate from Al-MMT in soil simulating conditions (at both neutral and acid conditions) were fitted to different kinetic models, namely zero-order, first order and Korsmeyer–Peppas models described in Paragraph “Mathematical modelling of glyphosate release” (Experimental section). For each of the above-mentioned model, fitting equation, R² values and release constants were determined (Table 3).

Table 3. Modelling of glyphosate release data from Al-MMT in 0.01 CaCl₂, at pH 6.7 and pH

3

Kinetic model	Test conditions	Linearized fitting equation	R ²	K
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Zero-order	CaCl ₂ , pH 6.7	$C_t = 34.61 + 0.39t$	0.6526	0.39
	CaCl ₂ , pH3	$C_t = 19.45 + 0.43t$	0.8362	0.43
Pseudo first-order	CaCl ₂ , pH 6.7	$\log C_t = 1.80 - 0.005t$	0.6764	0.12
	CaCl ₂ , pH3	$\log C_t = 1.90 - 0.004t$	0.8398	0.09
Korsmeyer–Peppas	CaCl ₂ , pH 6.7	$\log C_t = 1.61 + 0.21 \log t$	0.9902	0.94
	CaCl ₂ , pH3	$\log C_t = 1.48 + 0.32 \log t$	0.9947	0.33

Results clearly show that glyphosate released from Al-MMT follows the Korsmeyer–Peppas kinetic equation. Indeed, for both neutral and acidic pH conditions, R² for zero-order and first-order model ranges from 0.65 to 0.84, while the first seven datapoints (representing release of up to approximately 60% of the loaded glyphosate) showed a R² value higher than 0.99 when computed by Korsmeyer–Peppas model.

Korsmeyer–Peppas *n* diffusional exponent was consequently calculated, obtaining *n*=0.21 and 0.32 for neutral and acidic pH conditions, respectively. Accordingly, the release of glyphosate from Al-MMT support appears to be diffusion controlled, following a quasi-Fickian model.

Finally, the release rate constant (*K*) is equal to 0.94 hours^{-0.21} and 0.33hours^{-0.32} for neutral and acid pH, respectively. The kinetic parameters obtained were used to calculate release of glyphosate according to the Korsmeyer and Peppas model (Figure 6) which was in satisfactory agreement with the experimental data.

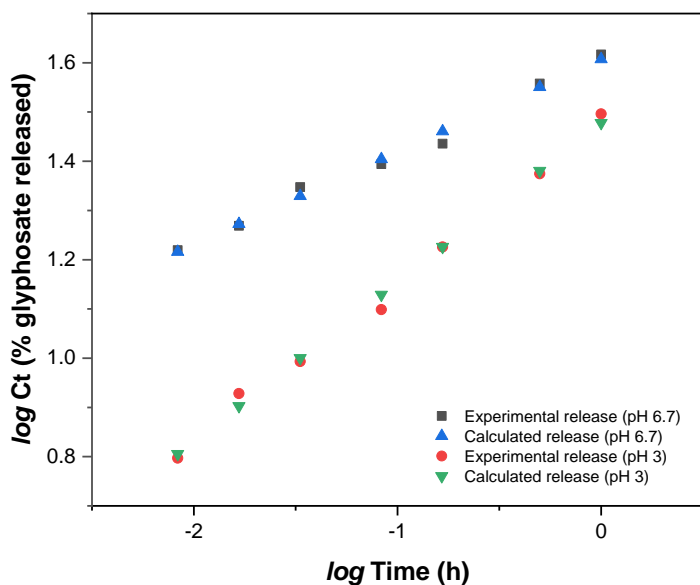


Figure 6. Release kinetics for glyphosate from Al-MMT. Experimental and calculated values according to linearized Korsmeyer and Peppas model.

To the best of our knowledge, no other studies investigating the kinetic models describing the release of glyphosate in controlled release applications are nowadays present in literature.

3.6 Real sample application

The efficacy of Al-MMT in the controlled release of glyphosate was finally tested in a bench scale plant. A laboratory self-made system was setup with a glass bottle filled with a known aliquot of tap water (typically used for irrigation) and soil according to the procedure previously described (see “Water/soil bench-scaled system” paragraph in Materials and Method Section, §2.7). Through this apparatus, the release of the herbicide was assessed considering not only the dissolution in water medium, but also the competitive adsorption equilibrium of soil, thus simulating a real application in

field or in a flowerpot. Releasing performances of impregnated Al-MMT were compared with those of a glyphosate commercial formulation and both kinetic plots are represented in Figure 7:

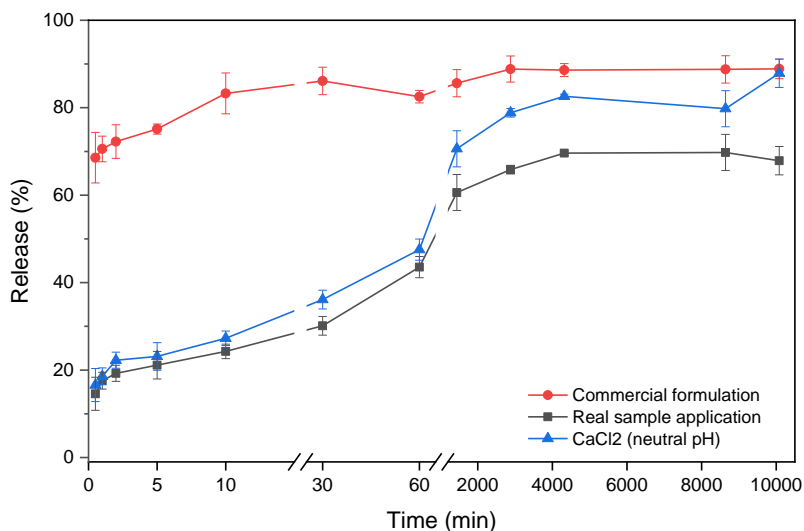


Figure 7: Desorption profile of glyphosate in bench scaled system (tap water/soil suspension, pH 6.8) from Al-MMT. Releases from glyphosate commercial formulation and from Al-MMT in CaCl₂ media, at pH 6.7 were compared. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

As shown by the dissolution curves, the bench system confirmed the good performances of Al-MMT as support for the prolonged release of glyphosate, with about 40% of the herbicide still retained after 3 days. The presence of a complex matrix such as real soil particles does not significantly affect the release trend. Moreover, the releasing kinetic of Al-MMT is clearly slower than the one obtained with the commercial formulation, which was almost quantitatively dissolved within 30 seconds after its application (89%). It should be remarked how, in the presence of soil

particles, the observed final release of glyphosate applied as commercial formulation is less than 100%, probably due to the herbicide adsorption by the soil particles [57].

4. Conclusions

Mesoporous silica and clay supports were innovatively presented as releasing systems of glyphosate for application in soils. This practice has the advantage to avoid air-dispersion pollution and worker exposure to glyphosate. This study highlighted that the enhancement of interactions between the support and glyphosate is of paramount importance to achieve a prolonged release of the herbicide. In this regard, the Al-MMT system proved to be the most promising encapsulating support due to: i) Al-glyphosate complexation (through phosphorous moiety); ii) electrostatic interactions between glyphosate and clay surface. Release performances of Al-MMT support (about 10-20% of glyphosate still retained on the support after 7 days) were confirmed both in ultrapure water, and in experimental conditions simulating acid rains and soil composition and was poorly affected by any competitive interaction between the Al-MMT surface and other species. The non-uniform particle size distribution of Al-MMT promoted a semi-Fickian diffusion mechanism which is responsible for the release of glyphosate from the support, as described by the Korsmeyer–Peppas equation (n diffusion exponential < 0.5). The bench scale application of Al-MMT in a tap water/ soil suspension system fully demonstrated the applicability of Al-MMT in the prolonged release of glyphosate in real world applications.

Authorship contribution statement

Luca Rivoira: data validation and interpretation, conceptualization, manuscript writing and revision. **Stefano Frassati:** investigation and writing – original draft. **Silvia Cordola:** investigation. **Michele Castiglioni:** data validation and interpretation. **Barbara Onida:** data interpretation, manuscript revision and revision. **Silvia Ronchetti:** data interpretation, review and manuscript

editing and revision. **Irene Ingrando**: visualization; **Maria Concetta Bruzzoniti**: conceptualization, data interpretation, manuscript revision, funding acquisition.

Declaration of Competing Interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication.

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Encapsulation of the glyphosate herbicide in mesoporous and soil-affine sorbents for its prolonged release

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Abstract

The increase in herbicide consumption, in particularly glyphosate, is causing considerable health and environmental concerns, due to its possible carcinogenic effects. Indeed, its widespread and intensive use promotes its diffusion in the surrounding environment. Additionally, the operator's exposure to the herbicide is not negligible.

In this work the encapsulation of glyphosate into three selected, eco-friendly silica- and clay- based supports, namely SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT) to promote both a punctual application and a prolonged release of glyphosate is innovatively presented.

Preliminary, substrates were characterized pre and post encapsulation through XRD and nitrogen adsorption measurements, to assess the incorporation of the herbicide. Release studies were performed in aqueous matrices of different composition, namely ultrapure water, 0.02M oxalic pH 3 (simulating acid rains) and 0.01M CaCl₂ solution (simulating soil salinity). Within all these media, Al-MMT exhibited a slow-releasing mechanism, with about 10-20% of glyphosate still retained on the support after 7 days, ascribed to complexation and electrostatic interactions.

Three different kinetic models usually applied within controlled-releasing processes, i.e. zero order, pseudo-first order and Korsmeyer–Peppas models, were used to describe glyphosate release from Al-MMT in CaCl₂ solutions, with Korsmeyer–Peppas model providing the best fit to experimental data ($R^2 > 0.990$). Finally, a water/soil bench-scaled system was efficiently tested, confirming the successfully applicability of Al-MMT in the prolonged release of glyphosate in real systems.

1. Introduction

Weed control is the botanical component of pest control that is used to prevent weeds from reaching a matured crop which is ready for cultivation [1]. Both physical and chemical methods are exploited to reduce weeds that are harmful to agricultural plants and fodder. Among them, herbicides are the dominant tool used for weed control in modern agriculture.

Nowadays, it is recognized that, to ensure the effectiveness of crop production, herbicides are often applied at exceeding dosages [2] and that current formulations generally release the compound into the environment practically instantaneously [3].

In the light of the information described above, a wide use of herbicides is evident, thus leading all the countries of the world to face different problems, such as the rapid evolution of herbicide-resistant weeds [4, 5], the environmental impact of these compounds, [6], and the impact on human health, with particular attention to worker exposure [7, 8], with 170,000 workers worldwide employed in the agricultural died every year. On these incidences, a correlation between deaths and exposure to toxic pesticides through spray, drift and direct contact cannot be excluded [9].

