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Innovative wastewater treatment based on electrodeposited thin film: Systematic studies of interfacial processes between birnessite 2 and Mn(II) for a better efficiency

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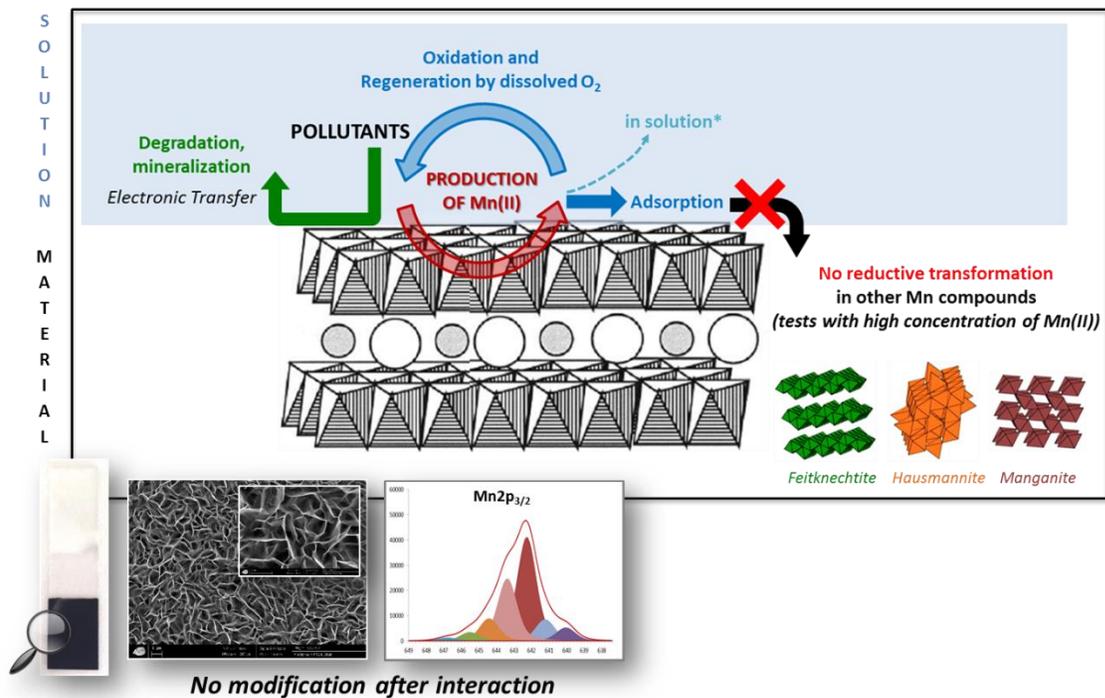
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GRAPHICAL ABSTRACT

***Electrodeposited birnessite thin film :
A robust material for the spontaneous degradation of persistent organic pollutants.***



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ABSTRACT

10 Electrodeposited birnessite thin films have remarkable properties for spontaneous degradation of
11 organic pollutants until mineralization via a complex mechanism of charge transfer reactions. But,
12 birnessite may be transformed into passivated material by reaction with Mn(II) species generated
13 during the reduction of birnessite due to oxidation of organic pollutants. Such modification could

1 imply a possible inhibition of the degradation process, a depreciated condition for future
2 applications. This paper focuses on the determination of the real robustness of electrodeposited
3 birnessite thin films and their quality for innovative wastewater treatment. Systematical studies
4 were performed with solutions containing different Mn(II) concentrations in presence and in
5 absence of oxygen to have unfavorable conditions. Samples were characterized at macroscopic
6 scales (SEM and XRD) in addition to a focused study on the chemical modification at the extreme
7 near surface by XPS. Open circuit potential (OCP) was also followed to complete the study.
8 Similar characterizations were performed after interaction with organic pollutants solutions. As a
9 result, nature and structure of the bulk and the near surface of birnessite stay unchanged after long
10 times even in absence of oxygen or in presence of organic pollutants at high concentrations,
11 proving their very good robustness and real interests for future applications.

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14 **KEYWORDS:** Electrodeposition; Manganese oxides; Depollution; Glyphosate; AMPA;
15 Pesticide.

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1 1. INTRODUCTION

2 Birnessite, a layered manganese oxide, is closely studied since many years in different
3 fields such as energy production and/or storage [1-3], or pollutants treatments [4-9]. Majority of
4 studies used birnessite powder, however electrodeposited birnessite thin films appear as very
5 interesting tools for wastewater treatment. For example, previous works have demonstrated the
6 high efficiency of such samples for eliminating heavy metals by sorption [8] or degrading and
7 mineralizing organic pollutants as dyes [10,11] and pesticides (e.g. glyphosate and AMPA, its
8 main by-product) [12] by spontaneous electronic transfers. These remarkable results were based
9 on interactions between solution and birnessite thin film in very soft conditions by a simple contact
10 between the film and the solution without causing damage [8,10-12]. Moreover, the yield and/or
11 the kinetic of the process degradation of organic pollutants can be largely even enhanced by
12 coupling with electrochemistry but with very low electrical input [13].

13 Birnessite thin films are synthesized by electrodeposition, which is a well-adapted method
14 to form adherent, crystallized and very homogeneous thin films in very reproducible conditions on
15 conductive substrates with a good control of the amount and the thickness [14-17]. The synthesis
16 is fast, performed in aqueous solution at room temperature, and at low costs. Moreover, the use of
17 material as thin films has many advantages for applications such as no filtration step after synthesis
18 and uses, and the possibility of regeneration and reuse of the material [8,10-13]. That is why, these
19 non-toxic material as thin films appear as very promising for developing efficient and eco-friendly
20 water depollution processes.