In order to prevent the above-mentioned issues and given the public pressure to reduce the overall pesticide use, new integrated weed management strategies are now strongly encouraged [10, 11]. Among these, an important part is devoted to the development of new methods for the application of herbicides on soils.

Among the several herbicide formulations that are applied, glyphosate is probably the most used in the world (about 720k tons production in 2012) [12]. Glyphosate (N-(phosphonomethyl)glycine) is a broadspectrum post-emergence herbicide used both in agriculture and for the conservation of green spaces, such as parks and gardens [13]. The more common methods of glyphosate use include broadcast, aerial, spot, and directed spray applications [14]. It should be remarked that despite glyphosate is typically spread on leaves, its absorption through roots has been clearly assessed [15] and application to soils are also reported, i.e. for fungicidal aims [16].

Despite its huge consumption, glyphosate has been the subject of controversial discussions over its impact on the environment and human health in recent years, with IARC (International Agency for Research on Cancer) classifying glyphosate as *a probable human carcinogen compound* (class 2A), oppositely to EFSA (European Food Safety Authority) stating that this herbicide *is unlikely to pose a carcinogenic hazard to humans*.

Despite this still-open discussion, on December 12, 2019 European Union renewed the licence for the sale of glyphosate for five years [17], even if some countries (for example Italy) has already introduced some restrictions on the use of this herbicide [18].

The impact of glyphosate on the environment has been extensively studied, as traces of glyphosate and its metabolites could be found both in water basins, in soils and even in the atmosphere [19]. Therefore, selected approaches are nowadays exploited to face the emergency caused by the use of glyphosate. Most of them are post-use remedies, and are mainly based on the development of new technologies for the removal of the herbicide from the environmental compartments [20, 21]. However, it is also appropriate to evaluate some approaches defined "a priori" which, on the contrary, are based on the reduction of the quantity of glyphosate released into the environment.

The incorporation of active formulations inside specific carriers to obtain a controlled release in the environment has been extensively explored for agricultural applications, in order to set-up the concentration of the active principle within a range spanning from the minimum effective concentration to the maximum concentration safe for the operator [22]. Applications reporting the encapsulation of fungicides [23], herbicides [24], insecticides [25], acaricides [26], as well as of compounds intended for the stimulation of plant growth and productivity [27] are frequently presented in the scientific literature. Conversely, research concerning glyphosate is under-investigated and light controlled [28] and supramolecular [29] systems are the only solutions proposed.

Mesoporous silica and clay based materials exhibit adsorption properties that were exploited for the preparation of sorptive substrates [30, 31] and in water remediation technologies [32, 33]. In

particular, the removal of herbicides using both types of supports through selective bonds between silica or clay supports with the active compounds is demonstrated [34].

Hence, this work aimed at the innovative encapsulation of glyphosate into selected silica- and clay- based supports. The encapsulation of the herbicide allows the application of the loaded support, promoting both a punctual application and the controlled release of glyphosate, thus limiting human exposure to glyphosate, during application. To the best of our knowledge, this manuscript represents the first study specifically devoted to the encapsulation of glyphosate into mesoporous sorbents, which indeed have a structure affine to the composition of the soil.

For this study, three different types of environmental-friendly mesoporous silica and clay-based supports were selected, namely: SBA-15, montmorillonite (MMT) and Al pillared montmorillonite (Al-MMT). MMT and Al-MMT can be also considered low cost and then their use appears feasible in the proposed application. After physicochemical characterization of the pre- and post-impregnated supports, tests on the release of glyphosate were performed simulating different environmental conditions, such as acid rains or soil leaching. Data obtained within release tests were fitted to kinetics models typically used to describe desorption of active principles from mesoporous supports. Finally, the sorbent showing the best releasing performances was chosen for a real sample application, in a water/soil bench-scaled system.

2. Experimental

2.1 Materials and reagents

A highly stable mesoporous silica sieve (Santa Barbara Amorphous, hereafter called SBA-15), montmorillonite K-10 (MMT) and Al pillared montmorillonite (Al-MMT) were purchased from Sigma-Aldrich (Darmstadt, Germany).

Glyphosate, sodium hydroxide solution (grade >98%), ethanol, hydrochloride acid (40%), oxalic acid (98%) and calcium chloride were from Sigma-Aldrich (Darmstadt, Germany).

High purity water (18.2 MΩ cm resistivity at 25 °C), produced by an Elix Milli Q Academic system (Millipore, Vimodrone, MI, Italy) was used for standard and eluent preparation.

2.2 Instrumental setup and calibration

The release profiles of glyphosate from the tested substrates were evaluated by means of suppressed ion chromatography as recently optimized by our research group [20]. A DX-100 ion chromatograph (25-μL injection loop) from Dionex, Thermo Scientific, (Sunnyvale, CA, USA) equipped with a conductivity detector was used. An IonPac AG16 (50 × 4 mm) and IonPac AS16 (250 × 4 mm) were used as guard and analytical columns, respectively. Mobile phase was 35 mM NaOH at a flow rate of 1.0 mL/min. Detection was performed by electrochemical suppressed conductivity (100mA current set-up) using a 4-mm ESRS-300 membrane suppressor. Chromatographic data were collected by PeakNet 2.8 software.

For calibration curve, a 100 mg/L glyphosate stock solution was used to prepare standard solutions (six levels, from 0.5 to 15 mg/L). Each level was injected in triplicate and a new calibration curve was run, weekly. Limits of detection and limits of quantifications of the chromatographic method were calculated according to Shrivastava and Gupta and were 0.1 mg/L and 0.3 mg/L, respectively [35].

2.3 Impregnation of the supports with glyphosate

The impregnation of supports with glyphosate was achieved using water as solvent through the incipient wetness impregnation technique [36], by which a volume of a solution containing the active ingredient to be incorporated is put in contact with the support itself. Consequently, the solution is forced to spread by capillary within the available pores, by means of a manual or a

mechanical mixing. Finally, the impregnated material is dried as to evaporate the excess of solvent and to allow the deposition of the desired molecules inside the support.

In detail, a saturated solution of glyphosate was prepared by dissolving 0.4 g of glyphosate in 33 mL of water (solubility=12 g/L, at room temperature [37]). Subsequently, 1 mL of such solution was added dropwise to 0.6 g of each support, thus obtaining a homogenous slurry, which was finally oven dried at 60°C for 24 hours. The impregnation procedure was performed at room temperature and was repeated until the glyphosate saturated solution was totally consumed. The procedure allowed to obtain 40% glyphosate impregnation in respect to the total weight of the support.

2.4 Physicochemical characterization of the supports pre- and post-impregnation

X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert Powder (Cu K α radiation) diffractometer. The measurements were performed by means of a circular sample holder with diameter of 30 mm and thickness of 2 mm. Field Emission Scanning Microscopy (FESEM) images were recorded with a Merlin instrument (Zeiss, Germany). Nitrogen adsorption isotherms were measured using a Quantachrome (FL, USA) AUTOSORB-1 instrument. Prior to nitrogen adsorption, samples were outgassed (393 K, 5 h). BET specific surface areas (SSA) were calculated in the relative pressure range 0.04–0.1.

2.5 Release of glyphosate from supports in aqueous solutions

The release of encapsulated glyphosate from the different tested supports in aqueous solutions, was evaluated simulating different environmental conditions. In detail, 0.25 g of each impregnated material was put in contact with 15 mL of the following aqueous solutions: i) ultrapure water, pH 6.5; ii) 0.02 M oxalic acid (pH 3), to simulate acid rains; iii) 0.01 M CaCl₂ solution, to simulate soil salinity (experiments were performed both at neutral and acidic pH). The suspension was stirred in an orbital shaker up to 7 days at room temperature, withdrawing 100 μ L-aliquots from each solution at scheduled times, namely: 0 and 30 seconds, 1, 2, 5, 10, 30, 60, 1140 (1 day), 2880 (2 days), 4320 (3

days), 8640 (6 days) and 10080 minutes (7 days). The cumulative sampled volume was less than 5% of the initial volume (15 mL), thus it can be assumed that the influence of the volume change on the release pattern is negligible. Release tests were performed separately for each support, in order to avoid any competitive equilibrium, and were repeated in triplicates.

Each sampled solution was then diluted 1:1000 with ultrapure water prior to IC analysis. The concentration of the glyphosate released (C_r) was derived through the calibration curve previously commented. The percentage of glyphosate released (*Release %*) was calculated according to the following equation:

$$Release\% = \left(\frac{1000 * C_r}{C_{max}} \right) * 100.$$

Where C_{max} is the maximum concentration that could be released from each support, according to the encapsulation procedure and the nominal glyphosate content (i.e. 40 % w/w), namely 6400 mg/L. This concentration was chosen to match the content of glyphosate in commercial formulations (e.g. 64-66% for granular RoundUp product) in consideration of the amount of commercial product to be applied in real applications (about 10 g of granules per liter, according to the manufacturer indications).

2.6 Mathematical modelling of glyphosate release

The profiles of glyphosate release from the studied supports were mathematically modelled to better understand the dissolution profile. Within this work, several models were evaluated, as hereafter listed. Even if all models were originally developed for drug delivery from polymeric and non-polymeric supports, they are commonly applied for the release of herbicides [38, 39] as well.

Zero-order model (*Release %* vs. time) [40]

The release rate is supposed to be independent from the concentration of herbicide, And the same amount of compound is expected to be released per unit of time, according to eq. 1.

$$C_t = C_0 + K_0 t \quad (1)$$

where C_t is the amount of herbicide (mg/L) dissolved at the time t (expressed in hours), C_0 is the initial amount of the herbicide dissolved in the solution and K_0 is the zero-order release constant, expressed as mg/L/h.

Pseudo first-order model (log of *Release %* vs. time) [41]

Differently to the zero-order model, in the first-order kinetic, the release rate depends on the concentration. The linearized model is expressed by eq. 2:

$$\log C_t = \log C_0 - Kt/2.303 \quad (2)$$

where C_t is the concentration of herbicide (mg/L) released at t time (expressed in hours), C_0 (mg/L) is the initial dissolved concentration of herbicide in the media and K is first order constant (1/hour).

Korsmeyer and Peppas model (log of *Release %* vs. log of time) [42]

The Korsmeyer-Peppas model (eq. 4) can be used to discriminate between Fickian diffusion or non-Fickian (anomalous) diffusion [43]. The linear relation is expressed by eq. 3

$$\log C_t = \log K + n \log t \quad (3)$$

where C_t is the concentration of drug released at time t (mg/L), K (hour⁻ⁿ) is the release rate constant and n is the diffusional exponent (adimensional). This kinetic equation is claimed valid only for the first 60% of the released active principle [42].

For a dispersed, non-swellable system, the value of n gives an indication of the release mechanism, as hereafter listed [44]: i) $n < 0.5$, quasi-Fickian diffusion, ii) $n = 0.5$, Fickian diffusion mechanism, iii) $0.5 < n < 1$, non-Fickian diffusion, iv) $n = 1$, case II transport (zero-order release), v) $n > 1$, super case II transport.

It should be noted that for $n=0.5$, a Fickian diffusion is present. Accordingly, eq. 3 simplifies into the Higuchi's equation (eq.4):

$$C_t = K_H t^{0.5} \quad (4)$$

where C_t is the amount of drug released (mg/L) at time t (expressed in hours) and K_H is the release rate constant of H (hour^{-1/2}).

2.7 Water/soil bench-scaled system

The release of glyphosate from the most promising support among the four tested (Al-MMT) was evaluated in a real soil/water system and compared in parallel with the release of glyphosate from a commercial formulation. Soil was collected from a public garden in the town of Torino (Valentino Park) and was chosen to have the representative composition of typical soils intended for horticulture uses [45], where glyphosate is mostly employed. In detail, 0.25 g of each formulation was added to 15 g soil/15 ml tap water dispersion in a glass bottle. pH of the suspension was measured and was equal to 6.8. At selected times after herbicide application (from 0 min to 7 days, as for the water release studies), the bottles were hand-shaken, the contents were allowed to settle, and 100 μ L of the supernatant solution were filtered and analysed by IC to determine the glyphosate concentration released. The periodic sampling of such a small amount of supernatant was assumed not to have any influence on the release pattern. Release kinetics were evaluated in triplicate.

3. Results and Discussions

3.1 Physicochemical characterization

The Incipient Wetness Impregnation technique is a protocol frequently exploited for the encapsulation of active principles in supporting materials, since it does not require specific reagents or procedures, and since it guarantees quantitative impregnation of the supports [6].

To investigate how glyphosate was encapsulated in the tested materials, physicochemical characterization of SBA-15, MMT and Al-MMT was performed.

Particle size and morphology of SBA-15, MMT and Al-MMT were evaluated by FESEM analysis (Figs. S1, S2 and S3 in the Supplementary Material, respectively). MMT and Al-MMT are characterized by irregular and heterogenous particles (with size ranging roughly from about 40 nm to 200 nm). Conversely, SBA-15 showed its typical hexagonal, elongated particle shape, with length from sub-micron size up to a few μ m.

Specific surface area (SSA_{BET}) and pore volume of each substrate, obtained by nitrogen sorption analysis before and after impregnation (Figure S4, S5 and S6 in the Supplementary Material) are reported in Table 1.

Table 1. Specific surface area (SSA) and pore volume of the four tested materials, before and after the encapsulation of glyphosate. Brunauer–Emmett–Teller (BET) model was used for calculations.

	SSA_{BET} (m^2/g)	Pore volume (m^3/g)
SBA-15	701	0.99
SBA-15 impregnated	492	0.74
MMT	279	0.42
MMT impregnated	83	0.15
Al-MMT	250	0.26
Al-MMT impregnated	6	0.017

The three sorbents cover a wide range of porosity (from 0.26 to 0.99 m^3/g pore volume and from 250 to 700 m^2/g SSA).

The impregnation with glyphosate resulted, for all the supports, in a significant modification of nitrogen adsorption-desorption isotherms (Figure S4, S5 and S6 in the Supplementary Material) and a reduction of SSA and pore volume (Table 1). These results indicate the location of glyphosate molecules inside the mesopores of the materials. This evidence is dramatic for Al-MMT (around 98% and 96% reduction of SSA and pore volume, respectively), suggesting that in this case the original mesoporous structure has been fully occupied by the herbicide. Indeed, the adsorption-desorption isotherms of N_2 on Al-MMT (Figure S4) reveal that the hysteresis loop, typical of disordered mesoporous materials, almost disappeared after the inclusion of glyphosate (red-triangled line).

The almost complete filling of pore volume for Al-MMT by glyphosate, at variance with SBA-15 and MMT, is in agreement with the lowest pore volume measured for Al-MMT ($0.26 \text{ m}^3/\text{g}$) when compared to those of SBA-15 ($0.99 \text{ m}^3/\text{g}$) and MMT ($0.42 \text{ m}^3/\text{g}$), considering that the same amount of glyphosate (0.40 g) per gram of support is present in the three impregnated materials.

In order to characterize the glyphosate in SBA-15, MMT and Al-MMT, XRD measurements were also performed (Figure 1).

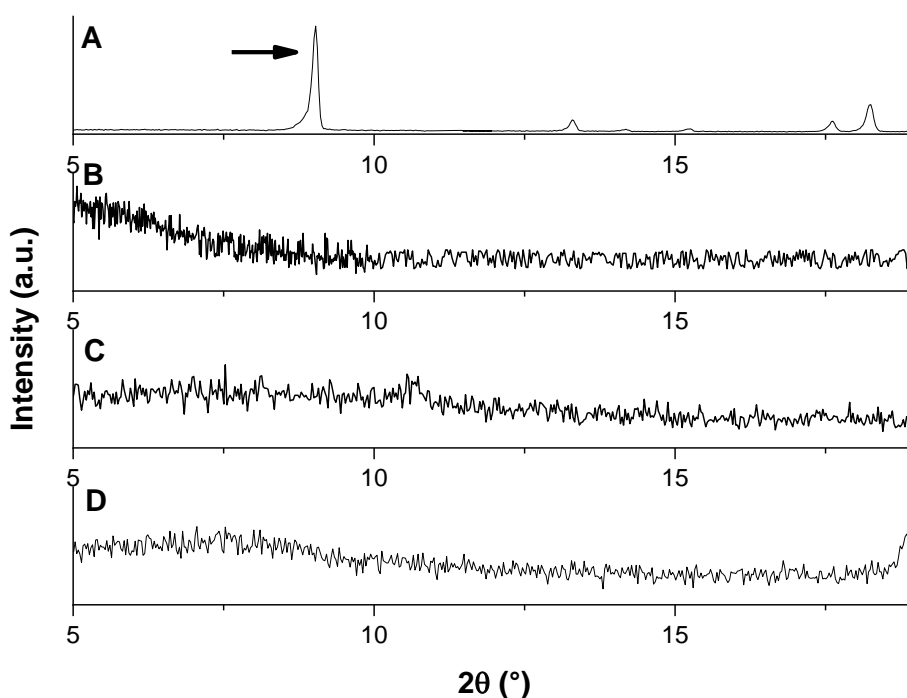


Figure 1. XRD patterns of glyphosate (A) and post-impregnated support: B - SBA-15, C- MMT, D- Al-MT. Black arrow points the main peak of crystalline glyphosate ($2\theta = 8.9^\circ$)

Results showed that the main peak of crystalline glyphosate ($2\theta = 8.9^\circ$, Fig.1A) is absent for all sorbents (1B, 1C, 1D). The lack of crystalline glyphosate signal is indicative for a complete amorphization of glyphosate. This is ascribed to the location of molecules inside materials mesopores, preventing crystallization [46] , and to their interaction with the surface sorbents.

The location of glyphosate molecules inside mesopores was confirmed by small angle XRD patterns (see Supplementary Material). In details, to what concern SBA-15 a decrease of the intensity of the

peak (100) is observed (Figure S7), being indicative of the pore filling, in agreement with the decrease of the scattering contrast between the pores and the walls [47]. As far as MMT (Figure S8) and Al-MMT (Figure S9) are concerned, the location of glyphosate molecules in the interlayer spacing of the clays is evidenced by the vanishing of the typical basal peak (related to d001), indicating that the interlayer has expanded due to the inclusion of glyphosate [46].

3.2 Desorption tests in ultrapure water

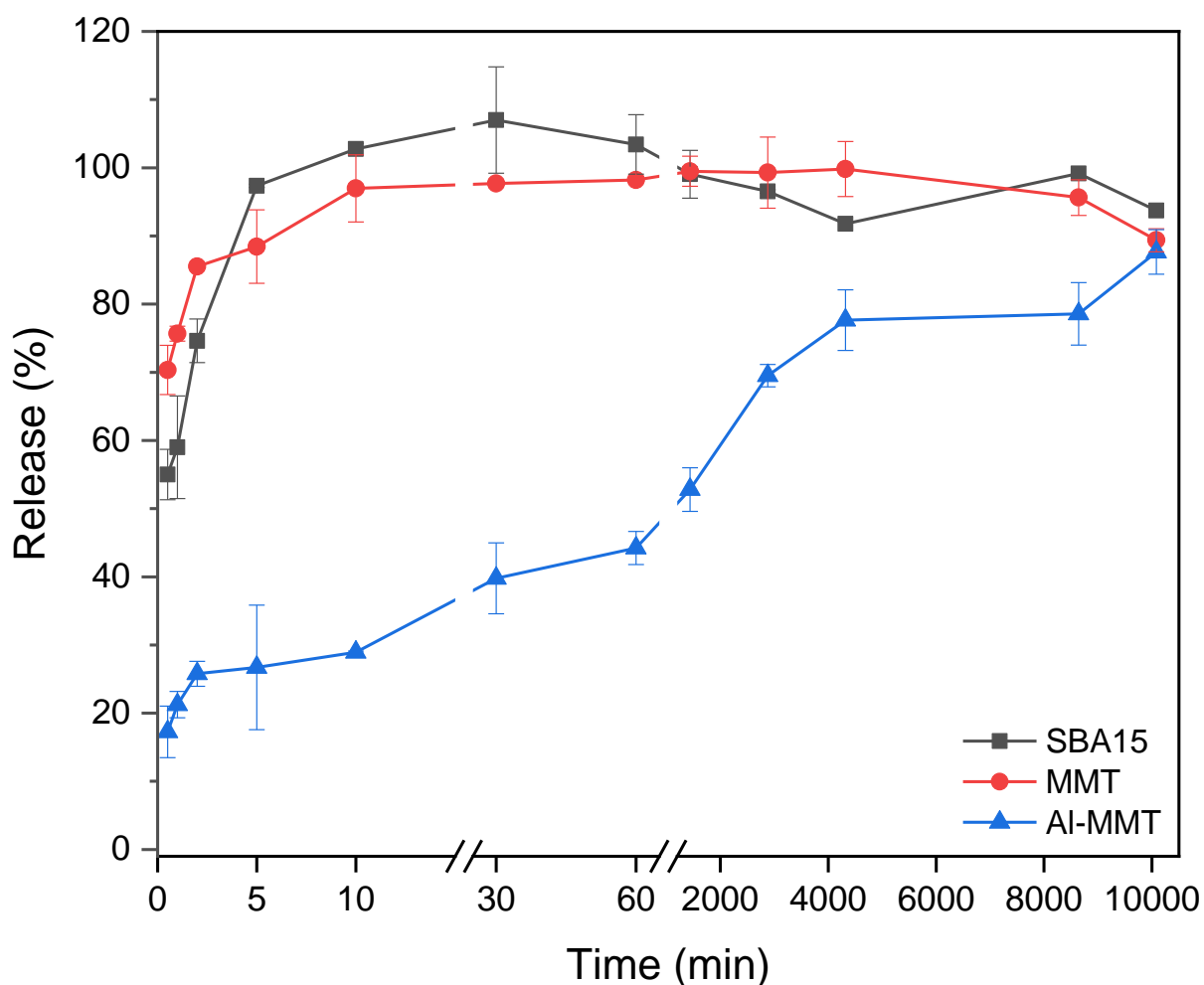


Figure 2. Desorption kinetics of glyphosate in ultrapure water from impregnated supports SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and

hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Ultrapure water (pH 6.5) was chosen as the first aqueous medium to be tested in order to avoid any competition of external species which could affect the release of glyphosate from supports.