21 The high efficiency of this degradation treatment is due to birnessite, which belongs to
22 manganese oxides. Indeed, these non-toxic compounds present natural sorption and oxidant

1 properties. They exist in soils and play key role in environment by geochemistry [18, 19]. Among
2 manganese oxides, birnessite presents the most important redox and sorption properties due to its
3 specific structure. It is a non-stoichiometric oxide with a very open and malleable layered structure
4 formed by MnO_6 octahedra sharing edges due to the substitution of Mn(IV) by Mn(III) or Mn(II),
5 the negative charges being compensated by the presence of hydrated cations inserted inside the
6 layered structure [18,19].

7 Nevertheless, the redox mechanism, which takes place at the interface between birnessite
8 and solution containing pollutants is complex [9-12, 20-25]. The organic pollutants are oxidized
9 and degraded until mineralization, while Mn(IV) and/or Mn(III) present in the birnessite structure
10 are reduced into soluble Mn(II) species. Previous works have admitted the hypothesis that these
11 Mn(II) species generated by this reduction may be adsorbed onto the birnessite surface [9-12,24].
12 Two pathways are possible: (i) dissolved oxygen in the solution may oxidize adsorbed Mn(II) to
13 regenerate oxide, or (ii) adsorbed Mn(II) species may react by reduction reaction with birnessite
14 leading to its possible transformation. Some studies performed with birnessite powder have
15 described many possible evolutions of birnessite structure after interaction with solutions
16 containing different Mn(II) concentrations at fixed pH during a couple of days. As a result, it has
17 been observed spontaneous redox transformations of birnessite powder into new materials such as
18 feitknechtite ($\beta\text{-MnOOH}$), hausmannite (Mn_3O_4) or manganite ($\gamma\text{-MnOOH}$) [26,27]. Another
19 study focused on reduction of birnessite thin films induced by electrochemical methods confirmed
20 also the possible transformation of birnessite in similar compounds in presence of Mn(II) in
21 solution [23]. The major problem is that these materials are passivating and inhibit the surface
22 reactivity [23,27], which could put the brakes on pollutants degradation.

1 In the present work, thin films synthesized by electrodeposition on conductive substrate
2 (≈ 2 microns) were used rather than birnessite powder in order to study systematically the behavior
3 of the material after spontaneous interactions with solution containing various concentrations of
4 Mn(II) during long durations (e.g. from few days to several months). Oxygen influence was also
5 studied in order to highlight the material regeneration step. After interaction, materials were
6 investigated at macroscopic scale by Scanning Electron Microscopy (SEM) and X-Ray Diffraction
7 (XRD), and at microscopic scale by X-Ray Photoelectron Spectroscopy (XPS) to focus on any
8 chemical transformation on the extreme surface of the solid. Indeed, XPS is a very well
9 characterization method for determining the oxidation states at the near surface of materials (10 to
10 20 nanometers). This is a key point for understanding precisely these spontaneous electronic
11 transfers in interfacial processes even if the XPS spectra of manganese oxides in terms of Mn
12 oxidation states can be complex [20,21, 25, 28-30]. The great advantage of the electrodeposited
13 thin films compared to powder samples is a direct characterization without any preparation due to
14 their good conductivity (no charge effect). In addition, Open Circuit Potential (OCP) was also
15 followed during these different interactions with Mn(II) solutions in presence and in absence of
16 oxygen.

17 To complete this work, interactions with pollutants were realized in conditions previously
18 studied to investigate the behavior of our samples in real settings [12,13]. Glyphosate and AMPA
19 (aminomethylphosphonic acid) were chosen because these compounds represent respectively the
20 pesticide the most used in the world and its main metabolite, which becomes a real problem due
21 to its persistence and its toxicity [31,32]. Samples were systematically characterized at the extreme
22 near surface by XPS after the interaction in order to validate the real robustness of the birnessite
23 thin film, a key point for future applications.

1 **2. EXPERIMENTAL SECTION**

2 **2.1. Chemical products**

3 Reagents, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (ACS Reagent Aldrich), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (ACS Reagent Sigma
4 Aldrich), glyphosate (PESTANAL® analytical standard Fluka), AMPA (aminomethylphosphonic
5 acid) (99% Sigma Aldrich) were used without further purification. Solutions were prepared with
6 Milli-Q water and the pH was free.

7 **2.2. Electrodeposition of birnessite thin films**

8 The electrochemical synthesis of pure birnessite thin films was performed according to our
9 previous studies from oxidation of Mn(II) [8,12,13,16]. Electrodeposition was carried out in a
10 solution prepared with Milli-Q water (Na_2SO_4 0.4 M; $[\text{Mn(II)}] = 1.6 \cdot 10^{-3}$ M; pH free (5 - 6), with
11 no buffer) in presence of dissolved oxygen (no deaeration). Electrodeposition was performed at
12 room temperature in a classical electrochemical cell set-up using three electrodes: a Mercurous
13 Sulfate Electrode (MSE: +0.656 V vs Normal Hydrogen Electrode (NHE)) as reference electrode,
14 a twisted wire of platinum as counter electrode, and a fluorine doped tin oxide coated glass
15 substrate ($\text{SnO}_2\text{:F}$ or FTO from SOLEMS; $120 \text{ } \Omega/\text{cm}^2$; $S = 3 \text{ cm}^2$) as working electrode.
16 Electrodeposition were performed by chronoamperometry (+0.6 V vs MSE) with a fixed electric
17 charge thanks to a Microautolab potentiostat from Metrohm and GPES software. In these
18 experimental conditions, pure H-Birnessite thin film was obtained whatever the value of the fixed
19 electrical charge [8,30,33,34]. For this study, the electrical charge was fixed to $Q = 1.8 \text{ C}$, which
20 is the optimal value for samples dedicated to spontaneous degradation of organic pollutants

1 [12,13]. After electrodeposition, thin films were rinsed with Milli-Q water and dried in ambient
2 air. They may be used several days after their preparation.