The dissolution profiles of glyphosate in ultrapure water from SBA-15, MMT and Al-MMT are shown in Figure 2. The values on the left y-axis are given as percentages of the total amounts of glyphosate present in the dissolution vessel and, for all release curves, a 100% release corresponds to 6400 mg/L glyphosate concentration (for more details, see Experimental Section, §2).

When focusing on the short sampling times, it is observed that more than 50% of the glyphosate is released from both SBA-15 and MMT after only 30 seconds, reaching a quantitative release after 10 minutes. Hence, no prolonged release of the herbicide was observed for such sorbents. For SBA-15, less than 10% of the herbicide is still retained after 5 minutes and a complete release is observed after 10 minutes of contact with water, suggesting that weak interactions occur between glyphosate molecules and SBA-15 surface. This behaviour is in agreement with adsorption results previously obtained [20], showing negligible interactions between glyphosate and SBA-15 at neutral pH, whereas partial adsorption was observed only at acidic pH (see next paragraph).

A similar behaviour was observed also for MMT (96.9% release after 10 minutes). Despite several works report that selective interactions between glyphosate and MMT can occur, in particular at acidic pH (< 4) [48, 49], desorption tests here presented are performed at a neutral pH, which is higher than the point of zero charge (PZC) of MMT (about 3.4). In such conditions, the clay mineral surface is negative [48] and the negatively charged glyphosate [20] could hardly be retained by the negatively charged surface adsorption sites due to electrostatic repulsion. Such behavior is responsible for the fast and quantitative release rate of glyphosate within the short sampling time.

Differently to what previously discussed for MMT and SBA-15, the trend of Al-MMT indicate a slower kinetic release. Indeed, after 2 minutes only 28% (of impregnated glyphosate was released

in the solution from Al-MMT, suggesting that the interactions between the herbicide and the support are stronger than those occurring in SBA-15 and MMT. To explain this behavior, it should be mentioned that Al-MMT is characterized by the presence of Al³⁺ ions that could be complexed with glyphosate, mainly through phosphate-Al interaction [50], forming monomeric and dimeric complexes [51]. This interaction is, therefore, proposed to be responsible for the slower release of the herbicide from Al-MMT. As regards the releasing mechanism, it should be mentioned that the complexation constants of Al-glyphosate are lower than Al-H₂O constants [51]. Hence, a competition of water molecules, interacting with aluminium, could occur.

Al-MMT system exhibits a prolonged release of glyphosate which appears appealing for the proposed application. The slow release observed for Al-MMT is ascribed to strong interactions between glyphosate molecules and internal surface of the support. Moreover, the diffusion of glyphosate molecules from the internal pore structure may at same extent control the release. The location of glyphosate molecules in the interlayer spacing of the pillared clay is evidenced by the XRD pattern at small angles (Figure S6 in the Supplementary Material), as previously discussed. The release of glyphosate by Al-MMT is in agreement with the work of Siepmann and co-workers, in which the drug release was shown to be kinetically longer for supports in which the active principle was encapsulated in the material core [52].

The performances of Al-MMT (20% of the herbicide still inside the support after 7 days) were compared with those reported in the only two literature papers on the release of glyphosate. Data show that Al-MMT exhibits better or at least similar prolonged release performances (i.e. slower dissolution profiles) than biochar-attapulgite (quantitative glyphosate release of glyphosate after 2 hours) [28], and supramolecular organic guest intercalated layered double hydroxides (40% release after 24 hours) [29] systems, respectively.

3.3 Desorption tests in simulated acid rain solution

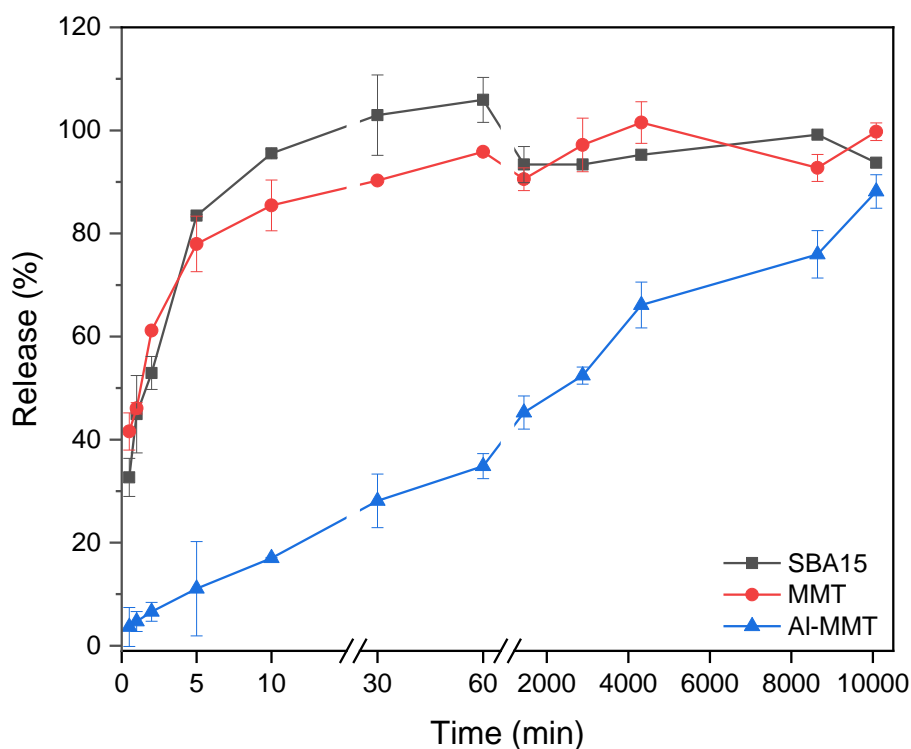


Figure 3. Desorption kinetics of glyphosate in 0.02M oxalic acid (pH=3) from SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Once assessed the desorption behaviours in ultrapure water, the same tests were replicated at pH 3, simulating worst conditions of rain acidity [53] (Figure 3).

The dissolution profiles of Figure 3 showed that, also at acidic conditions, Al-MMT was the only support characterized by a prolonged release of glyphosate (about 13% still retained after 7 days), with a partial slowdown of the kinetic in comparison to the one obtained in ultrapure water (Table 2, column A vs B). A slowdown was also observed for pure MMT (Table 2, column C vs D), despite this support quantitatively release glyphosate after 60 minutes.

Table 2. Comparison of glyphosate release up to 3 days between ultrapure water medium (UP) and 0.02M oxalic acid, pH3 (pH3). Gray cells show sampling times in which quantitative release of glyphosate is reached.

Glyphosate release (%)				
	Al-MMT		MMT	
	pH3 (A)	UP (B)	pH3 (C)	UP (D)
0.5 min	3.6	17.3	41.6	70.3
1 min	4.7	21.2	46.1	75.7
2min	6.6	25.8	61.2	85.5
5min	11.1	26.7	78.0	88.4
10min	17.0	28.9	85.4	97.0
30min	28.1	39.8	90.3	97.7
60 min	34.9	44.2	95.9	98.2
1 day	45.3	52.8	90.5	99.5
2 days	52.4	69.5	97.2	99.3
3 gg	66.1	77.6	101.5	99.8

To explain the slowdown of Al-MMT and MMT kinetics, both acid-base equilibrium of glyphosate and surface properties of montmorillonite should be considered. Indeed, at pH 3 glyphosate is present with a protonated carboxylic, and a monovalent phosphonic group (Figure 4A).

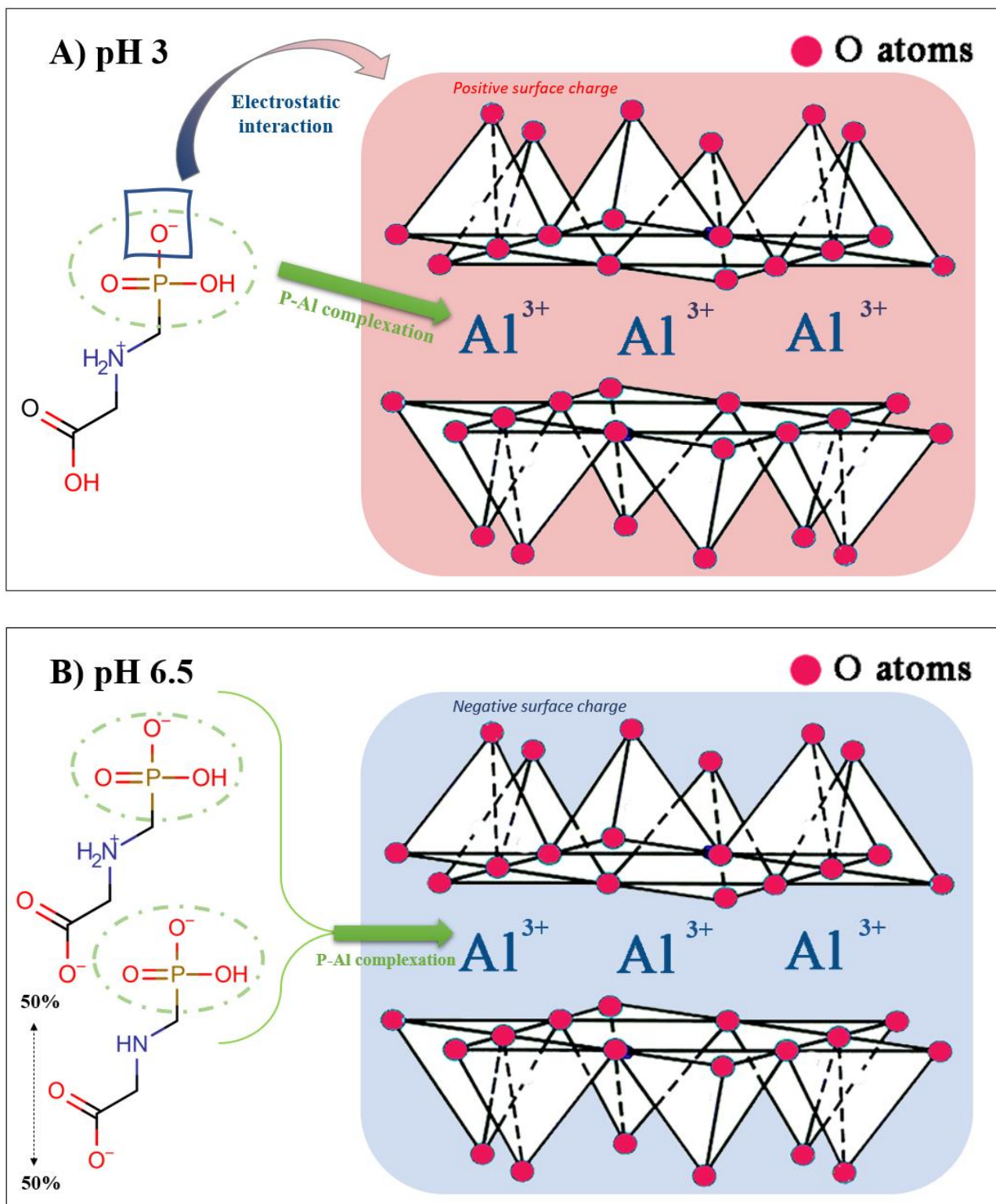


Figure 4. Surface charge of Al-MMT and chemical dissociation of glyphosate at pH 3 (A) and pH 6.5 (B). Main interaction occurring at both pH values are also highlighted.

Since pH conditions are lower than Al-MMT PZC (about 4.3 [54]), the surface of montmorillonite has to be considered positively charged (Figure 4A). Conversely, in ultrapure water (pH around 6.5) glyphosate is present with the same monovalent phosphonic group but with the deprotonated carboxylic, (Figure 4B) and the surface of montmorillonite has to be considered negatively charged, being above its PZC. Therefore, electrostatic repulsions occur in ultrapure water, which instead are not present at pH 3.

Summarizing, for Al-MMT at pH values close to neutrality, the effect of both P-Al interactions and electrostatic repulsion influence the release of glyphosate, thus justifying the lower retention of glyphosate, and hence the faster kinetic release, observed in respect to acidic pH conditions where only P-Al interactions occur. Moreover, despite the zwitterionic form of glyphosate at pH3, electrostatic attractive interactions between the negative phosphonic group and the positive surface of Al-MMT may give a further contribution to the retention, besides the complexation of Al³⁺ ions by glyphosate.

A fast release was observed for SBA-15 since more than 85% of glyphosate is released after 5 minutes. However, after 30 seconds about 35% release was observed at pH 3, against 55% in ultrapure water, thus supporting the role of surface charge also in the interaction between SBA-15 and negatively charged glyphosate. Indeed, pH 3 may be considered below the PZC of SBA-15 PZC (5.2), whereas at pH around 6.5 the surface of SBA-15 has to be considered mainly negatively charged [55].

3.4 Desorption tests in simulated soil conditions

Previous tests were performed without considering any competing species. However, the presence of the soil matrix can affect the release of glyphosate from encapsulating support. Competitive interactions between surface moieties and soil salts, such as calcium chloride [56], can be established, with charged species potentially promoting a faster release of the herbicide.

Experiments were performed on Al-MMT only, since MMT and SBA-15 were shown to exhibit a fast release, not compatible with prolonged applications. Glyphosate desorption from Al-MMT in 0.01M CaCl₂ solution was studied, roughly simulating the ionic strength of soil solutions [56].

Dissolution profiles obtained in 0.01M CaCl₂ at pH conditions acidic (pH=3) and close to neutrality (pH=6.7) are reported in Figure 5 (triangled blue- and squared black- lines, respectively), together with desorption profiles obtained in ultrapure water and oxalic acid solution (starred green- and pointed red- lines, respectively) for a better comparison.

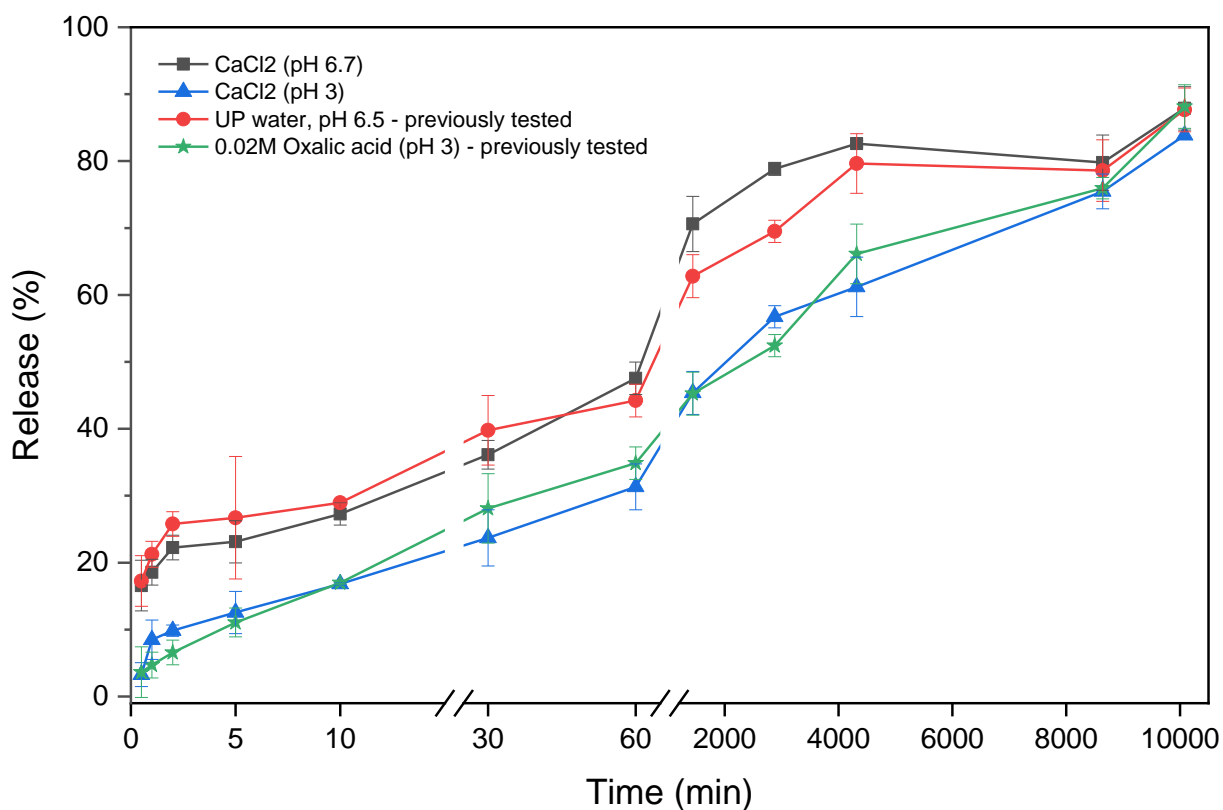


Figure 5. Desorption profiles of glyphosate 0.01M CaCl₂ solution, at acidic (pH 3) and almost neural (pH 6.7) conditions. Release percentage in ultrapure water (UP water) and 0.02 oxalic acid solution are overlaid. For an easier comprehension, sampling time is expressed both as minutes and

hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

Results confirmed that, within the standard deviation of the measurements, glyphosate release is not affected by CaCl₂, thus suggesting the absence of significant competitive interactions between Al-MMT and CaCl₂. It is important to highlight that after 7 days, about 10-15% of the herbicide is still adsorbed on the support and that the prolonged release of Al-MMT is confirmed also when simulating soil salinity conditions. Furthermore, the slower kinetic in acidic conditions (as discussed in the “Desorption tests in simulated acid rain solution” paragraph) is still confirmed in CaCl₂ solution (green and blue lines -obtained in 0.02M oxalic acid solution and in CaCl₂, pH3 respectively- have a similar trend and are well separated from red and black ones -obtained at neutral conditions-).

3.5 Computational treatment of release data through kinetic models

The release data of glyphosate from Al-MMT in soil simulating conditions (at both neutral and acid conditions) were fitted to different kinetic models, namely zero-order, first order and Korsmeyer–Peppas models described in Paragraph “Mathematical modelling of glyphosate release” (Experimental section). For each of the above-mentioned model, fitting equation, R² values and release constants were determined (Table 3).

Table 3. Modelling of glyphosate release data from Al-MMT in 0.01 CaCl₂, at pH 6.7 and pH

3

Kinetic model	Test conditions	Linearized fitting equation	R²	K
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<i>Zero-order</i>	CaCl ₂ , pH 6.7	$C_t = 34.61 + 0.39t$	0.6526	0.39
	CaCl ₂ , pH3	$C_t = 19.45 + 0.43t$	0.8362	0.43
<i>Pseudo first-order</i>	CaCl ₂ , pH 6.7	$\log C_t = 1.80 - 0.005t$	0.6764	0.12
	CaCl ₂ , pH3	$\log C_t = 1.90 - 0.004t$	0.8398	0.09
<i>Korsmeyer–Peppas</i>	CaCl ₂ , pH 6.7	$\log C_t = 1.61 + 0.21 \log t$	0.9902	0.94
	CaCl ₂ , pH3	$\log C_t = 1.48 + 0.32 \log t$	0.9947	0.33

Results clearly show that glyphosate released from Al-MMT follows the Korsmeyer–Peppas kinetic equation. Indeed, for both neutral and acidic pH conditions, R² for zero-order and first-order model ranges from 0.65 to 0.84, while the first seven datapoints (representing release of up to approximately 60% of the loaded glyphosate) showed a R² value higher than 0.99 when computed by Korsmeyer–Peppas model.