3 **2.3. Interaction studies**

4 One sample of birnessite thin film was introduced into a cell containing 20 mL of
5 interaction solution. Various concentrations of Mn(II) (0, 10^{-3} M, 10^{-2} M and 10^{-1} M), with Na₂SO₄
6 at 10^{-5} M as electrolyte, were studied. The initial pH of the solutions was always free and no buffer
7 was added. The initial value of pH varied from 3.8 to 5.8 according to the concentration of Mn(II),

8 **Table 1.**

9 For each concentration, Open Circuit Potential (OCP) was measured in continuous during
10 the first day, and punctually (several hours) during long durations (until 95 days). For that, a two-
11 electrode setup was used: the reference electrode was MSE and the working electrode was the
12 birnessite sample in interaction with the studied solution. Between each measurement, the cells
13 were put in the dark and covered with a paraffin film to avoid evaporation of the solution. The pH
14 were measured at the end of the interaction after 95 days, **Table 1**. The influence of oxygen was
15 also studied. For that, some interactions were performed into degassed solutions of Mn(II) at 10^{-1}
16 M with Na₂SO₄ at 10^{-5} M as electrolyte. In this case, the solution was degassed by a continuous
17 flow of argon and OCP was measured in continuous during 8 days.

18 Some interactions were also carried out in presence of pollutants, such as glyphosate and
19 AMPA, in presence of oxygen. For that, solutions with 110 μ M of each pollutant, corresponding
20 to 18.5 mg/L for glyphosate and 12.2 mg/L for AMPA respectively, were prepared from powders
21 of glyphosate and AMPA. The pH of the solution was free ($\approx 4 - 5$) and no buffer was added. Two
22 durations were studied based on our previous studies, e.g. 90 h and 168 h for glyphosate and

1 AMPA respectively, corresponding to the optimal conditions of degradation of each pollutant
2 [12,13]. All interactions were performed at room temperature.

3 **2.4. Characterization of thin films**

4 The characterizations were made directly without preparation. The surface morphology of
5 the films was observed by Scanning Electron Microscopy (SEM) using a Zeiss Merlin compact
6 microscope (applied voltage fixed to 10 kV). The crystalline structure of the films was identified
7 by X-Ray diffraction (XRD) with a Bruker diffractometer using Cu K α 1 radiation ($\lambda = 1.5405 \text{ \AA}$),
8 in the classical Bragg-Brentano set-up. The extreme surface of the thin films (few nanometers)
9 was analyzed using a Thermofisher Scientific K-Alpha X-Ray Photoelectron Spectroscopy (XPS)
10 system, with Al K α micro-focused monochromator. The monochromatic Al K α line was used as
11 X-ray excitation with 1486.68 eV. X-ray spots (400 μm) were usually used to probe the surface.
12 The interpretation of the XPS spectra of manganese oxides in terms of Mn oxidation states was
13 based on studies of Nesbitt *et al.* [20-22,25,28]. Semi-quantitative analyzes were extracted from
14 standardized XPS spectra and on the base on peak deconvolution allowing the determination of
15 different chemical states of the metal [29,30].

16 **3. RESULTS AND DISCUSSION**

17 **3.1. OCP measurements: influence of Mn(II) concentration and oxygen.**

18 **Fig. 1** presents OCP measurements performed punctually during 8 days when
19 electrodeposited birnessite thin films were in contact with solutions of Na₂SO₄ 10⁻⁵ M (as
20 electrolyte) containing various Mn(II) concentrations, from 0 to 0.1 M, in presence of oxygen. In
21 absence of oxygen, OCP measurements were performed in continuous during 8 days. Some

1 measurements were also realized until 95 days, and the global results in term of pH and potential
2 values, are regrouped in **Table 1**.

3 In absence of Mn(II), OCP increases to reach a constant value around 0.2 V vs MSE during
4 the first 24 hours (no peak). After 95 days, OCP drops to zero Volts with a significant increase of
5 pH (from 5.8 to 7.5). The evolutions of potentials are different when measurements were
6 performed in presence of Mn(II) species. Indeed, the values of OCP increase more rapidly, and in
7 direct relation with the augmentation of Mn(II) concentration. Moreover, the OCP amplification
8 is reflected systematically by “a peak” in presence of Mn(II), with OCP maximum values equal to
9 0.140, 0.250 and 0.325 V vs MSE after 12 hours of interaction in solution containing 10^{-3} M, 10^{-2}
10 M and 0.1 M Mn(II) respectively. In addition, OCP and pH stay stable in time and particularly for
11 the higher Mn(II) concentrations (10^{-2} and 0.1 M).

12 The evolution of OCP in absence of oxygen by argon degassing during 8 days, is similar
13 to the experiment performed in presence of oxygen with a similar concentration (e.g. 0.1 M
14 Mn(II)). This result signifies that the absence of dioxygen in solution did not affect the behavior
15 of the solid. Furthermore, the thin films stay systematically adherent and visually unchanged
16 during all experiments whatever the conditions signifying that they are stable in these solutions
17 during long durations, and even in unfavorable conditions. However, it is necessary to confirm if
18 the material was modified by characterization at macroscopic and microscopic scales, particularly
19 in the more unfavorable conditions (e.g. 0.1 M Mn(II) in presence or in absence of oxygen).

20

21

3.2. Characterization of materials after interaction with concentrated solutions of Mn(II) in presence or in absence of dissolved oxygen

3.2.1. Observations by Scanning Electron Microscopy (SEM)

SEM observations (x 3000; inset: x 20000), reported on **Fig. 2**, were performed directly on the conductive thin films after synthesis (**Fig. 2A**), and after interactions with 0.1 M Mn(II) solutions in presence (**Fig. 2B**) or in absence of dissolved oxygen (**Fig. 2C**). The surface of the electrodeposited birnessite thin film after synthesis and before interaction presents a very covering texture (**Fig. 2A**). Large nano-sheets are visible with homogeneous grain size around 2 μm as already observed previously [10-13,30]. Despite the interaction with concentrated solutions of Mn(II) (0.1 M) during a long time (112 days) (**Fig. 2B**), and even in unfavorable conditions in absence of dissolved oxygen during 8 days (**Fig. 2C**), the surface morphology was not modified. Moreover, the shapes and sizes of the birnessite sheets are preserved. These observations show that these electrodeposited thin films seem robust at this macroscopic scale.