Korsmeyer–Peppas *n* diffusional exponent was consequently calculated, obtaining *n*=0.21 and 0.32 for neutral and acidic pH conditions, respectively. Accordingly, the release of glyphosate from Al-MMT support appears to be diffusion controlled, following a quasi-Fickian model.

Finally, the release rate constant (*K*) is equal to 0.94 hours^{-0.21} and 0.33hours^{-0.32} for neutral and acid pH, respectively. The kinetic parameters obtained were used to calculate release of glyphosate according to the Korsmeyer and Peppas model (Figure 6) which was in satisfactory agreement with the experimental data.

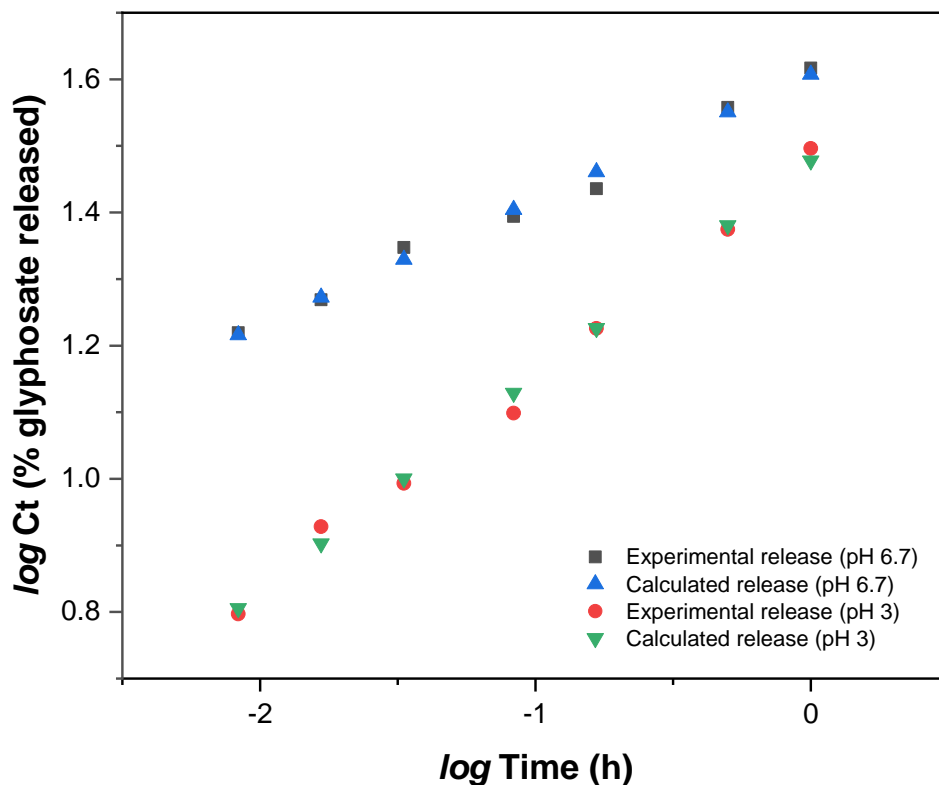


Figure 6. Release kinetics for glyphosate from Al-MMT. Experimental and calculated values according to linearized Korsmeyer and Peppas model.

To the best of our knowledge, no other studies investigating the kinetic models describing the release of glyphosate in controlled release applications are nowadays present in literature.

3.6 Real sample application

The efficacy of Al-MMT in the controlled release of glyphosate was finally tested in a bench scale plant. A laboratory self-made system was setup with a glass bottle filled with a known aliquot of tap water (typically used for irrigation) and soil according to the procedure previously described (see “Water/soil bench-scaled system” paragraph in Materials and Method Section, §2.7). Through this apparatus, the release of the herbicide was assessed considering not only the dissolution in water medium, but also the competitive adsorption equilibrium of soil, thus simulating a real application in

field or in a flowerpot. Releasing performances of impregnated Al-MMT were compared with those of a glyphosate commercial formulation and both kinetic plots are represented in Figure 7:

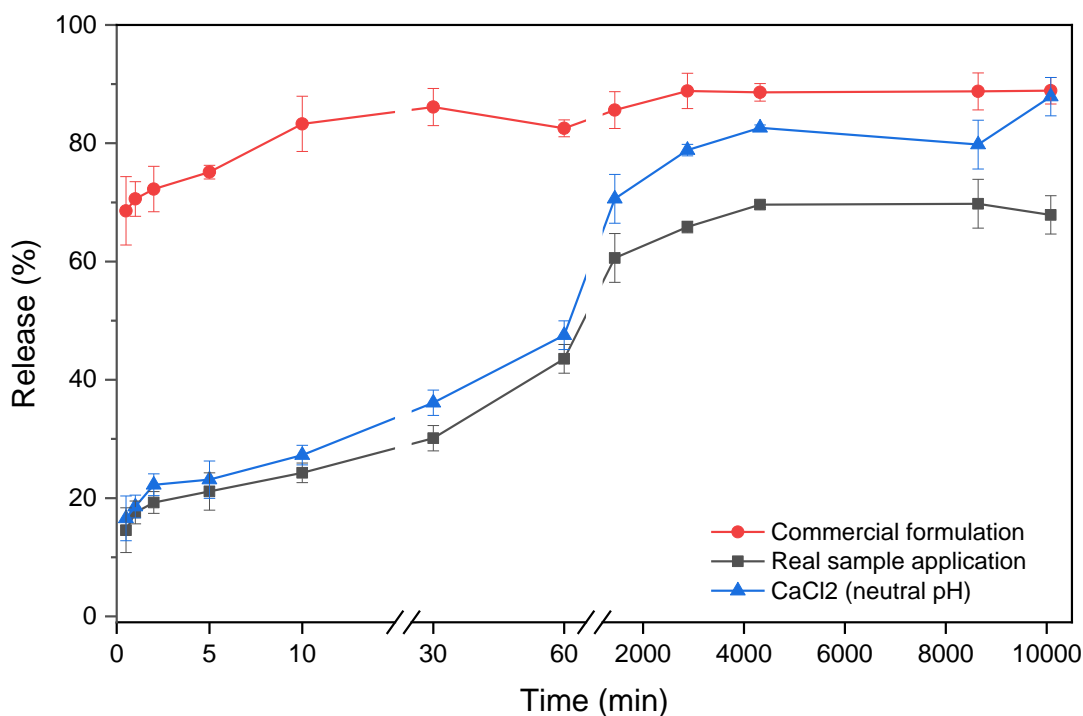


Figure 7: Desorption profile of glyphosate in bench scaled system (tap water/soil suspension, pH 6.8) from Al-MMT. Releases from glyphosate commercial formulation and from Al-MMT in CaCl₂ media, at pH 6.7 were compared. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

As shown by the dissolution curves, the bench system confirmed the good performances of Al-MMT as support for the prolonged release of glyphosate, with about 40% of the herbicide still retained after 3 days. The presence of a complex matrix such as real soil particles does not significantly affect the release trend. Moreover, the releasing kinetic of Al-MMT is clearly slower than the one obtained with the commercial formulation, which was almost quantitatively dissolved within 30 seconds after its application (89%). It should be remarked how, in the presence of soil

particles, the observed final release of glyphosate applied as commercial formulation is less than 100%, probably due to the herbicide adsorption by the soil particles [57].

4. Conclusions

Mesoporous silica and clay supports were innovatively presented as releasing systems of glyphosate for application in soils. This practice has the advantage to avoid air-dispersion pollution and worker exposure to glyphosate. This study highlighted that the enhancement of interactions between the support and glyphosate is of paramount importance to achieve a prolonged release of the herbicide. In this regard, the Al-MMT system proved to be the most promising encapsulating support due to: i) Al-glyphosate complexation (through phosphorous moiety); ii) electrostatic interactions between glyphosate and clay surface. Release performances of Al-MMT support (about 10-20% of glyphosate still retained on the support after 7 days) were confirmed both in ultrapure water, and in experimental conditions simulating acid rains and soil composition and was poorly affected by any competitive interaction between the Al-MMT surface and other species. The non-uniform particle size distribution of Al-MMT promoted a semi-Fickian diffusion mechanism which is responsible for the release of glyphosate from the support, as described by the Korsmeyer–Peppas equation (n diffusion exponential < 0.5). The bench scale application of Al-MMT in a tap water/ soil suspension system fully demonstrated the applicability of Al-MMT in the prolonged release of glyphosate in real world applications.

Authorship contribution statement

Luca Rivoira: data validation and interpretation, conceptualization, manuscript writing and revision. **Stefano Frassati:** investigation and writing – original draft. **Silvia Cordola:** investigation. **Michele Castiglioni:** data validation and interpretation. **Barbara Onida:** data interpretation, manuscript revision and revision. **Silvia Ronchetti:** data interpretation, review and manuscript

editing and revision. **Irene Ingrando**: visualization; **Maria Concetta Bruzzone**: conceptualization, data interpretation, manuscript revision, funding acquisition.

Declaration of Competing Interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication.

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Table 1. Specific surface area (SSA) and pore volume of the four tested materials, before and after the encapsulation of glyphosate. Brunauer–Emmett–Teller (BET) model was used for calculations.

	SSA_{BET} (m²/g)	Pore volume (m³/g)
SBA-15	701	0.99
SBA-15 impregnated	492	0.74
MMT	279	0.42
MMT impregnated	83	0.15
Al-MMT	250	0.26
Al-MMT impregnated	6	0.017

Table 2. Comparison of glyphosate release up to 3 days between ultrapure water medium (UP) and 0.02M oxalic acid, pH3 (pH3). Gray cells show sampling times in which quantitative release of glyphosate is reached.

Glyphosate release (%)				
	Al-MMT		MMT	
	pH3 (A)	UP (B)	pH3 (C)	UP (D)
0.5 min	3.6	17.3	41.6	70.3
1 min	4.7	21.2	46.1	75.7
2min	6.6	25.8	61.2	85.5
5min	11.1	26.7	78.0	88.4
10min	17.0	28.9	85.4	97.0
30min	28.1	39.8	90.3	97.7
60 min	34.9	44.2	95.9	98.2
1 day	45.3	52.8	90.5	99.5
2 days	52.4	69.5	97.2	99.3
3 gg	66.1	77.6	101.5	99.8

Table 3. Modelling of glyphosate release data from Al-MMT in 0.01 CaCl₂, at pH 6.7 and pH

3

Kinetic model	Test conditions	Linearized fitting equation	R²	K
<i>Zero-order</i>	CaCl ₂ , pH 6.7	$C_t = 34.61 + 0.39t$	0.6526	0.39
	CaCl ₂ , pH3	$C_t = 19.45 + 0.43t$	0.8362	0.43
<i>Pseudo first-order</i>	CaCl ₂ , pH 6.7	$\log C_t = 1.80 - 0.005t$	0.6764	0.12
	CaCl ₂ , pH3	$\log C_t = 1.90 - 0.004t$	0.8398	0.09
<i>Korsmeyer–Peppas</i>	CaCl ₂ , pH 6.7	$\log C_t = 1.61 + 0.21 \log t$	0.9902	0.94
	CaCl ₂ , pH3	$\log C_t = 1.48 + 0.32 \log t$	0.9947	0.33

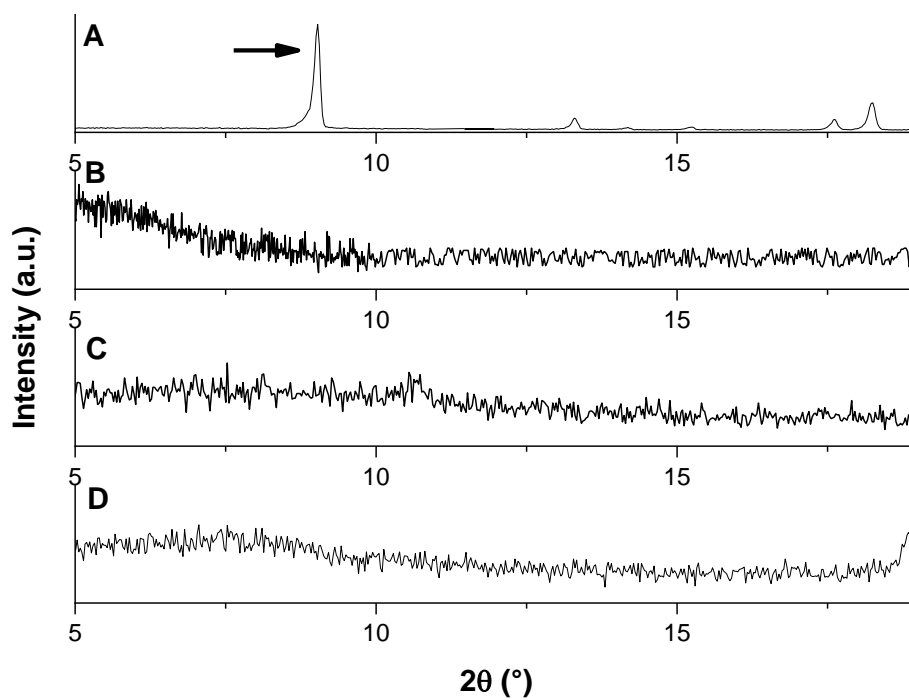


Figure 1. XRD patterns of glyphosate (A) and post-impregnated support: B - SBA-15, C- MMT, D- Al-MT. Black arrow points the main peak of crystalline glyphosate ($2\theta = 8.9^\circ$)

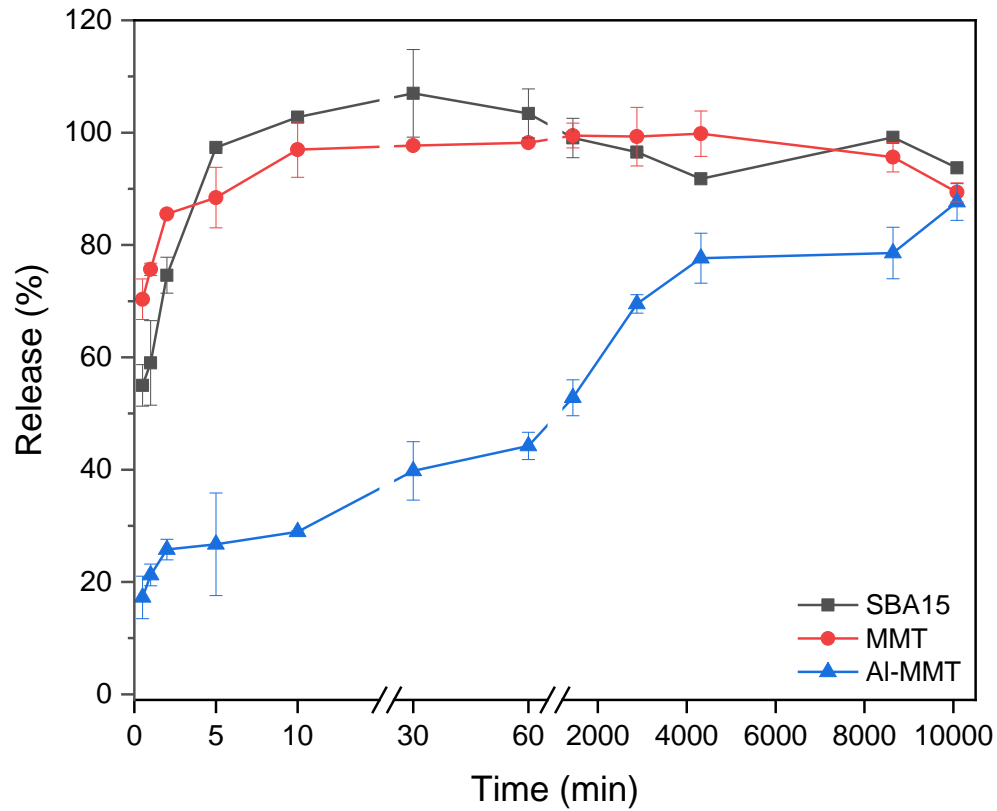


Figure 2. Desorption kinetics of glyphosate in ultrapure water from impregnated supports SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

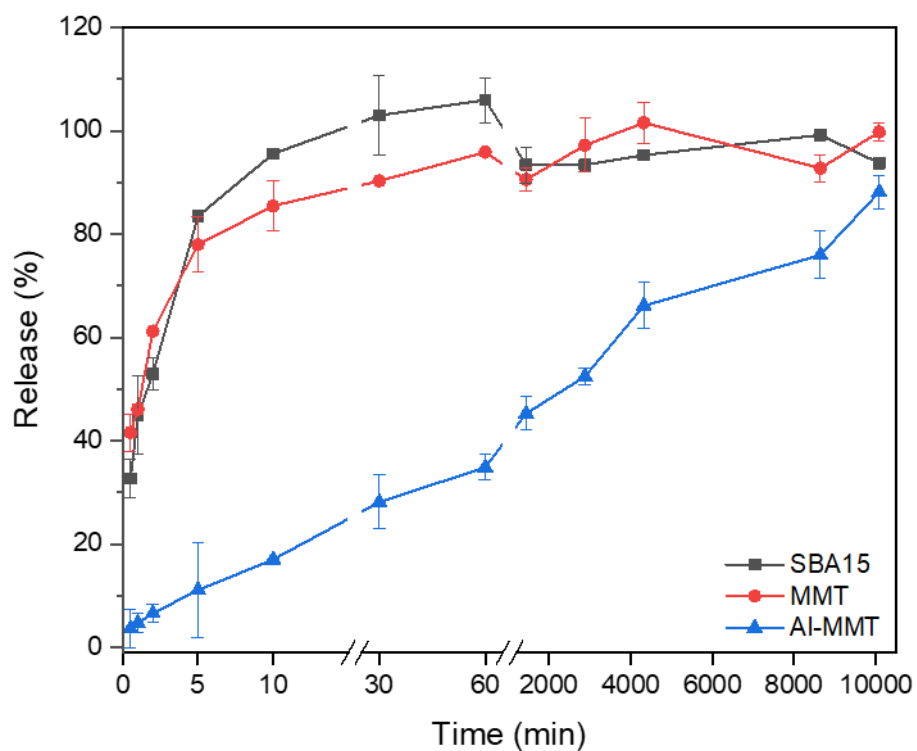


Figure 3. Desorption kinetics of glyphosate in 0.02M oxalic acid (pH=3) from SBA-15, MMT and Al-MMT. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

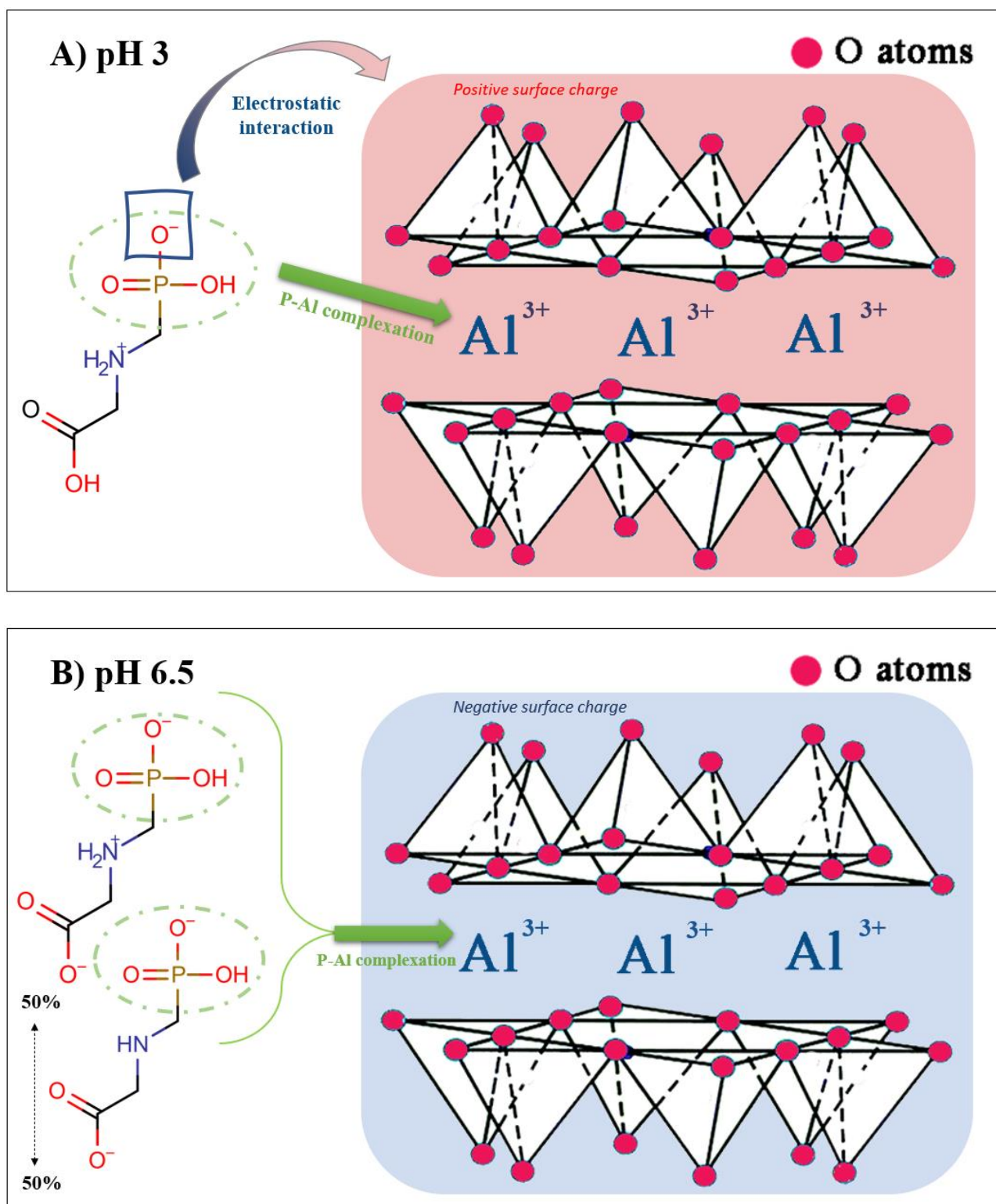


Figure 4. Surface charge of Al-MMT and chemical dissociation of glyphosate at pH 3 (A) and pH 6.5 (B). Main interaction occurring at both pH values are also highlighted.