3.2.2. Identification of the crystalline structure by X-Ray Diffraction after interaction

Fig. 3 presents XRD measurements recorded on the birnessite thin films after interaction with 0.1 M Mn(II) solutions in absence (**b**) or in presence (**c**) of dissolved oxygen in comparison to one thin film after synthesis (**a**). Only the characteristic peaks of birnessite can be identified on the different diffractograms, according to JCPDS 23-1239 card, expected the peaks attributed to SnO₂ substrate (JCPDS 41-1445 card).

1 However, some modification was observed on diffractograms after interaction. The peak
2 at 12.13° disappears but the other ones are always present, and no characteristic peaks of other
3 manganese compounds are present. This point is crucial because this loss of peak has been already
4 observed in previous studies performed by Elzinga [26], after the interaction of birnessite powder
5 with Mn(II) solutions at $2 \cdot 10^{-3}$ M and $4 \cdot 10^{-3}$ M during 10 days at fixed pH 7, and other materials
6 such as feitknechtite (β -Mn^{III}OOH) and manganite (γ -Mn^{III}OOH) had been respectively identified
7 by XRD measurements. The presence of others manganese oxides confirm the real redox
8 transformation of birnessite powder by Mn(II) at this pH. In the present study, the experiments
9 were reproduced in extreme conditions with very high Mn(II) concentration (0.1 M) and during
10 long durations in presence (112 days) or in absence of oxygen (9 days), and neither the film
11 morphology nor the structure of birnessite change after interaction in such conditions.

12 *3.2.3. Characterization of the extreme surface by X-ray Photoelectron Spectroscopy (XPS)*

13 To complete the characterization of the bulk of material by SEM and XRD, the extreme
14 surface of birnessite thin films was probed directly without preparation by X-ray Photoelectron
15 Spectroscopy (XPS). XPS spectra of the Mn(2p_{3/2}) and O(1s) regions of electrodeposited birnessite
16 thin films were collected for various samples depending on the interaction conditions, **Fig. 4A, 4B**
17 **and 4C**. In these figures, the red solid curve corresponds to the fit of the XPS data and the colored
18 areas represent the fitted Mn(2p_{3/2}) and O(1s) multiplet peaks. The corresponding compositions
19 are gathered in **Table 2**.

20 First, the unreacted birnessite was characterized, **Fig. 4A**. Previous studies had reported in
21 the literature analyzes of Mn(2p_{3/2}) and O(1s) spectra of birnessite and the attribution of the
22 different peaks [20-22,25,28,30]. The energy peak position and the feature of the Mn(2p_{3/2})
23 spectrum obtained on the electrodeposited thin film was typical of birnessite reported in the

1 literature [28]. Indeed, a maximum is observed near to 642 eV, attributed to Mn(IV) (orange peak)
2 but with a contribution at higher binding energy (centered at 643.5 eV), attributed to the presence
3 of Mn(III) (pink peak), which is characteristic of birnessite. At lower binding energy, another
4 contribution centered at 640 eV, reveals also the presence of Mn(II) (grey peak). Other peaks are
5 present without specific attribution because they may result from the contribution of mixed
6 oxidation degrees of manganese, as it has been already reported in the literature [28].

7 The O(1s) spectrum of unreacted birnessite, **Fig. 4A**, shows a well-defined peak, centered
8 on 530 eV, corresponding to oxide O^{2-} (blue peak) in largest majority, OH^- (purple peak) centered
9 at 531.5 eV, and minor attached water H_2O (red and green peaks) as expected. This O(1s) spectrum
10 is typical of birnessite according to the literature [28]. These results are in good agreement with
11 our previous *in situ* XRD and XAS measurements during electrodeposition of thin films, which
12 confirmed that H-birnessite in particular was synthesized in these experimental conditions [33,34].
13 The corresponding compositions are gathered in **Table 2**.

14 **Fig. 4B and 4C** show respectively the Mn(2p_{3/2}) and O(1s) spectra of birnessite thin films
15 after interaction with a Mn(II) solution at 0.1 M, in presence and in absence of dioxygen in
16 solution. Mn(2p_{3/2}) and O(1s) spectra show the same peak positions and features that those
17 analyzed on the birnessite thin film before interaction (**Fig. 4A**). The additional contribution of
18 birnessite, near the peak centered at 642 eV on Mn(2p_{3/2}) spectra, is always observed, as a well-
19 defined peak corresponding to the oxide species O^{2-} on the O(1s) spectra. Moreover, the surface
20 composition does not change significantly and stays similar after the interaction with Mn(II)
21 solution in presence or in absence of oxygen, **Table 2**. Nevertheless, the surface composition in
22 atomic percentage of Mn(II) tends to increase lightly after the interaction of the thin film with the

1 solutions. This could be due to the possible adsorption of Mn(II) present in high concentration in
2 solution, which is more pronounced in absence of oxygen (no oxidation reaction of Mn(II)).

3 Despite these extreme conditions imposed to birnessite thin films in terms of Mn(II)
4 concentration and duration, the XPS spectra stay comparable to those of the unreacted birnessite
5 thin film, indicating that the extreme surface is not modified. This observation is different from
6 the results reported in the literature with birnessite powder, which has been reduced into manganite
7 (γ -Mn^{III}OOH) after interaction with Mn(II) [26]. This latter compound, characterized by Nesbitt
8 and Banerjee by XPS [28], has a O(1s) spectrum with an equal proportion of O²⁻ and OH⁻ and also
9 a Mn(2p_{3/2}) spectrum with multiple peaks with equal intensity. These spectra are strongly different
10 from those reported in **Fig. 4A and 4B** and confirm the absence of the transformation of birnessite
11 thin films.

12 **3.3. Characterization of the extreme surface of thin films after interaction with high** 13 **concentrated solutions of pollutants: Examples of glyphosate and AMPA**

14 Similar XPS characterizations were performed on birnessite thin films after their
15 interaction with solutions containing pollutants such as glyphosate and AMPA during 90 hours
16 and 168 hours respectively. These conditions were chosen according to our previous studies, which
17 report the degradation of these pollutants by electrodeposited birnessite thin films by a simple
18 contact [12] or as electrode materials [13].

19 In the case of a simple contact, the interaction leads to the degradation of the pollutants and
20 the reduction of birnessite with the production of Mn(II) in solution due to spontaneous redox
21 reactions, as shown by Ndjeri et al. [12]. However, the concentration of Mn(II) found in solution
22 were lower than expected for this rate of degradation and mineralization of the pollutant. This
23 suppose that Mn(II) ions were adsorbed onto the solid, and (i) can be oxidized by dissolved oxygen

1 present in solution to regenerate birnessite, or (ii) they can induce the reduction of birnessite by
2 redox reactions. The aim of these experiments was to identify formally the effect of these
3 spontaneous degradation reactions on birnessite thin film, to determine the chemical composition
4 of the extreme surface after reaction, and the real effect of Mn(II) produced. These points are very
5 important for future applications.

6 **Fig. 5A and 5B** show respectively the XPS spectra of electrodeposited birnessite thin films
7 after interaction with glyphosate and AMPA, and the corresponding compositions of the extreme
8 surface in each case are gathered in **Table 3**. No difference is observed on the Mn(2p_{3/2}) and O(1s)
9 spectra compared to the initial XPS spectra of birnessite thin film after synthesis and before
10 interaction with solution (**Fig. 4A**). This result is significant since it proves the lack of the surface
11 transformation. Only the proportion of Mn(II) increases slightly (**Table 3**), due to the adsorption
12 of Mn(II) produced during the degradation of pollutants as it has been proposed [12]. The proof of
13 adsorbed Mn(II) on the film surface is then in good agreement with the degradation process.
14 Moreover, the fact that the extreme surface of birnessite is unchanged even after several days of
15 interaction, while pollutants are degraded, are very encouraging for the development of this
16 innovative treatment.

17 **4. CONCLUSION**

18 Electrodeposited birnessite thin film is a very interesting material for developing
19 innovative treatment. Remarkable properties of degradation have been already established by
20 previous studies and to complete them it has been shown here that birnessite thin film is also a
21 robust material. The film is able to resist to extreme and unfavorable conditions without being
22 altered. Nature and structure of the bulk and the near surface of the material stay unchanged after
23 long times of interaction with a Mn(II) concentrated solution, and even in absence of oxygen. Same

1 results were observed in presence of pollutants as glyphosate and AMPA at high concentrations,
2 due to a very efficient in continuous regeneration of birnessite, which is very encouraging for
3 future applications.

4

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11

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1 **Figure captions:**

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4 **Fig.1:** Open Circuit Potential (OCP) measurements punctually recorded during the first 8 days of
5 interaction with solutions containing various Mn(II) concentrations with Na₂SO₄ 10⁻⁵ M as
6 electrolyte. The hashed line corresponds to continuous OCP measurements performed during
7 interaction in anoxic conditions in 0.1 M Mn(II) solution with Na₂SO₄ 10⁻⁵ M as electrolyte.

8 **Fig.2:** SEM observations (x 3000; inset: x 20000) of birnessite thin films synthesized by
9 electrodeposition on FTO substrate. **(A)** After synthesis and before interaction; **(B)** After
10 interaction with Mn(II) solution at 0.1 M during 112 days in oxic condition; **(C)** After interaction
11 with Mn(II) solution at 0.1 M during 8 days in anoxic condition.

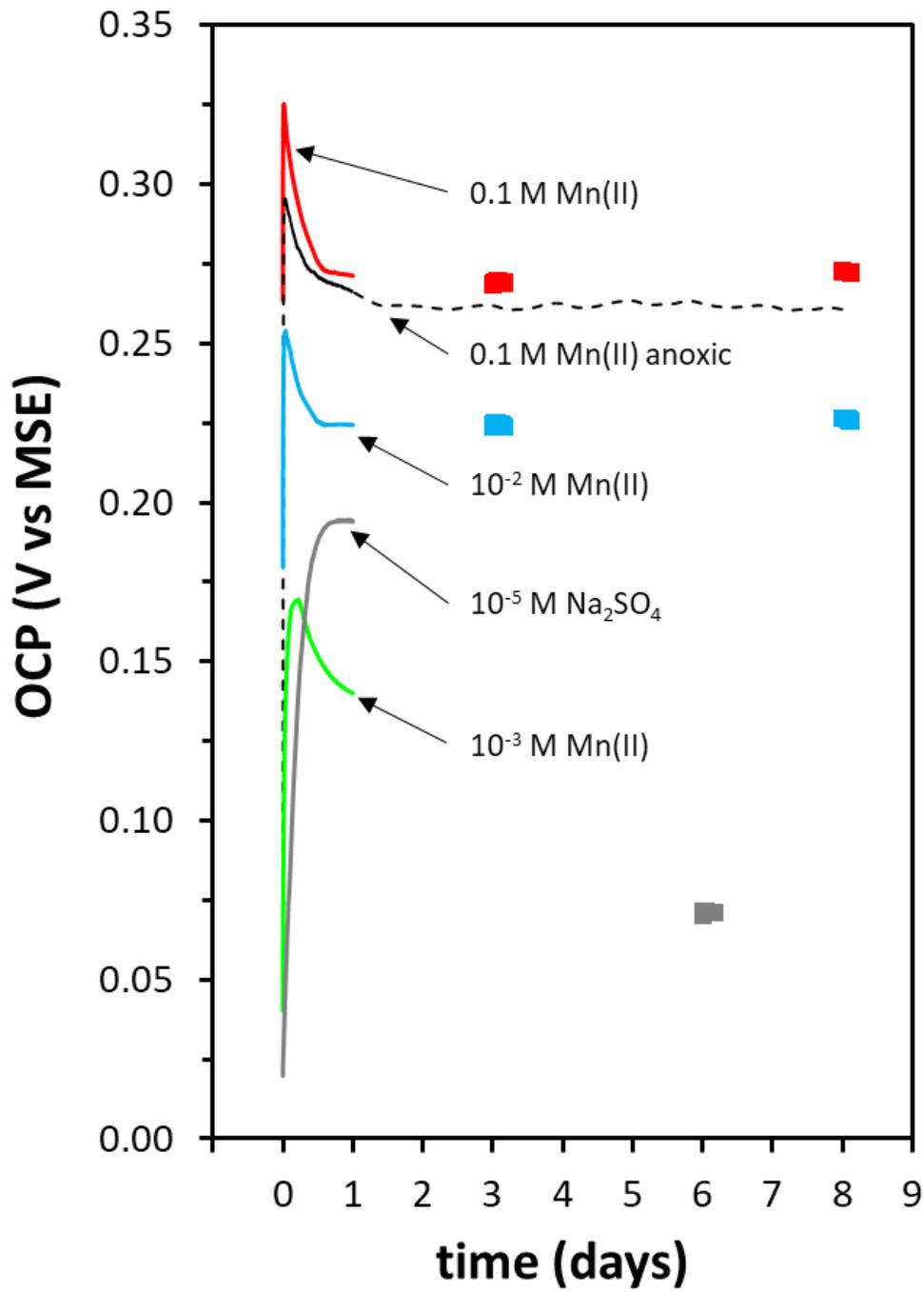
12 **Fig.3:** XRD measurements of electrodeposited birnessite thin films: **(a)** After synthesis and before
13 interaction; **(b)** After interaction in anoxic Mn(II) solution at 0.1 M with Na₂SO₄ 10⁻⁵ M as
14 electrolyte during 8 days; **(c)** After interaction in oxic solution of 0.1 M Mn(II) with Na₂SO₄ 10⁻⁵
15 M as electrolyte during 112 days. H-birnessite peaks and SnO₂ peaks have been attributed
16 according to JCPDS 23-1239 and JCPDS 41-1445 cards respectively.

17 **Fig.4:** XPS Mn(2p_{3/2}) and O(1s) spectra of electrodeposited birnessite thin film **(A)** After
18 synthesis; **(B)** After interaction with 0.1 M Mn(II) solution during 112 days in oxic conditions; **(C)**
19 After interaction with 0.1 M Mn(II) solution without O₂ during 8 days.

20 **Fig.5:** XPS Mn(2p_{3/2}) and O(1s) spectra of electrodeposited birnessite thin films **(A)** After
21 interaction for 90 h with an aqueous solution containing 110 μM of glyphosate **(B)** After
22 interaction for 168 h with an aqueous solution containing 110 μM of AMPA.

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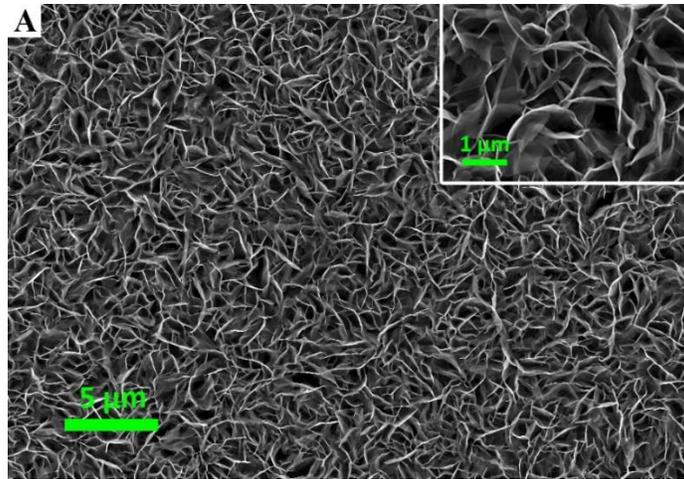
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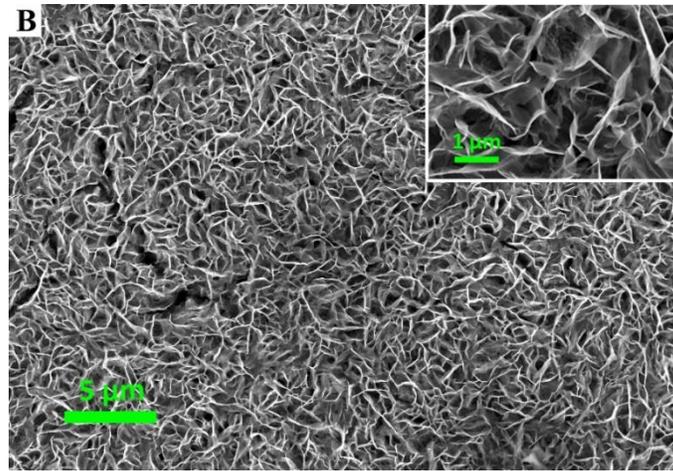
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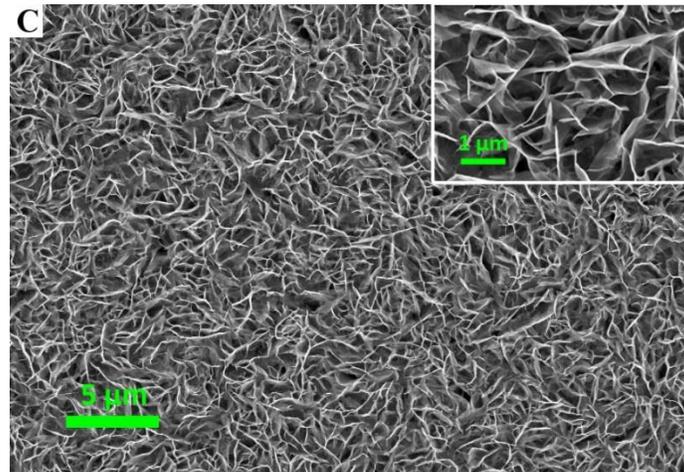
Fig.1



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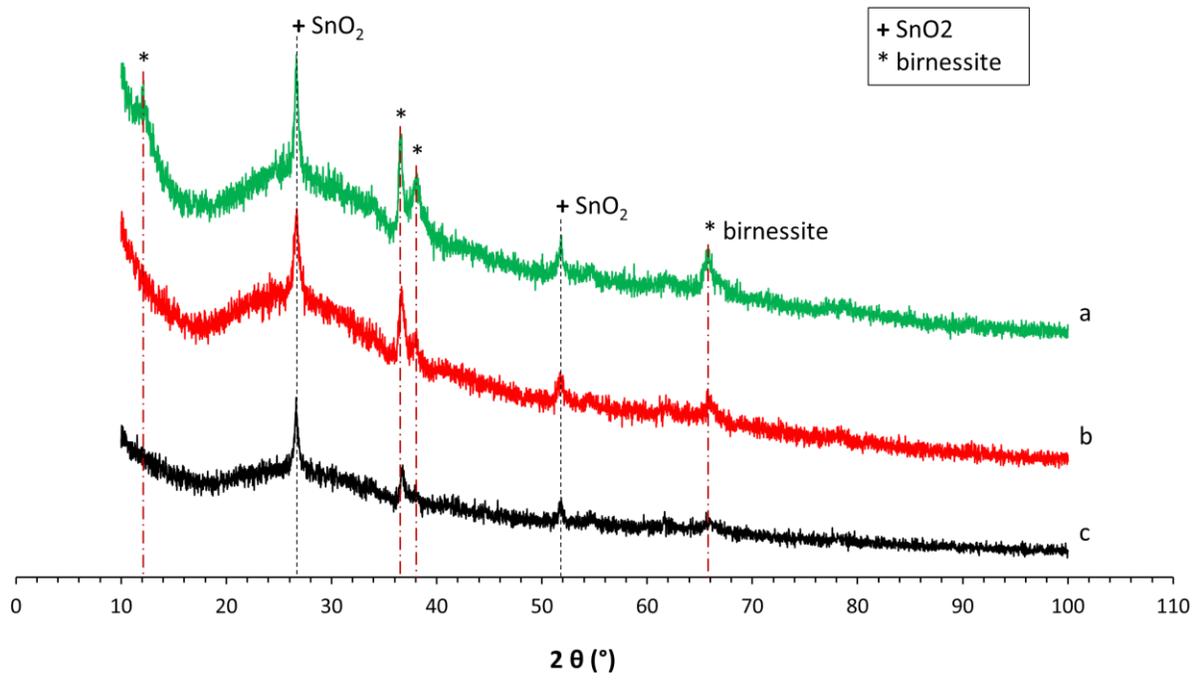
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Fig.2

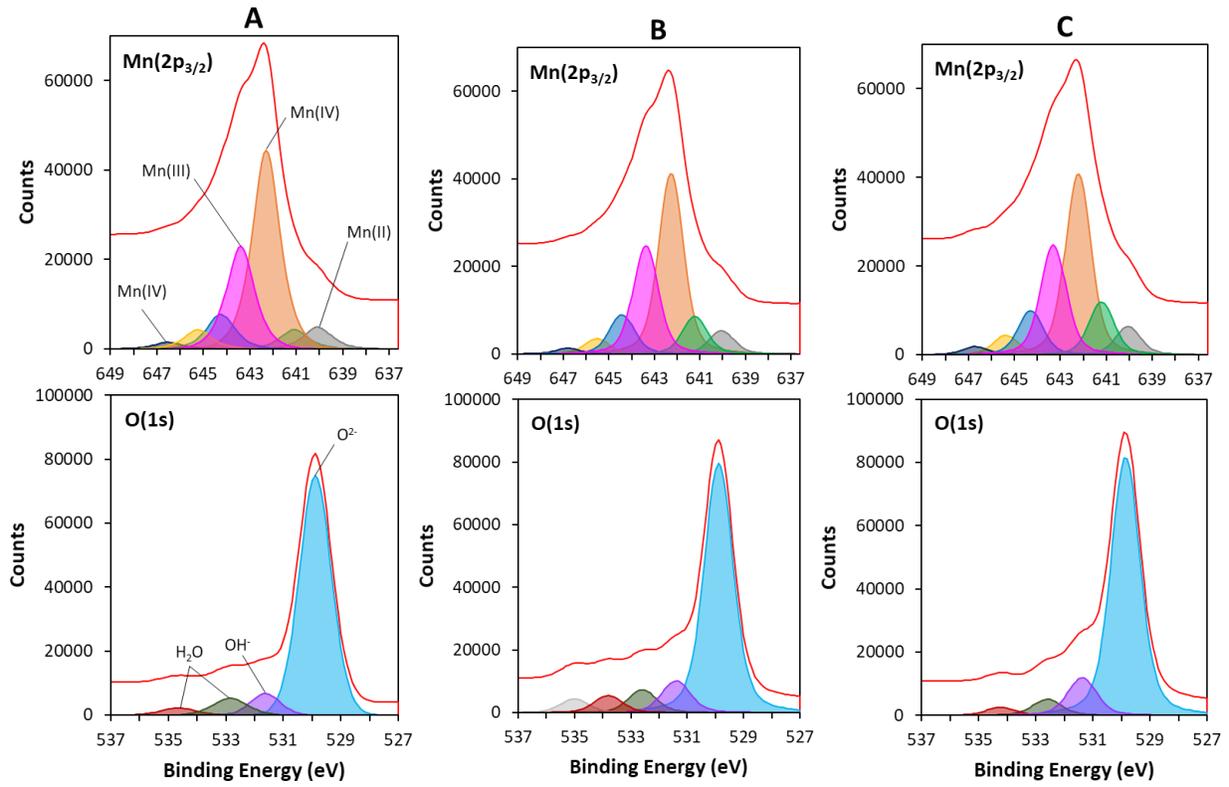
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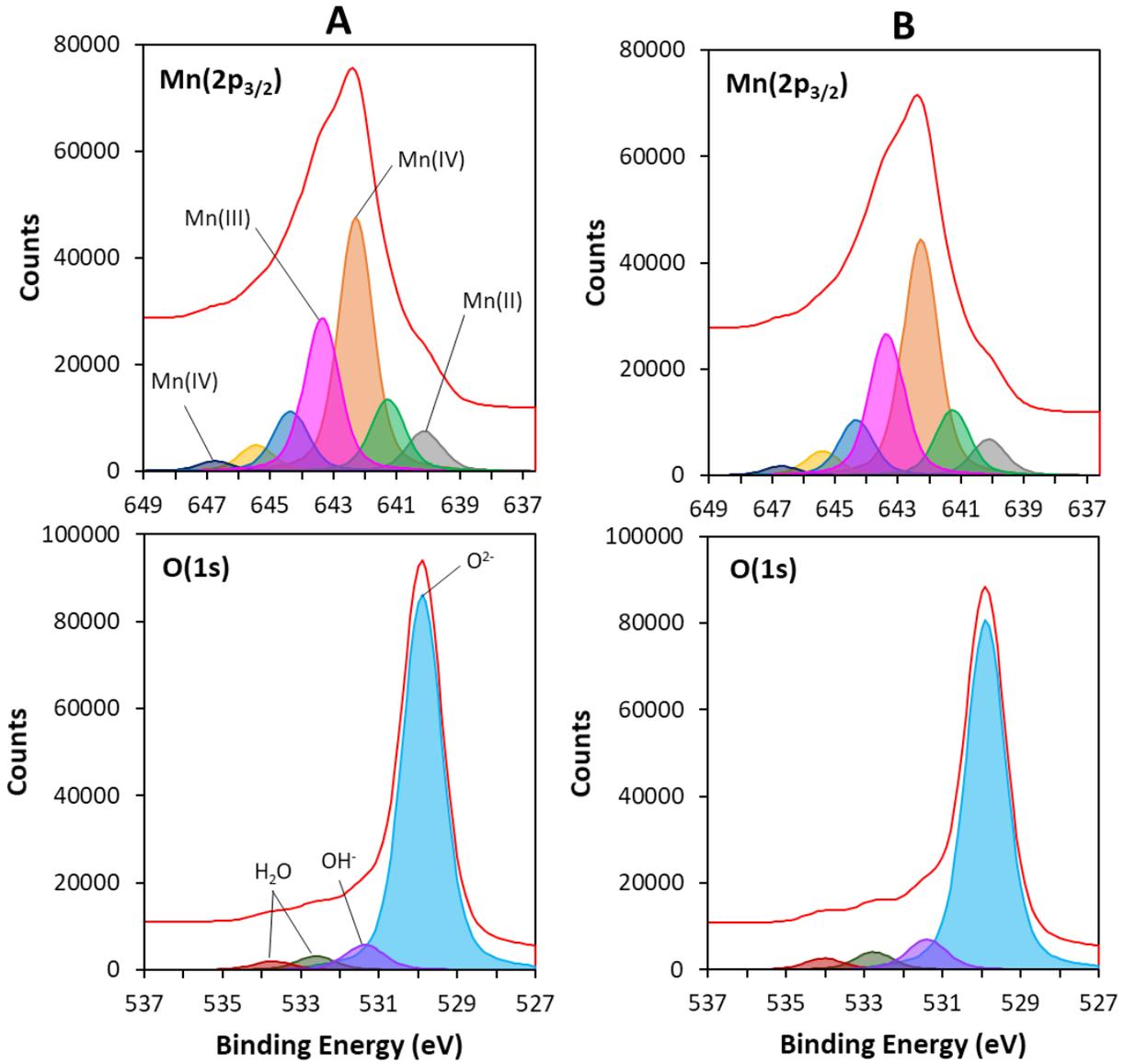
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Fig.4

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Fig.5

1 **Tables:**

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4 **Table 1:** Values of pH (initial and final) and recording of open circuit potentials (OCP) during
5 long interactions in oxic conditions between birnessite thin film and Mn(II) solutions with different
6 concentrations in presence of Na₂SO₄ 10⁻⁵ M as electrolyte.

7

[Mn(II)] (M)	Initial pH	OCP (V vs MSE) after						pH after 95 days
		1 day	3 days	8 days	35 days	65 days	95 days	
10 ⁻¹	3.7	0.27	0.27	0.27	0.27	0.27	0.28	3.5
10 ⁻²	4.6	0.22	0.22	0.22	0.21	0.17	0.15	5.8
10 ⁻³	5.5	0.14	-	-	0.01	0.00	-0.01	6.7
0	5.8	0.19	-	-	-0.02	-0.04	-0.07	7.5

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2 **Table 2:** Manganese and Oxygen proportions in electrodeposited birnessite thin film near-surface
3 before and after interaction with 0.1 M Mn(II) solutions, with Na₂SO₄ 10⁻⁵ M as electrolyte, in
4 presence or in absence of oxygen.

5

Species	After synthesis and before interaction (%)	After interaction in oxic conditions during 112 days (%)	After interaction in anoxic conditions during 8 days (%)
Mn(II)	6.8	7.9	8.3
Mn(III)	31.7	34.2	34.7
Mn(IV)	61.5	57.9	57.0
O²⁻	89.6	78.0	81.0
OH⁻	7.5	11.0	12.5
H₂O	2.9	11.0	8.0

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2 **Table 3.** Manganese and Oxygen proportions in electrodeposited birnessite near surface before3 and after interaction with aqueous solutions containing glyphosate (110 μ M) or AMPA (110 μ M).

4

Species	Before interaction (%)	After interaction for 90 hours with a solution of glyphosate (%)	After interaction for 168 hours with a solution of AMPA (%)
Mn(II)	6.8	9.0	8.0
Mn(III)	31.7	33.0	33.0
Mn(IV)	61.5	58.0	59.0
O²⁻	89.6	91.8	86.0
OH⁻	7.5	6.2	7.0
H₂O	2.9	2.0	7.0

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