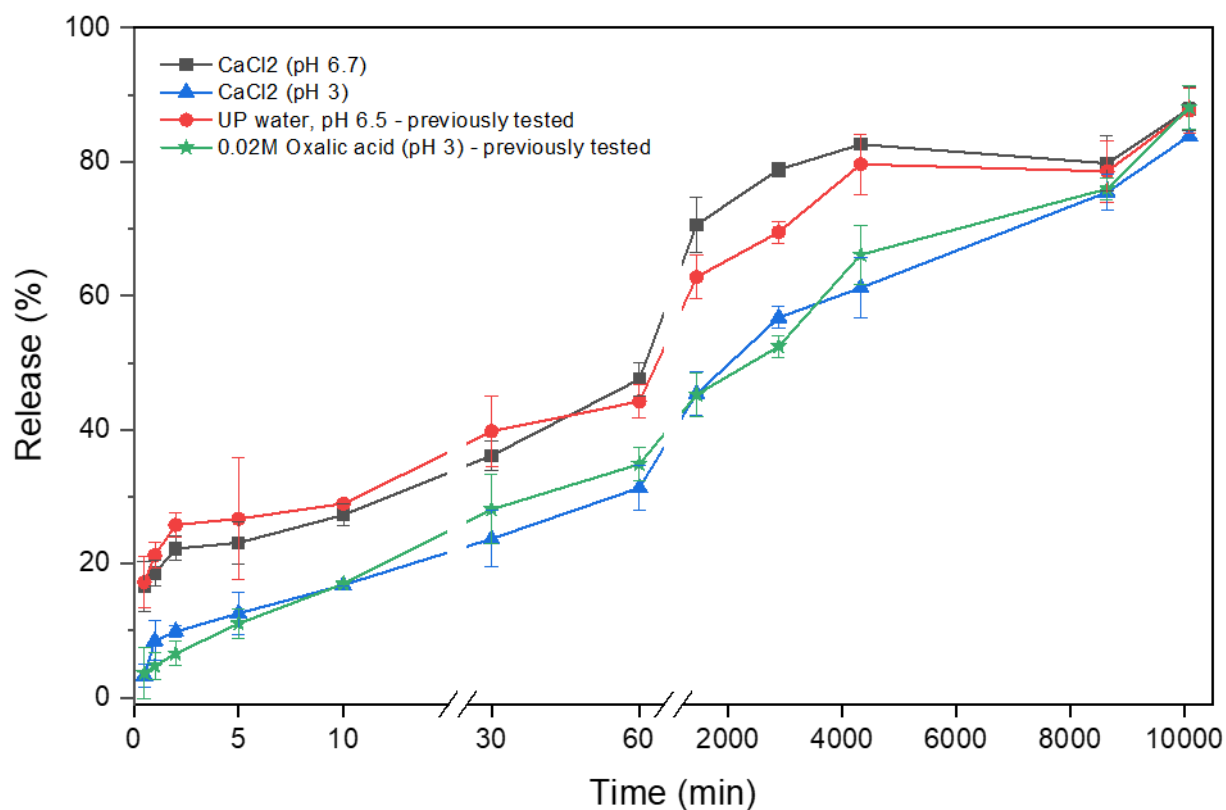


Figure 5. Desorption profiles of glyphosate 0.01M CaCl₂ solution, at acidic (pH 3) and almost neutral (pH 6.7) conditions. Release percentage in ultrapure water (UP water) and 0.02 oxalic acid solution are overlaid. For an easier comprehension, sampling time is expressed both as minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed in Experimental Section.

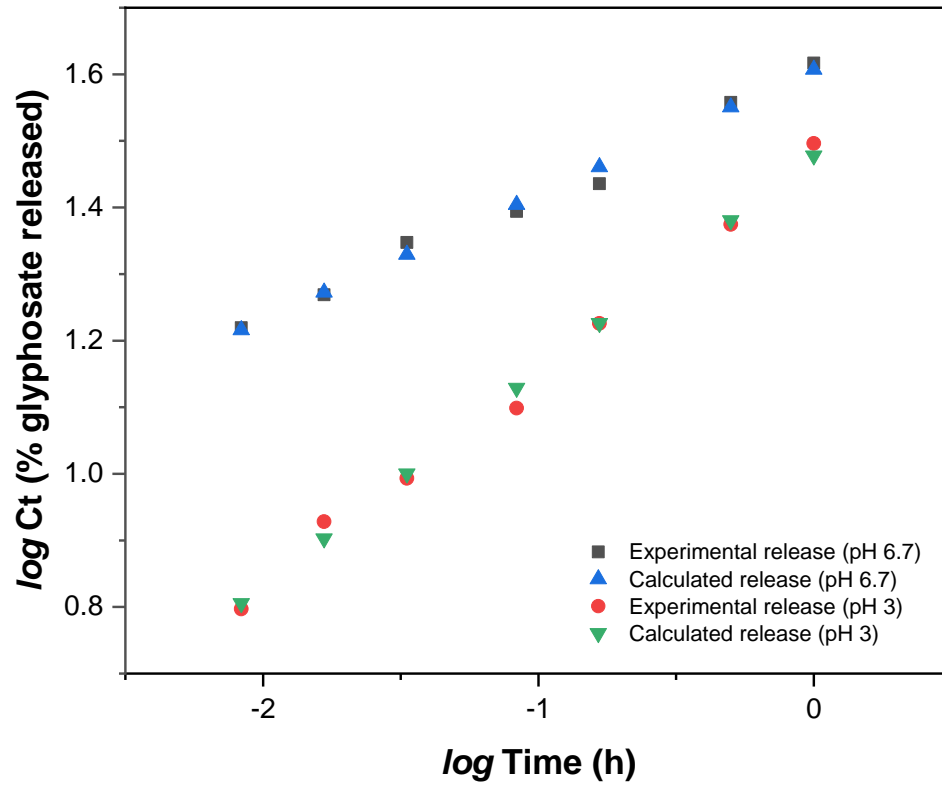
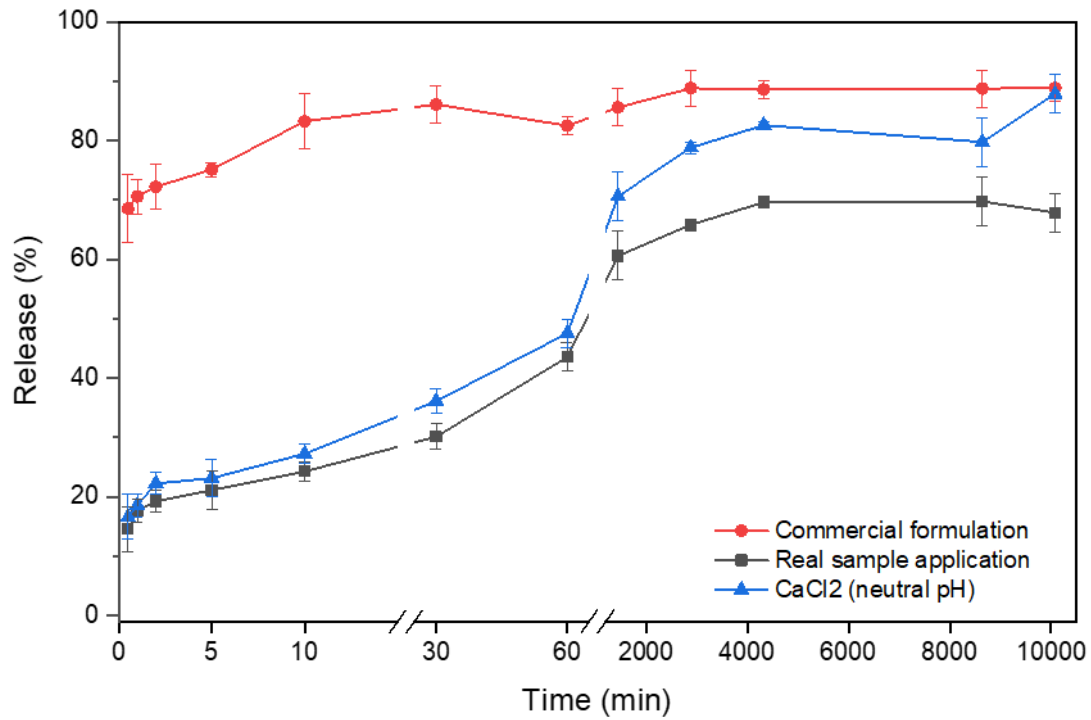


Figure 6. Release kinetics for glyphosate from Al-MMT. Experimental and calculated values according to linearized Korsmeyer and Peppas model.



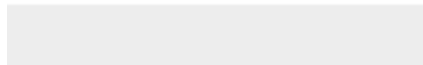
1

2 *Figure 7: Desorption profile of glyphosate in bench scaled system (tap water/soil suspension, pH*
 3 *6.8) from Al-MMT. Releases from glyphosate commercial formulation and from Al-MMT in CaCl₂*
 4 *media, at pH 6.7 were compared. For an easier comprehension, sampling time is expressed both as*
 5 *minutes and hours in the lower and upper X axis, respectively. Experimental conditions are detailed*
 6 *in Experimental Section.*

7



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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: