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An efficient eco-friendly water depollution process based on electrodeposited birnessite thin films coupled to electrochemistry: Application to methylene blue degradation as phenothiazines model molecule

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ABSTRACT

This paper describes successful use of nanostructured birnessite thin films as electrode to remediate aqueous solutions containing methylene blue, which can be a model molecule of phenothiazines largely used in industries. Such electrodeposited thin films, noted HB1, can spontaneously degrade dye, but the reactivity is limited by organic molecules sorption. The use as electrode improves largely efficiency for total discoloring in very soft conditions with very low energy inputs, even at high concentrations. The discolored solutions analyses by ion chromatography report the significant presence of non-toxic small organic compounds and inorganic ions confirming the degradation. Characterization of materials by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Raman spectroscopy confirm that no organic compound were adsorbed onto surface, with no modification of birnessite due to an efficient regeneration by electrochemistry in continuous. For better understanding reactions in real time, *in situ* measurements by UV-Visible spectroscopy were performed on solution confirming the real interest of coupling to electrochemistry. In complement, another type of sample with lower birnessite amount, noted HB4, was tested with success. These HB1 and HB4 samples used as electrodes present high degradation capacities towards methylene blue equal to 934 mg g^{-1} of HB1 and 2222 mg g^{-1} of HB4, without any modification of material. These results are very promising for future eco-friendly applications due to good efficiencies, very simple conditions, without toxic products and wastes, and with low energy needs, both for synthesis and depollution processes.

1. Introduction

Nowadays, water pollution is only growing with a multitude of wastes, which come from industrial, natural, agricultural, or even urban pollution mainly due to the large increasing anthropogenic activities [1–3]. Most pollutants are well treated by wastewaters treatment plants (WWTP); however, some persistent organic pollutants such as pesticides or their main metabolites, organic dyes, or drug residues can be poorly eliminated or degraded, and then found in environment with dramatic consequences for fauna, flora, and human health [1,4–6]. For example, phenothiazine molecules, largely used as organic dyes, insecticides, or drugs, are particularly recalcitrant towards conventional treatments performed in WWTP [5].

In the dyes category belonging to the family of phenothiazine molecules, methylene blue has potential applications in pharmaceutical, pa-

per, dyeing, medicine, and food industries, and is the most common in the textile field [1–4]. Usually, textile industries release in natural water sources, a huge amount of MB dye, which can be harmful to human health due to its toxicity. Not only MB is toxic, but it is also carcinogenic and has destructive effects on environment [1,2,7]. To overcome this problem of increasing pollution, several methods were developed to remove methylene blue from water, such as biodegradation, photocatalysis, advanced oxidation processes or even vacuum membrane distillation system [1–3]. However, all these methods have advantages and constraints concerning cost and feasibility, efficiency, and in particular environmental impact, and that is why it is necessary to improve them continuously.

In this context, we have reported previously the real efficiency of electrodeposited birnessite thin films to degrade and mineralize spontaneously organic compounds, such as glyphosate, a pesticide, and AMPA

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(amino methyl phosphonic acid) its main by-product more toxic and persistent than glyphosate (at 50 °C) [8], and organic dyes like indigo carmine or methylene blue (MB) [9,10]. These same birnessite thin films were also optimized to have very high sorption capacities towards heavy metals, such as soluble lead or cadmium, for an efficient wastewater depollution [11].

Developing novel eco-friendly processes with this non-toxic natural material seems particularly interesting for treating wastewaters containing organic pollutants such as phenothiazine molecules. Indeed, birnessite is the major mineral phase among manganese compounds in many soils [12,13]. This corresponds to a class of non-stoichiometric oxides due to the substitution of some Mn (IV) by Mn (III) or Mn (II), with a layered structure formed by MnO_6 octahedra sharing edges, in complement to hydrated cations in the interlayers for compensating the small overall negative charge [13,14]. Associated with its very open structure, this complex material exhibits the largest adsorption capacity on heavy metals than others manganese compounds [11,15]. Moreover, all kind of birnessite compounds can spontaneously oxidize organic compounds. In summary, this compound is a considerable interest as inexpensive and non-toxic material to depollute water.

Most studies with birnessite focus on powder synthesis and/or uses [13], and very few on nanostructured electrodeposited thin films [16,17] while thin films directly deposited on conductive substrates present very attractive advantages for potential applications in wastewaters treatments in particular [18–20]. Moreover, such samples have higher robustness compared to powder due to a very efficient self-regeneration [18]. However, the spontaneous reactivity of birnessite thin films can be limited at room temperature for some persistent pollutants such as AMPA, or methylene blue [8,9]. Indeed, in the latter case, we have shown previously that the degradation of this cationic phenothiazine dye was blocked by the adsorption of intermediate organic compound (thionin) onto the surface of birnessite. Nevertheless, one of solution, which can significantly increase the efficiency of this material, is to apply electrochemical methods during the interaction, by using these birnessite thin films as electrodes, in the aim to improve the degradation reaction with very low energy inputs, as already reported with success for the degradation of AMPA [19].

Therefore, the major aim of the present article was to study in details the effect of coupling electrochemistry to spontaneous oxidant properties of birnessite applied to the degradation of methylene blue as phenothiazines model molecule. First, the standard samples already optimized specially for the (electro)degradation of organic pollutants, noted HB1, were used. For understanding the mechanism of MB degradation by birnessite thin film used as electrode, various complement techniques were employed for analyzing aqueous solutions, such as UV-Visible spectroscopy and ion chromatography, in complement to the characterization of the solids by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Raman spectroscopy. It is important to highlight that thin films present many advantages for fundamental studies because the characterizations of the solid are performed directly without any preparation, and the solutions can be analyzed directly without any treatment (no filtration step). In addition, the same sample can be characterized before and after interaction allowing robust and rigorous results. In complement, *in-situ* measurements by UV-Visible spectroscopy, with or without electrochemistry, can be realized to scrutinize reactions in solution in real time. This original experimental approach allowed us to have a good comprehension of interfacial mechanisms at solid-liquid interfaces for concluding about the real interest of coupling with electrochemistry. In a second part, another type of samples with very low amount of birnessite (noted HB4), specially optimized previously for heavy metal sorption [20], was also studied for determining their capacities to degrade organic compounds in comparison to HB1 samples.

These all results appear particularly interesting and promising for future applications because electrodeposited thin films of birnessite

present many advantages for possible developments at high scales, with no filtration steps, in very soft conditions, and especially with very low energy inputs compared to other methods, as discussed in the last part.

2. Experimental

2.1. Chemical compounds

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 Aldrich), NaOH (0.1 mol L^{-1} , ACS Reagent, Sigma Aldrich), H_2SO_4 (0.1 mol L^{-1} , ACS reagent, 95–98 %, Sigma Aldrich), $\text{MB} \cdot \text{xH}_2\text{O}$ (Riedel-de Haën, min 96 %, blue dye), Thionin acetate salt (Sigma Aldrich, 85 %, purple dye) were used without further purification for electrodeposition and interaction experiments. DL-Tartaric acid (99 % ACS Reagent, Sigma Aldrich) and oxalic acid (99 % ACS Reagent, Sigma Aldrich) were used for preparation of cationic chromatography eluent. Reagents, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (ACS reagent, 99 %, Sigma Aldrich), KMnO_4 (ACS reagent, > 99 %, Sigma Aldrich), $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (ACS reagent, > 99 %, Sigma Aldrich) were used to determine the Average Oxidation State (AOS) of manganese by potentiometric titration. All solutions were prepared by using Milli-Q water.

2.2. Electrodeposition of nanostructured birnessite thin films

The electrodeposition of birnessite thin films was performed using a potentiostat/galvanostat system (Microautolab or Autolab, Eco Chemie) controlled by a Dell Computer using the GPES software package.

The electrochemical setup was classical with three electrodes. The working electrode was a glass plate covered with tin dioxide doped fluoride, noted SnO_2 (SOLEMS, 120 Ω/cm^2) and used after cleaning in a crystallizer into an ultrasonic bath for 5 min into acetone, 5 min into ethanol, and 5 min into Milli-Q water. The surface in contact with electrolyte ($S = 3 \text{ cm}^2$) was delimited by an adhesive mask. The counter electrode was a platinum wire spiraled to have a total surface higher than the working electrode. The reference electrode was a commercial Ag/AgCl electrode (Silver Chloride Electrode with a KCl 3 mol L^{-1} solution, Radiometer analytical, $E = 0.210 \text{ V/SHE}$).

Thin films of birnessite were electrodeposited at room temperature in 80 mL of a solution prepared with 18.2 $\text{M}\Omega \cdot \text{cm}$ Milli-Q water containing $[\text{Na}_2\text{SO}_4] = 0.4 \text{ mol L}^{-1}$, as electrolyte, and $[\text{MnSO}_4] = 1.6 \cdot 10^{-3} \text{ mol L}^{-1}$, at free pH (~ 5.5). The solutions used without deaerating were always gently stirred continuously during electrodeposition (250 rpm). Each sample of pure birnessite thin films was electrodeposited by chronoamperometry at $E = 1.0 \text{ V}$ with an electric charge Q (in Coulomb, C) fixed to 1.80 C (0.60 C cm^{-2}), for samples noted HB1, or 0.45 C (0.15 C cm^{-2}) for samples noted HB4. After electrodeposition, thin films were rinsed with Milli Q water and dried in ambient air. Birnessite being a very stable compound, samples can be electrodeposited and stocked before characterization and use.

2.3. Interaction studies with MB solutions

The *ex situ* interaction studies coupling to electrochemistry were performed with a potentiostat/galvanostat system (Microautolab or Autolab Eco Chemie). For that, one birnessite thin film used as the working electrode (HB1 or HB4 type sample), was introduced into a cell at room temperature containing the MB solution with variable concentrations in presence of Na_2SO_4 at $10^{-5} \text{ mol L}^{-1}$ as electrolyte (10 mL; no degassed). In all cases, the pH of the solution was adjusted at 4.3 with addition of small aliquots of H_2SO_4 . A homemade reference electrode (Ag/AgCl with a NaCl solution at 0.1 mol L^{-1} ; $E = 0.290 \text{ V/SHE}$) and a platinum straight wire as counter electrode were used. The solution was gently stirring at 250 rpm during the imposition of the potential fixed to $E = 1.1 \text{ V}$ (chronoamperometry) for variable durations. This opti-

mal value of potential was chosen based on previous studies [19]. Experiments were performed in a transparent cell without any protection to light. Each condition was repeated several times to determine the reproducibility.

For comparison, some experiments were performed without electrochemistry (spontaneous reaction) in a thermostatic oven at 25 °C under 350 rpm either with only one HB1 sample, either with four HB1 samples for having a total discoloration of the solution, which was essential for ion chromatography analyses. In all cases, birnessite thin films were removed from the solution after interaction (spontaneous or with electrochemistry), rinsed with Milli Q water, and stocked for further characterization. The interaction solutions were stocked at 4 °C until analyses.

In complement, some experiments were performed in the same conditions with the substrate alone (SnO_2), with or without electrochemistry, for comparison.

2.4. Analysis of solution

Absorbance measurements of dyes, before interaction and punctually during the *ex-situ* interaction experiments, were performed by UV-Visible spectroscopy (Shimadzu UV-3600 plus series, UV Probe software) in an optical cell with length equal to $l = 1$ cm or 4 cm or 0.1 cm according to the initial concentrations of the studied solutions (law of Beer Lambert; $\epsilon_{\text{MB}} = 62,179 \text{ mol}^{-1} \text{ cm}^{-1}$). Calibration curves were established for MB and thionin.

To determine the discoloration rate after different durations during the *ex situ* experiments (6 h, 24 h and 65 h), a small aliquot of the solution was taken and reintroduced immediately after measurement. In these conditions, the absorbance was measured from 800 to 200 nm. A visual colorimetric scale was established to illustrate MB coloring according to its concentration (Fig. S1). For information, the solution appears visually uncolored when the absorbance, measured in an optical cell ($l = 1$ cm), is equal or inferior to 0.05, corresponding to a concentration of MB equal to 0.2 mg L^{-1} , and a discoloration rate of 98 % in the case of an initial concentration fixed to 10 mg L^{-1} .

In complement, totally discolored solutions after interaction were analyzed by chromatography. The anionic species were detected by ion chromatography (Integriion Dionex, column AS 19, detection: conductivity, gradient eluant KOH from $10^{-2} \text{ mol L}^{-1}$ to $5.2 \cdot 10^{-2} \text{ mol L}^{-1}$, flow rate: 1.0 mL min^{-1} , volume: $25 \mu\text{L}$). In addition, Mn (II) ions were quantified by cationic chromatography (Dionex, column SCS 1, detection: conductivity, eluant tartaric acid ($4 \cdot 10^{-3} \text{ mol L}^{-1}$) and oxalic acid ($2 \cdot 10^{-3} \text{ mol L}^{-1}$); flow rate: 1.0 mL min^{-1} , volume: $25 \mu\text{L}$).

2.5. Characterization of thin films

XRD measurements were performed by using a compact D2-Phaser diffractometer (Bruker) with Cu radiation ($\lambda_{\text{Cu}} = 1.540600 \text{ \AA}$). The crystal structures were determined based on JCPDS cards and our previous studies [9,19,22,23]. The surface morphology was directly observed without preparation by Scanning Electron Microscopy (SEM) (MEB-FEG MERLIN, Zeiss). Raman spectra of thin films were recorded with a compact Xplora (Horiba; LABSPEC6 software) with a 532 nm laser (0.1 %, x 100 objective, 1800 tr mm^{-1} grating, $100 \mu\text{m}$ slit and $500 \mu\text{m}$ hole). Two accumulations of 30 s from 100 to 1500 cm^{-1} were performed for solid characterization before interaction, and from 100 to 2200 cm^{-1} for solid characterization after interaction. The LABSPEC6 software was used for interpretation.

In complement, the average oxidation states of manganese (AOS) in the HB1 and HB4 type samples after synthesis were determined by a potentiometric titration method [21].

2.6. In situ measurements by UV-visible spectroscopy during interaction experiments: studies of the solution evolution in real time

For few selected conditions, some *in situ* measurements by UV-Visible spectroscopy were performed during interactions (spontaneous or coupled to electrochemistry) to have complementary information about the evolution of the solution in real time. All *in situ* measurements were performed by UV-Visible spectroscopy with a Shimadzu UV-3600 plus series (UV Probe software).

For *in situ* spontaneous interaction studies, one birnessite thin film (HB1 type sample) was introduced at room temperature into an optical cell containing the MB solution with variable concentrations in presence of Na_2SO_4 at $10^{-5} \text{ mol L}^{-1}$ as electrolyte (quartz cell with $l = 1$ cm or boro-silicate cell with $l = 4$ cm; no interference of HB1 sample with beam). As previously, the pH of the solution was adjusted at 4.3 with H_2SO_4 , and the solution was gently stirring during experiments (350 rpm), with no degassed in all cases. The volume of the MB solution in interaction with one birnessite thin film was function of the cell type (3.5 mL for the optical quartz cell with $l = 1$ cm, and 10 mL for the boro-silicate cell with $l = 4$ cm). During *in situ* spontaneous reaction measurements, scans were recorded every 5 min from 800 to 350 nm with a medium speed (1 nm of sampling interval and a slit width of 5 nm).

The *in situ* measurements performed during the interaction coupled to electrochemistry were performed with a potentiostat/galvanostat system (Autolab, Eco Chemie). For that, one birnessite thin film (HB1 or HB4 type sample) was used as working electrode. The other electrodes were the same that used for *ex situ* interaction experiments (*i.e.* platinum straight wire as counter electrode, and the homemade electrode reference Ag/AgCl with a NaCl solution at 0.1 mol L^{-1} ; $E = 0.290 \text{ V/SHE}$). As previously, the pH of the solution was adjusted at 4.3 with H_2SO_4 , with no degassed. The solution was gently stirring at 250 rpm during the imposition of the potential fixed to $E = 1.1 \text{ V}$ (chronoamperometry) for variable durations. The volume of the MB solution in interaction with one birnessite thin film was always fixed to 3.5 mL since only the optical quartz cell with $l = 1$ cm was used in this case. For *in situ* measurements performed during interactions coupled with electrochemistry, scans were recorded every minute from 800 to 350 nm with a fast speed (1 nm of sampling interval and a slit width of 5 nm).

For comparison, some *in situ* experiments were performed also in the same conditions with the substrate alone (SnO_2), with or without electrochemistry.

In all cases, the studied sample (electrodeposited birnessite thin film or the substrate alone) was always placed in direct contact with the optical cell surface to avoid interferences during UV-visible spectroscopy measurements of the solution. Therefore, all absorbance values reported in this study correspond only to the solution absorbance.

3. Results and discussion

3.1. Studies of birnessite thin film reactivity used as electrode material to degrade methylene blue: case of HB1 sample in presence of low dye concentrations ($\leq 10 \text{ mg L}^{-1}$)

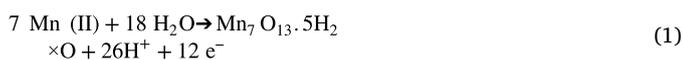
Previously, we have reported that electrodeposited birnessite thin films can spontaneously discolored and degraded methylene blue [9]. However, according to our proposed mechanism, birnessite surface is quickly blocked by the adsorption of thionin, the last organic compound produced before slow mineralization step [9]. In other studies, we have reported the significant effect of the electrochemistry during the degradation of a persistent pollutant (AMPA) with birnessite thin films used as electrode compared to spontaneous interaction [8,19].

Therefore, the aim of the present studies was to determine the possible effect of the electrochemistry during the degradation of MB. For that, these experiments were performed in first with HB1 type samples,

specifically developed for the degradation of organic pollutants by spontaneous reaction [8–10] or coupled to electrochemistry, as already reported for glyphosate (pesticide) and AMPA (by-product) [19].

3.1.1. Synthesis and characterization of HB1 type samples

Homogeneous black adherent thin films of H-birnessite, corresponding to HB1 samples, were electrodeposited onto SnO₂ by chronoamperometry at E = 1.0 V at fixed electric charge (1.80 C; 3 cm²), in neutral aerated solution containing sodium sulfate and manganese sulfate, such as described in detail elsewhere [22–24]. In these conditions, the mass of one HB1 type sample was equal to (1.07 ± 0.1) 10⁻³ g according to an average value based on sixty different samples measurements, Table 1. This value is in very good agreement with the theoretical mass expected for this value of electric charge (m_{theo} = 1.06 10⁻³ g), based on the electrochemical reaction, Eq. (1), and calculated according to the Faraday's law for H-birnessite (Mn₇O₁₃·5 H₂O; M = 683 g mol⁻¹; n = 12), Eq. (2):



$$m_{\text{theo}} = \frac{Q}{n.F} \cdot M \quad (2)$$

With Q, the electrical charge fixed; n, the number of electrons required for the formation of one mole of the studied compound; F: Faraday's constant (96,485 C mol⁻¹); M: molecular weight of the studied compound.

After synthesis, the samples were directly characterized without preparation by XRD, SEM and Raman spectroscopy. XRD measurements report that pure and well crystallized birnessite was obtained with the presence of the main peaks of H-birnessite according to JCPDS 23-1239 card for H-birnessite (Mn₇O₁₃·5H₂O), noted by an asterisk, and situated at 12.23°, 24.52°, 36.49° and 38.61°. In addition, the main peak of the SnO₂ substrate, situated at 26.61°, was identified according to JCPDS n° 41-1445 card (SnO₂; Cassiterite), Fig. 1A. The lamellar structure of H-birnessite with its hexagonal space group is therefore well correlated with the diffractogram results, and in good agreement with our previous studies [8–10,22–24].

A preferential orientation was observed according to the (110) plane (12.23°) as already reported previously [9,19,22,23]. In complement, the crystallite size was determined for the main peak situated at 12.23° with the Scherrer's law, Eq. (3). The determined crystallite size value, equal to 11.47 nm (Table 1) is coherent with our previous studies [9,19,22,23].

$$L = \frac{0.9 \lambda}{\beta \cos \theta} \quad (3)$$

With λ = 1.540600 Å (Copper anti cathode), β the width peak at half height and θ Bragg's diffraction angle from (hkl) reflexion.

Table 1

Main characteristics of the two samples of H-birnessite (Mn₇O₁₃·5H₂O) electrodeposited as thin film onto SnO₂ (S = 3 cm²) with a 3 electrodes system (reference electrode: Ag/AgCl with a KCl 3 mol L⁻¹ solution, E = 0.210 V/SHE; Counter electrode: Platine wire spiraled, working electrode: SnO₂) and 80 mL of a solution prepared with 18.2 MΩ.cm Milli-Q water containing [MnSO₄] = 1.6 10⁻³ mol L⁻¹ with, as electrolyte, [Na₂SO₄] = 0.4 mol L⁻¹ at free pH (~ 5.5).

	Weight (+/- 10 ⁻³ g)	Number of mole (mol)	Cut off charge (C)	Synthesis time (min)	Mn AOS (+/- 0.03)	Crystallite size (nm) (XRD)	Crystal size (SEM)
HB1	1.07	1.56.10 ⁻⁶	1.80	40–45	3.75	11.47	2 μm × 10 nm
HB4	0.27	3.95.10 ⁻⁷	0.45	10–15	3.78	9.17	1 μm × 10 nm

SEM images confirm also that the electrodeposited HB1 thin films are nanostructured with a very good homogeneity, Fig. 1B. Indeed, the characteristic sheets of H-birnessite are very well formed (layered structure), with nice, neat, and orderly nanosheets, with crystal size about 2 μm × 10 nm, Table 1. This result is in good agreement with the preferential orientation reported by XRD measurements.

In addition, the samples were characterized by Raman spectroscopy, Fig. 1C. The spectra present the typical five bands characteristic to birnessite, noted from a to e, as reported in literature for samples as powder [25]:

- Band a is considered as the symmetric stretching vibration m2 (Mn—O) of the out-of-plane MnO₆ groups
- Band b is attributed to the stretching vibration u3 (Mn—O) in the basal plane of MnO₆ sheets; this band traduces the rate of Mn (IV) in the material, [25]
- Band c is related to Mn—O vibrations as deformation.
- The origin of the bands d and e is not really defined in the literature; it can be related to the rate of hydration of the sample, to the crystallization of the sample or to the nature of cation inserted into the nanosheets of birnessite.

It should be noted that the Raman spectra are very reproducible as presenting on Fig. 1C that corresponds to the superposition of fifteen different HB1 samples spectra after synthesis, with always the intensity of band b inferior to the intensity of band a. These measurements confirm also that the electrodeposition of HB1 samples is very reproducible.

In complement, the Average Oxidation State of manganese (AOS) of such samples was determined by a potentiometric titration method [21]. The experimental value equal to (3.75 ± 0.03) for three different measurements is in good agreement with the expected value for H-Birnessite (Mn₇O₁₃·5H₂O) (3.71), Table 1, and in good coherence with our previous studies [9,11,20].

3.1.2. Control of spontaneous reactivity of HB1 type samples to degrade methylene blue as reference

➤ Solution

First, and as reference, the spontaneous reactivity of HB1 type samples was studied for comparison to interactions coupling with electrochemistry. For that, 10 mL of a solution of methylene blue at 10 mg L⁻¹ (3.12 10⁻⁵ mol L⁻¹) were put in interaction with two HB1 samples in a pill dispenser as illustrated on Fig. 2A. After 6 h, the interaction solution became clearer blue due to the spontaneous degradation of methylene blue into azures (Table 2), as already reported previously [9]. After 20 h, the solution appeared violet, which is the typical color of thionin in good coherence with the associated UV–Visible spectrum, Fig. 2A (thionin; λ_{max} = 601 nm; Table 2). According to this value of absorbance, the concentration of thionin present in solution was estimated to 2.04 mg L⁻¹ (7.76.10⁻⁶ mol L⁻¹) corresponding to 24.9 % of the initial MB amount.

In parallel, the same experiment was carried out with only the substrate (two plates of SnO₂ with a similar surface), under the same conditions. In this case, the solution remained dark blue, and even after 20 h of interaction, Fig. 2B. Thanks to the UV–Visible measurements, there was no discoloration compared to the initial MB solution at 10 mg L⁻¹.

These experiments confirm that HB1 type samples can spontaneously degrade methylene blue with efficiency by simple direct interaction at room temperature without electrical input, in good agreement with our mechanism proposed previously [9].

➤ Solid

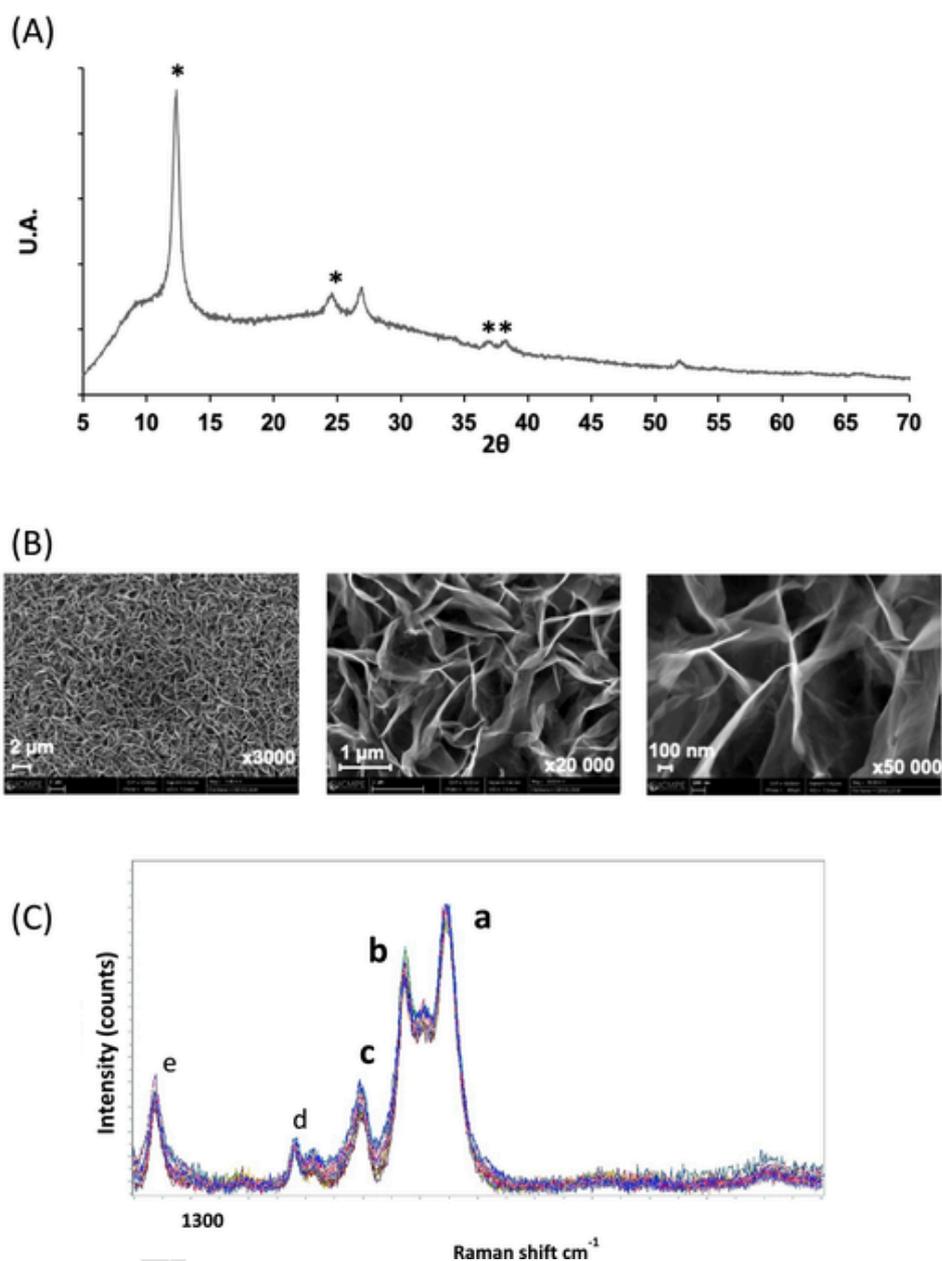


Fig. 1. HB1 sample characterization after synthesis: (A) Typical diffractogram with H-Birnessite peaks (*), (B) Typical SEM images at different magnifications, and (C) fifteen Raman spectra overlaid with the characteristic bands of birnessite (noted a to e).

After interaction, the HB1 samples remained visually intact, and well adherent onto the substrate that is why they were directly characterized by XRD, SEM and Raman spectroscopy without preparation, Fig. 3A, B and C.

On the diffractogram, the characteristic peaks of H-Birnessite are clearly present with the same preferential orientation that observed after synthesis, in addition to the main peak of SnO_2 situated at 26.61° Fig. 3A. The crystallite size, calculated after the spontaneous reaction, is equal to 10.27 nm, which is close to the value determined before interaction, Table 1. On SEM images, robust and ordered nanosheets are here despite the interaction, Fig. 3B. However, some crystals seem slightly nibbled at high magnification (inside the yellow square and pointed by the red arrows) confirming also the electronic transfers. Finally, in addition to the characteristic bands of birnessite (a, b, c), organic bands are clearly visible on the Raman spectrum, which can correspond to phenothiazine cycle (vibrations of $\text{C}=\text{C}$ and $\text{C}-\text{H}$ between 1200 and 1600 cm^{-1}), Fig. 3C. This observation is in good coherence

with our previous proposed mechanism, which reported that thionin was adsorbed onto the surface before slow mineralization step [9].

3.1.3. HB1 samples used as electrode for degradation of methylene blue: proofs of interest

> Solution

In this case, the sample HB1, used as the working electrode with a 3-electrodes system as described in the experimental section, was put in interaction with 10 mL of an aqueous solution of methylene blue at 10 mg L^{-1} ($3.12 \cdot 10^{-5}\text{ mol L}^{-1}$), as shown on Fig. 4A. The imposed potential chosen was $E = 1.1\text{ V}$, which is slightly higher than the synthesis potential. This value is optimal (i) to avoid the modification of H-birnessite, (ii) to have no parasite reactions (e.g. oxidation of water), and (iii) to have very low current intensities in order to limit the cost of energy, in good agreement with the development of a friendly environ-

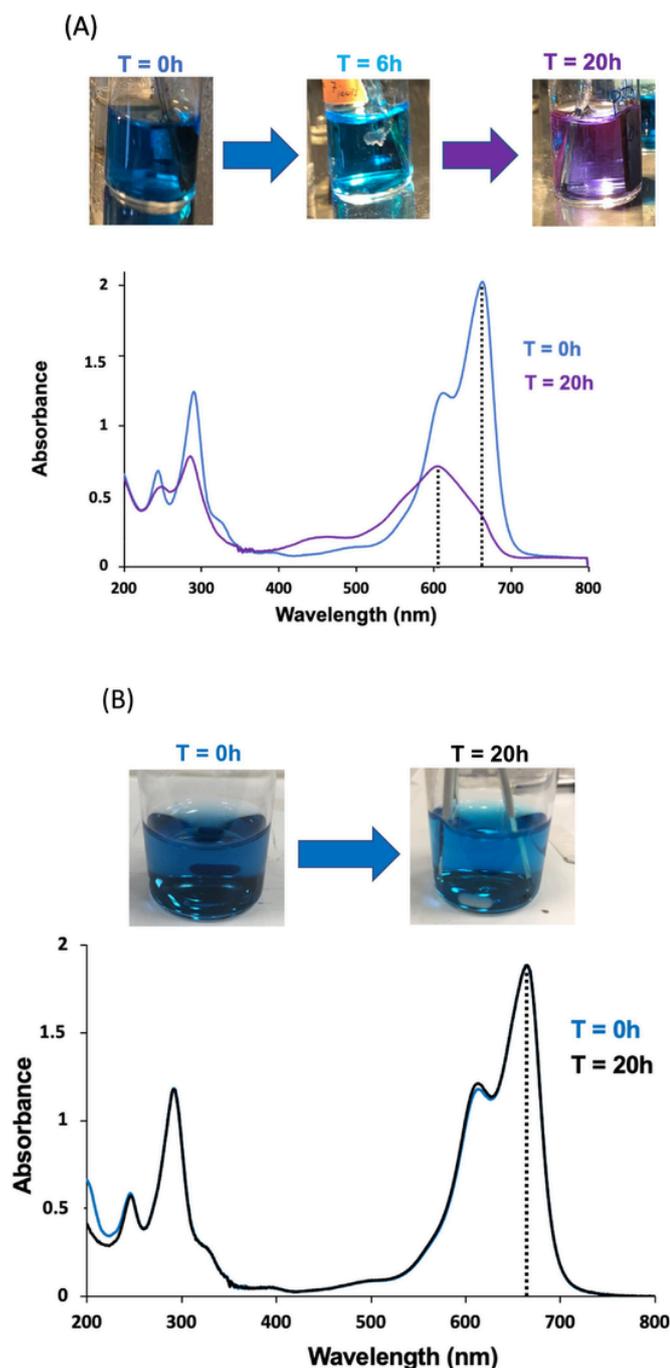
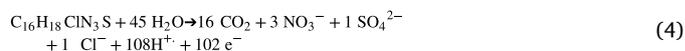


Fig. 2. Illustrations of spontaneous reactions with 10 mL of aqueous solution of MB at 10 mg L^{-1} : (A) with two HB1 samples from $t = 0 \text{ h}$ to $t = 20 \text{ h}$ and the corresponding UV-visible spectra; (B) with two SnO_2 plates (substrate) from $t = 0 \text{ h}$ to $t = 20 \text{ h}$ and the corresponding UV-visible spectra.

mental process, as already reported previously for other organic compounds (glyphosate and AMPA) [19].

In these conditions, a total discoloration of the solution was obtained after only 6 h, with intensity of current registered very low ($\sim 10^{-4} \text{ A}$) and a final average electric charge equal to (1.35 ± 0.20) Coulombs, Fig. 4A. For information, if methylene blue could be fully mineralized by electrochemistry (Eq. (4)), the expected theoretical electric charge, calculated with Faraday's law (Eq. (2)) for this amount of MB, would be equal to 3.07 C.



In parallel, the same experiment was carried out with the substrate alone (SnO_2). In these conditions, the solution remained clearly blue after 6 h with only 48 % of discoloration, and there was still MB in solution according to the associated UV-visible spectrum, Fig. 4B. The intensity of current recorded during this interaction was also very low ($< 10^{-5} \text{ A}$) with the final electric charge equal to 0.16 C. This partial discoloration of the solution could be attributed to the possible irreversible electro-oxidation and/or MB electropolymerization, [26] since an oxidation wave was observed onto SnO_2 by cyclic voltammetry measurements at this value of potential [27].

➤ Solid

After interaction, the HB1 samples remained visually intact and well adherent onto the substrate that is why they were directly characterized without preparation. The XRD characterization shows that they were not modified, with always the presence of the characteristic peaks of H-birnessite, and the same preferential orientation, in addition to the SnO_2 peak situated at 26.61° , Fig. 5A. The calculated crystallite size is equal to 10.14 nm, which remains in the same order of magnitude than before interaction, Table 1. SEM images show also that the samples are still intact with robust and homogeneous nanosheets, typical of birnessite, Fig. 5B.

In addition, the Raman spectrum is equivalent to a HB1 spectrum before interaction with no organic bands, Fig. 5C. Therefore, after 6 h of interaction with electrochemistry, there is no adsorption of organic compounds onto the surface of the material in contrary to the case of the spontaneous reaction (Fig. 3C). Moreover, the intensity value of the band b stays similar than for one sample after synthesis, indicating that the Mn (IV) rate in the material did not significantly decrease. This result highlights a possible regeneration of the material in continuous thanks to the imposition of a potential, as already reported in the case of the degradation of other organic compounds by coupling with electrochemistry [19].

3.2. In situ measurements for monitoring the reactivity of HB1 samples in real time: spontaneous reaction vs electrochemical way

The discoloration being very fast with electrochemistry, it is difficult to determine visually the mechanism. For that, *in situ* measurements by UV-Visible spectroscopy measurements were done on the solutions in real time to go further to understand interfacial mechanism.

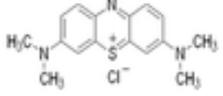
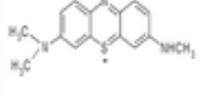
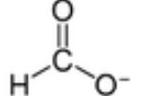
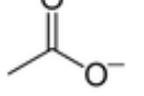
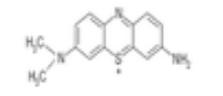
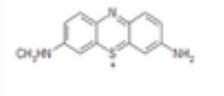
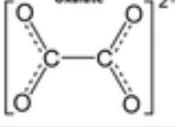
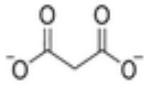
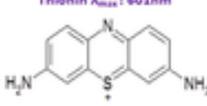
3.2.1. In situ UV-visible spectroscopy measurements of the solutions in real time

The UV-Visible spectrum presented in Fig. 6A demonstrates the efficiency of one HB1 sample ($1.56 \cdot 10^{-6} \text{ mol}$ of H-birnessite) for spontaneously degrading MB in 10 mL of a solution containing 1 mg L^{-1} ($3.12 \cdot 10^{-8} \text{ mol}$ of MB), put in an optical cell ($l = 4 \text{ cm}$). The total duration of this reaction was equal to 8 h 45.

When one HB1 sample was put in 10 mL of a 2 mg L^{-1} solution ($6.24 \cdot 10^{-8} \text{ mol}$ of MB) in the same optical cell ($l = 4 \text{ cm}$), the UV-Visible spectrum shows a blocking at $\lambda_{\text{max}} = 601 \text{ nm}$, characteristic of thionin, at the end of the spontaneous interaction experiment for an equivalent duration to the previous experiment Fig. 6B. The shift from 664 nm to 601 nm, passing through other wavelengths during all the duration of the experiment, corresponds to the formation of azures as mixture, in good coherence with the spontaneous degradation mechanism already proposed in previous work [9]. The amount of remaining thionin in solution was estimated to 0.10 mg L^{-1} ($3.80 \cdot 10^{-7} \text{ mol L}^{-1}$; $3.80 \cdot 10^{-9} \text{ mol}$ in 10 mL), corresponding to 6 % of the initial amount of MB. In addition, an isobestic point appears as the reaction progresses,

Table 2

Detection of the different species in solution after discoloration and MB degradation by spontaneous interaction and/or coupling to electrochemistry, and according to the initial concentration of MB.

Methylene Blue and its by-products detected by UV-visible Spectroscopy		Species detected by Ion Chromatography		
<p>Methylene Blue λ_{\max}: 664nm</p> 	<p>Azur B (AB) λ_{\max}: 638nm</p> 	<p>Formate</p> 	<p>Acetate</p> 	<p>Cl^-</p> <p>NO_3^-</p> <p>SO_4^{2-}</p> <p>CO_2</p> <p>Mn(II)</p>
<p>Azur A (AA) λ_{\max}: 628nm</p> 	<p>Azur C (AC) λ_{\max}: 618nm</p> 	<p>Oxalate</p> 	<p>malonate</p> 	
<p>Thionin λ_{\max}: 601nm</p> 		<p>Maleic acid</p> 		

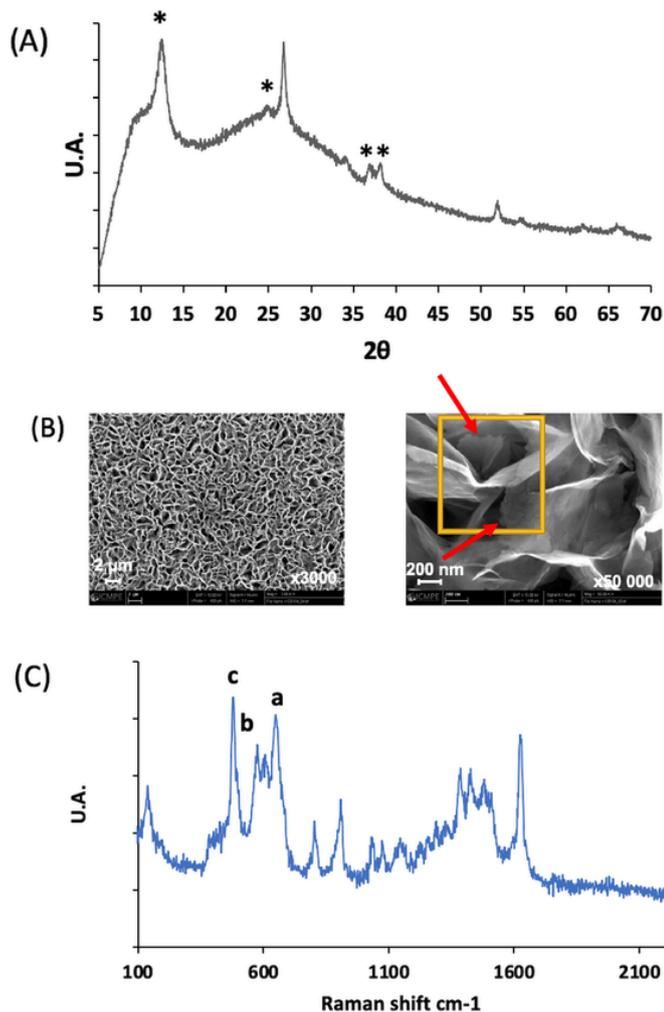


Fig. 3. Solid characterization after spontaneous interaction between 2 HB1 and 10 mL of aqueous solution of MB at 10 mg L^{-1} (A) Diffractogram with the characteristic peaks of birnessite (*), (B) SEM images, and (C) Raman spectrum.

Fig. 6B, indicating that the substances have the same extinction coefficient for this specific wavelength. The observation of an isobestic point proves that it is a one-step reaction resulting in the transformation of the starting compound into a product, or a mixture of end products, in fixed proportions. Moreover, there is a significant absorbance between 450 and 500 nm, which could be attributed to the mixture of dyes and/or the presence of Mn (II) complex in solution [28], however, the absorbance is largely amplified in this case due to the optical cell ($l = 4 \text{ cm}$).

When one HB1 sample was put in 3.5 mL of a MB solution at 10 mg L^{-1} in a quartz cell ($l = 1 \text{ cm}$; $1.09 \cdot 10^{-7} \text{ mol}$ of MB), the spontaneous degradation blocking is further accentuated as illustrated by the UV-Visible spectrum, Fig. 6C. In this case, the discoloration reaction was not total even after 18 h. In these conditions, the HB1 sample is partially effective because it blocks rapidly at the level of the production of azures (mixture), the solution staying dark blue at the end of the experiment.

The last spectrum reports the interaction between one HB1 sample and 3.5 mL of a MB solution at 10 mg L^{-1} in a quartz cell ($l = 1 \text{ cm}$; $1.09 \cdot 10^{-7} \text{ mol}$ of MB) but coupled with electrochemistry, Fig. 6D. In these conditions, the solution was totally discolored after only 2 h 35 in comparison to the spontaneous reaction blocked for an equivalent concentration, Fig. 6 C. Moreover, no shift of $\lambda_{\max} = 664 \text{ nm}$ was observed, signifying that MB was directly degraded without the significant production of azures or thionin. In addition, the intensity of current was very low during the interaction experiment ($< 10^{-5} \text{ A}$) and comparable to equivalent *ex-situ* experiments.

In complement, *in situ* experiments with the substrate alone (SnO_2) were carried out, and conclusions were equivalent to *ex situ* experiments: no significant discoloration concerning spontaneous reaction, and the same % of discoloration when SnO_2 was coupled to electrochemistry. These results confirm again the real efficacy of electrodeposited birnessite thin films to degrade MB.

3.2.2. Complementary characterization of solids by Raman spectroscopy

At the end of these different types of *in situ* measurements, Raman spectra were recorded on the samples, and the results are comparable to *ex situ* experiments. Indeed, the organic bands were observed in all cases after spontaneous interactions, and even for 1 mg L^{-1} , and no modification of birnessite was noted after interaction with electrochemistry, inset Fig. 6A to D.

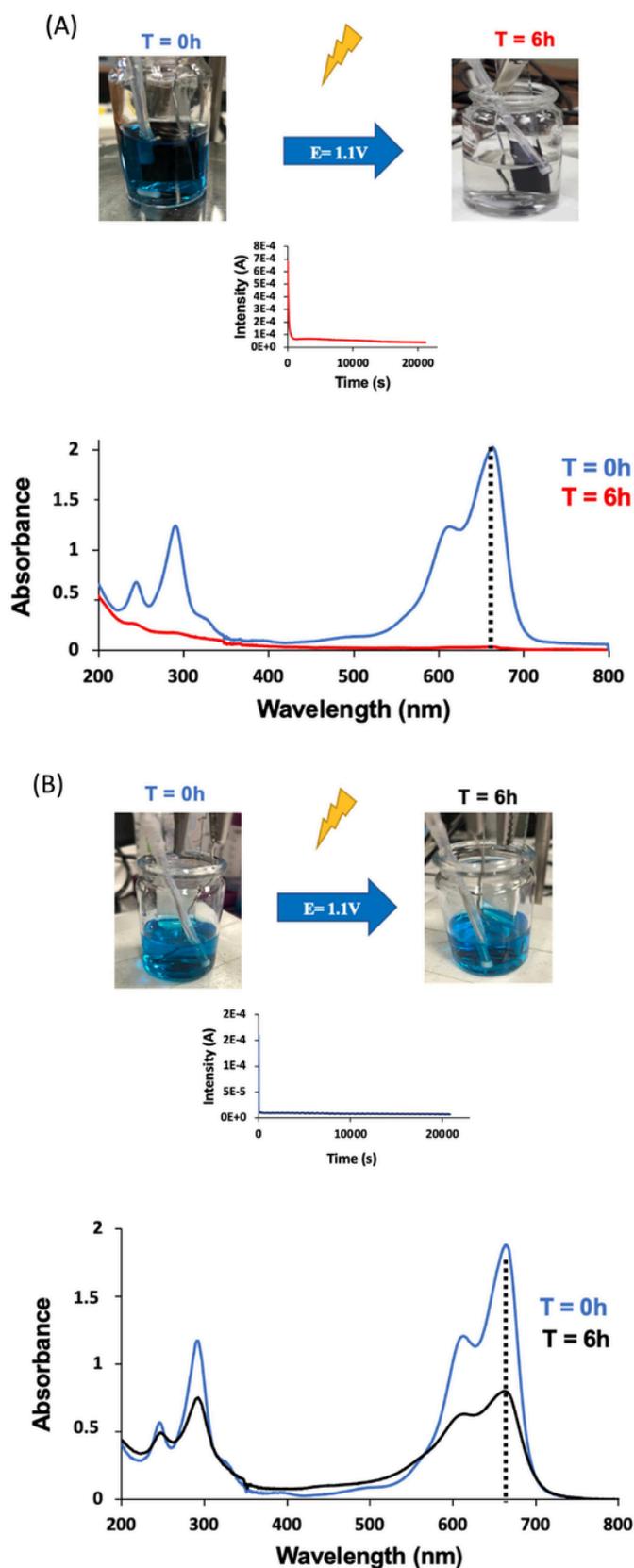


Fig. 4. Illustration of the interaction coupled with electrochemistry, and 10 mL of an aqueous solution of MB at 10 mg L^{-1} with the associated electrochemical curves and UV-visible spectra for (A) one HB1 sample, and (B) one plate of the substrate alone (SnO_2).

However, in the case of the coupling with electrochemistry, Raman spectra were carried out systematically when the solution was totally discolored. Perhaps in these conditions, the detection of the presence of organic compounds onto the surface cannot be possible due too low amounts. That is why, in complement, Raman spectroscopy measurements were performed at the very beginning of the interactions when the solution was still colored (blue).

Fig. 7 presents the monitoring of the solid evolution by Raman spectroscopy after 10, 30, 60 and 100 min, with the associated registered currents. In each case, the intensity of current was very low and comparable to an equivalent experiment in continuous. Clearly, there is no change in the Raman spectra compared to the original spectrum of HB1 whatever the duration.

Regarding the mechanism, methylene blue seems degraded directly without intermediate steps of organic sorption onto the surface, even at the beginning of the degradation (few minutes), and without any modification of birnessite.

3.3. Analysis of solutions by ion chromatography after interactions: spontaneous reaction vs electrochemical way

3.3.1. Spontaneous interaction case

To determine the produced species by ion chromatography, it was necessary to have uncolored solutions. For that, spontaneous interaction experiment was performed with four samples of HB1 during 24 h with 10 mL of a MB solution at 10 mg L^{-1} [9]. The final solution totally discolored was analyzed by anionic chromatography. Small non-toxic organic acids (formate and acetate ions), in addition to chloride, sulfate and nitrate ions, were detected (Table 2). The presence of such species confirms that MB molecule was really broken after spontaneous interaction, and that it was not only a sorption reaction.

In complement, cationic chromatography analysis was performed and a few amount of Mn (II) was detected in solution (1.66 mg L^{-1} ; $3.02 \cdot 10^{-5} \text{ mol L}^{-1}$), confirming also the spontaneous electronic transfers between MB and birnessite (*i.e.* Mn (IV) reduced into soluble Mn (II), Eq. (5)):



However, the concentration of Mn (II) found corresponds to 0.68 % of the initial amount of the manganese containing in the four HB1 samples, which is largely lower than the expected value for this rate of MB degradation. This result confirms then the spontaneous partial regeneration of birnessite in the presence of dissolved oxygen containing in the aqueous solutions, as already proposed generally in literature, and more particularly for the electrodeposited thin films [8–10,18].

3.3.2. Case of interaction coupled to electrochemistry

The discolored solutions obtained after 24 h by coupling with electrochemistry with an equivalent initial concentration (10 mL at 10 mg L^{-1} of MB), were also analyzed by anionic chromatography. As in the case of spontaneous interaction, in complement to chloride, sulfate and nitrate ions, the same non-toxic organic acids (formate and acetate ions) were detected in solution, but with higher concentrations for formate, confirming the interest of the electrochemistry coupling. The presence of these organic acids in solution confirms also the real degradation of the methylene blue in this case, and not only its discoloration.

In complement, cationic chromatography analysis was performed, and Mn (II) was not detected in solution in this case, validating the total regeneration of the material by imposition of potential (electrodeposition), which is another interest of the coupling to electrochemistry.

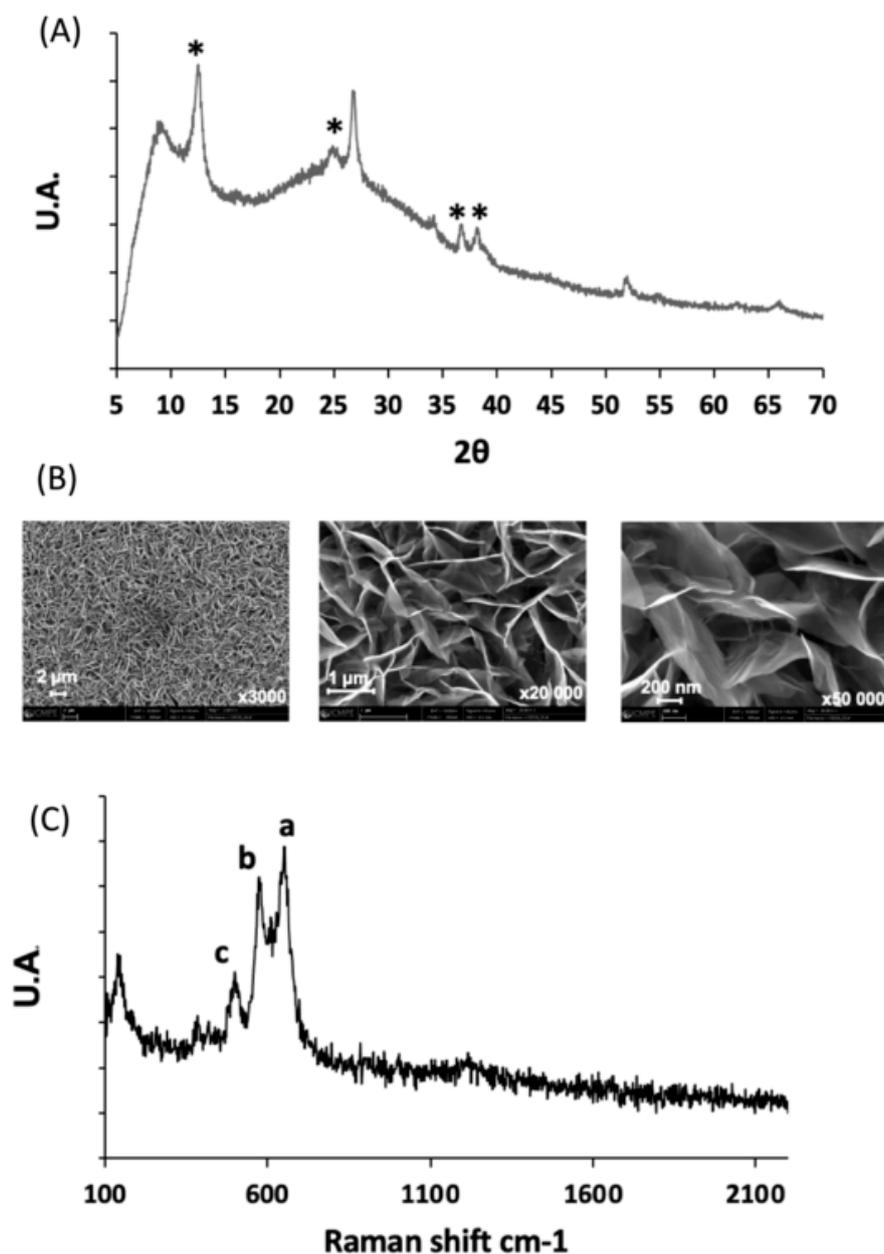


Fig. 5. Solid characterization after interaction coupled with electrochemistry between HB1 and 10 mL of aqueous solution of MB at 10 mg L⁻¹ with (A) the diffractogram with the characteristic peaks of birnessite (*), (B) SEM images, and (C) Raman spectrum.

3.4. HB1 samples used as electrode for methylene blue degradation: Determination of their capacity and robustness towards higher MB concentrations

The main objectives were (i) to determine the robustness and efficiency of HB1 samples used as electrode by increasing the concentrations of methylene blue present initially in solution (from 20 to 100 mg L⁻¹), and (ii) to scrutinize the mechanism when the pollutant was in excess compared to the birnessite amount.

3.4.1. Discoloration rates of solutions

For testing their efficiency, one HB1 sample used as electrode was interacted with 10 mL of aqueous solutions containing higher BM concentrations such as 20, 40, 60 and 100 mg L⁻¹. For that, UV-Visible spectroscopy measurements were performed after 6 h, 24 h and 65 h for the different solutions in the aim to determine the rate of discoloration at $\lambda = 664$ nm for each concentration, calculated according to

Eq. (6), in comparison to the case of 10 mg L⁻¹ studied previously, Fig. 8A.

$$\% \text{ discoloration} = \frac{(A_0 - A)}{A_0} \times 100 \quad (6)$$

With A_0 , the absorbance at $\lambda = 664$ nm at $t = 0$ h; A , the absorbance at $\lambda = 664$ nm at t (h).

It appears that the % of discoloration after 6 h slightly decreases with increasing the initial concentration; however, it stays around to 80 % regardless of the initial concentrations with the minimum being equal to 75.5 % for the initial concentration of 100 mg L⁻¹, Fig. 8A. For the highest concentrations (60 and 100 mg L⁻¹), small amounts of azures as mixture were observed for this duration.

After 24 h, the discoloration was total for the concentrations equal to 20 and 40 mg L⁻¹, and higher to 90 % for the highest concentrations (60 and 100 mg L⁻¹) that correspond to the cases of an excess of pollu-

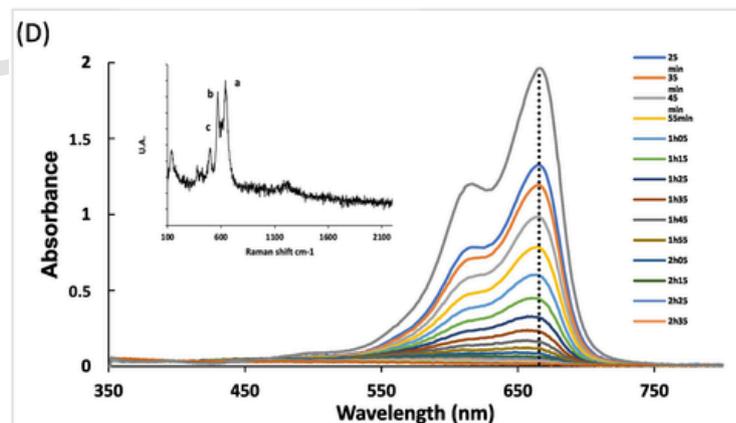
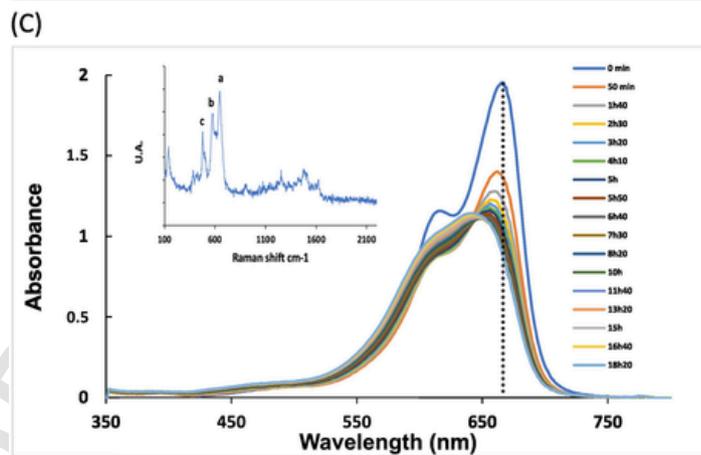
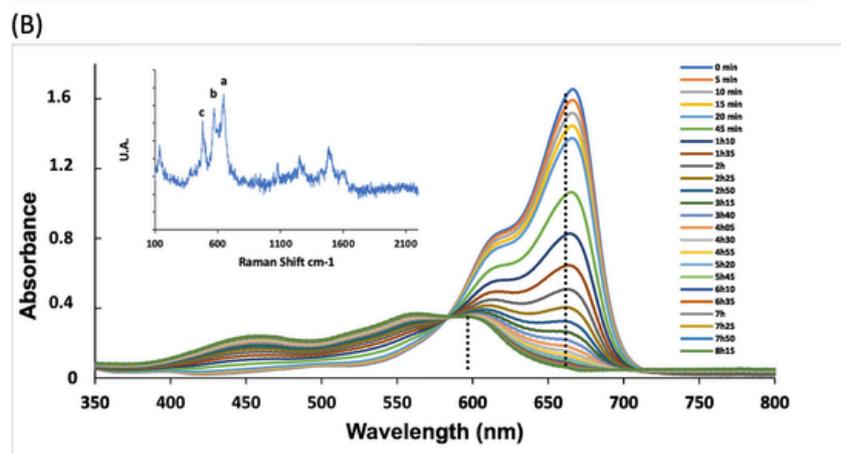
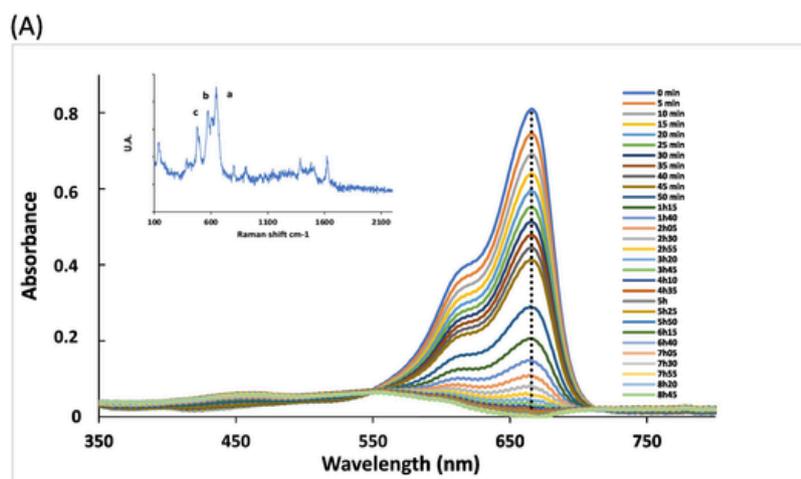


Fig. 6. UV-Vis spectroscopy measurements performed *in situ* and in real time for different cases with one HB1 sample: (A) Spontaneous interaction with 10 mL of MB solution at 1 mg L⁻¹ in a 4 cm boro-silicate cell under stirring at 350 rpm (B) Spontaneous interaction with 10 mL of MB solution at 2 mg L⁻¹ in a 4 cm boro-silicate cell with stirring at 350 rpm (C) Spontaneous interaction with 3.5 mL of a MB solution at 10 mg L⁻¹ in a 1 cm quartz cuvette with stirring at 350 rpm (D) An interaction coupled to electrochemistry with 3.5 mL of MB solution at 10 mg L⁻¹ under stirring at 250 rpm with a 3-electrode system (reference: Ag/AgCl homemade, working: sample HB1, CE: Pt wire). *Inset:* Raman spectrum associated measured on each sample at the end of experiment.

tant, in comparison to the amount of birnessite contained in one sample of HB1 (Fig. 8A). The total discoloration was obtained after 65 h for all initial concentrations, as illustrated on Fig. 8B for the initial concentration equal to 100 mg L⁻¹, which reports the final UV-visible spectrum in comparison to the initial spectrum.

3.4.2. Analysis of solutions by ion chromatography

In parallel, the discolored solutions, obtained in all cases after 65 h, were analyzed by anionic chromatography. According to the results, a perfect linear trend between the formate ions produced (mol L⁻¹) and the initial MB concentration (mol L⁻¹) is obtained, Fig. 8C. This indicates that there is no saturation phenomenon, whatever the initial concentration of MB, and traduces the great efficiency of such samples for dye degradation, and even when the pollutant is in excess. According to the value of the slope, two formate ions are produced simultaneously.

When the concentration of MB increases, in addition to formate and acetate ions, other non-toxic organic acids were detected as traces in solution such as oxalate and malonate, Table 2, in complement to the presence of a substantial peak of carbonate ions, not quantifiable because the reaction was made in the air without special precautions. The presence of such species confirms the total break of the organic cycles in good agreement with the final UV-Visible spectrum (no specific bands in the UV range), Fig. 8B.

In addition, cation chromatography analyses report that Mn (II) was not detected in solution after 65 h in all cases, confirming the continuous and efficient regeneration of the solid.

3.4.3. Characterization of HB1 samples after interaction

In complement, the thin films were characterized at the end of the experiments (65 h). When the reaction was coupled with electrochemistry, regardless of the concentration of MB (from 20 to 100 mg L⁻¹), there is no organic compounds adsorbed onto the HB1 surface, as shown by the Raman spectra reported in Fig. 9A for 20, 40 and 100 mg L⁻¹. Moreover, no other manganese oxides were produced since only typical bands of birnessite are observed on the spectra.

Moreover, the diffractogram of the sample HB1, after the interaction with a solution containing 100 mg L⁻¹, always reports the characteristic peaks of H-birnessite, Fig. 9B, in good agreement with the SEM observations, which confirm that the nanosheets are not modified, Fig. 9C. These all results validate the very good robustness and stability of these samples HB1 used as electrode, even after degradation of high MB concentrations (100 mg L⁻¹).

In complement, the evolution of the solid by Raman spectroscopy was performed for the highest concentration, corresponding to an excess of pollutant (100 mg L⁻¹), after different durations at the beginning of the discoloration and when the solution was still blue (from 10 to 190 min), Fig. 10. In all cases, the spectra present the typical main bands of birnessite, but adsorption of organic compounds (phenothiazine molecules) at the surface onto the solid was observed until 60 min of interaction. Then, there is a decrease of this adsorption phenomenon, until completely disappearing after 190 min, because after this duration the amount of birnessite was in excess to the amount of the pollutant. In fact, the associated UV visible spectrum (not shown) reports that 50 % of MB were degraded after 190 min (concentration of MB equal to 50 mg L⁻¹), that is why there is no more adsorption of MB onto surface.

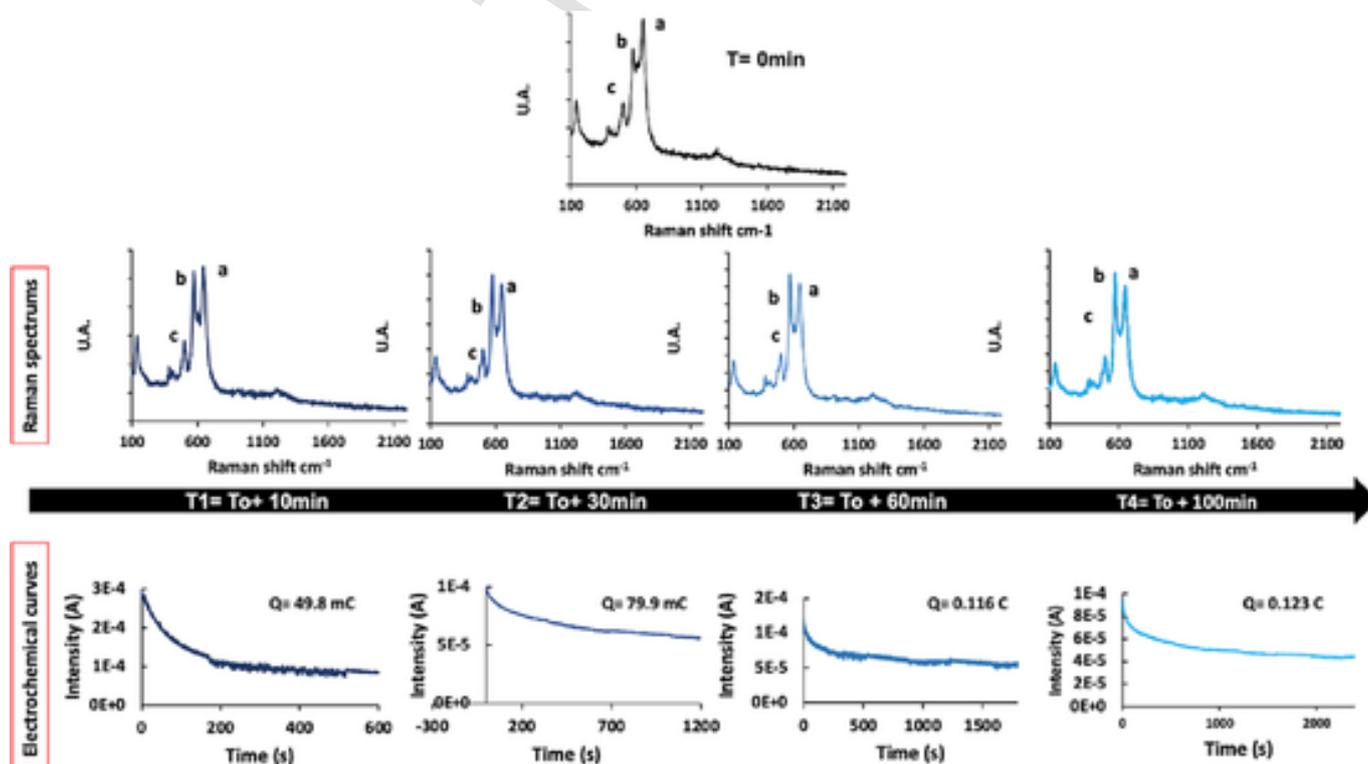


Fig. 7. Characterization by Raman spectroscopy of one HB1 sample during the interaction coupled to electrochemistry with 10 mL of a MB solution at 10 mg L⁻¹ and the associated electrochemistry curves. Measurements after 10 min, 30 min, 60 min, and 100 min in comparison to the initial Raman spectrum of the HB1 sample before interaction.

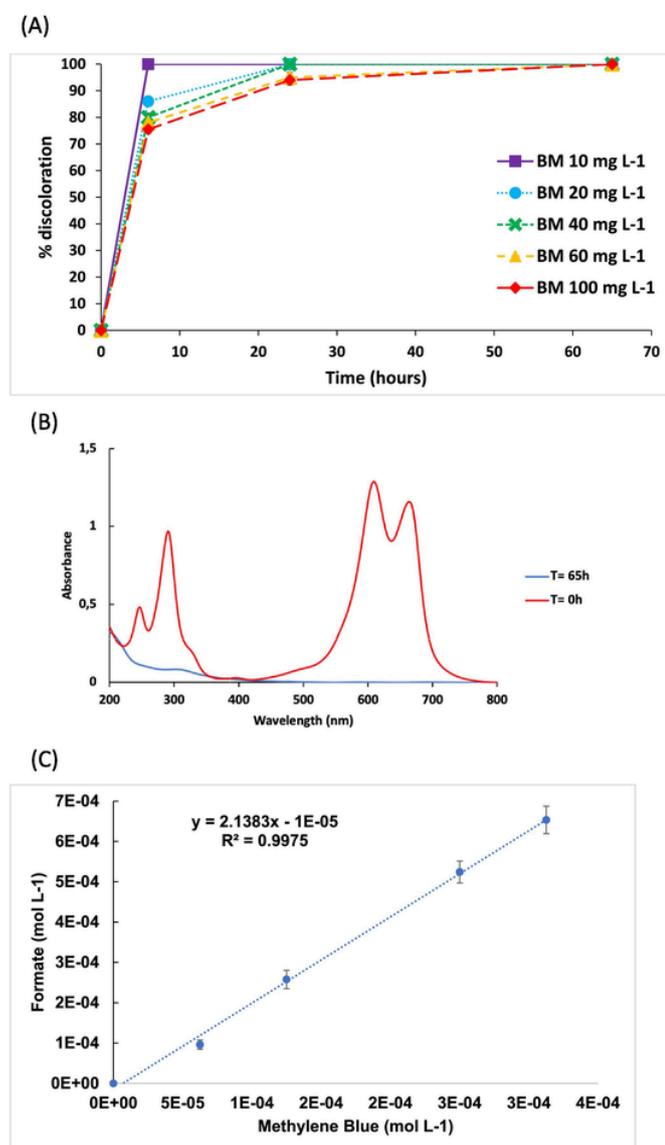


Fig. 8. (A) % of degradation for different durations at $\lambda = 664$ nm for different initial concentration of MB in interaction with one HB1 sample used as electrode. (B) UV-vis spectrum of the initial MB solution at 100 mg L^{-1} and after 65 h in interaction with one HB1 sample used as electrode, both measurements realized into a 0.1 cm quartz cell, and (C) formate content in mol L^{-1} after 65 h of interaction between one HB1 used as electrode and a MB solutions at different concentrations.

3.4.4. Discussion

According to the analyses of solutions and characterization of solids, it appears that the final results after 65 h are equivalent whatever the initial concentration, with a total discoloration and no modification of the solid due to a total regeneration (no Mn (II) in solution) with the same crystalline structure (no modification of Raman spectra and diffractogram). However, it appears also that for shorter durations, the amount of birnessite, in comparison to the pollutant amount, seems slightly orientated the production of the intermediary species (azures), and/or species adsorbed onto the surface as illustrated on Fig. 11.

Indeed, if the amount of birnessite (in mol) is higher than the number of MB mol, the dye was degraded directly into small organic acids and minerals without intermediate steps (no production of azures in solution and no organic species adsorbed onto the birnessite surface), with the electrochemical coupling. This can be due by immediate breaking of the molecule degraded onto the birnessite surface thanks to

the capture of the pollutant at the level of two adjacent sites. Then, thanks to the birnessite quantity in excess, and due to the total and continuous regeneration of the material, the surface is never saturated, and the reaction is linked very quickly.

In contrary, when methylene blue is in excess in solution compared to birnessite, the solid can have rapidly its sites saturated in the beginning of the reaction, and cannot be able to cling the pollutant due to few sites, leading to the presence of intermediate species in solution (azures and thionin) and organic species adsorbed onto the surface (Raman spectra). In this case, MB molecule cannot be break directly (no adjacent sites). However, this phenomenon seems rapidly disappeared as soon as the amount of pollutant becomes inferior to the amount of birnessite, and then the degradation is total without modification of the solids, despite these intermediate steps.

According to these results, it appears that one HB1 sample used as an electrode material is able to totally discolored and degraded 1 mg of MB containing initially in 10 mL of solution with an initial concentration equal to 100 mg L^{-1} , which corresponds to a capacity equal to 934 mg of MB per gram of HB1 material, Eq. (7):

$$\text{Degradation capacity} = \frac{\text{Mass MB degraded (mg)}}{\text{Mass of birnessite (g)}} \quad (7)$$

This degradation capacity seems high compared to other data in the literature. Indeed, for example, Kara et al. report a q_{max} equal to 90.91 mg g^{-1} using periodiated modified nanocellulose for elimination by sorption with no degradation, [29], or a q_{max} of 67% MB removal for an initial MB concentration of 100 mg L^{-1} using nano manganese oxides and birnessite at $80 \text{ }^\circ\text{C}$, for the elimination of organic dyes by sorption with no degradation [4].

Our eco-friendly degradation method is comparable to electro-oxidation with active chlorine of selected dyes in chlorine solutions using undivided cells with DSA-type electrodes, metals, and graphite as anodes at $20\text{--}30 \text{ }^\circ\text{C}$; however, the intensity of currents, fixed to 20 mA cm^{-2} [30], is largely higher than our recorded intensities. Indeed, in both cases, for 80 mg L^{-1} of MB, there is 100% of color removal (94% COD decay [30]), and 100% of MB degradation with our eco-friendly process but with very lower energy inputs. Other composite films in the literature such as $\text{Ag-Cu}_2\text{O}$ can degrade MB with photocatalytic activities. For example, 4.5 cm^2 of $\text{Ag-Cu}_2\text{O}$ is used as electrode, with 50 mL of MB solution at 30 mg L^{-1} and the photodegradation rate of MB reaches 95.1% compared to 100% for our method in near conditions (10 mL of MB solution at 100 mg L^{-1} with H-birnessite surface of 3 cm^2) [31].

Our results are very promising for future applications. However, it appeared interesting to study the possibility of decreasing the birnessite amount, and not the geometric surface of sample, since the degradation appears as an interfacial reaction performed onto the surface of the material, as currently reported in the literature for birnessite [8–10,13].

3.5. Which is the effect of birnessite amount containing in thin film used as electrode material to degrade methylene blue? Case of HB4 sample

The main objective was to determine if the decrease of the material amount via the thickness could limit the interfacial discoloration/degradation reaction. For that, another type of birnessite samples with very low amount of material, four times less quantity than HB1 samples (noted HB4) were used. This type of sample was specially optimized previously for elimination of heavy metal by sorption [20]. Similar experiments were carried out therefore with HB4 samples used as electrode material for studying the reactivity and the kinetics of the degradation of organic compounds, in comparison to HB1 samples, in addition to determine their robustness.

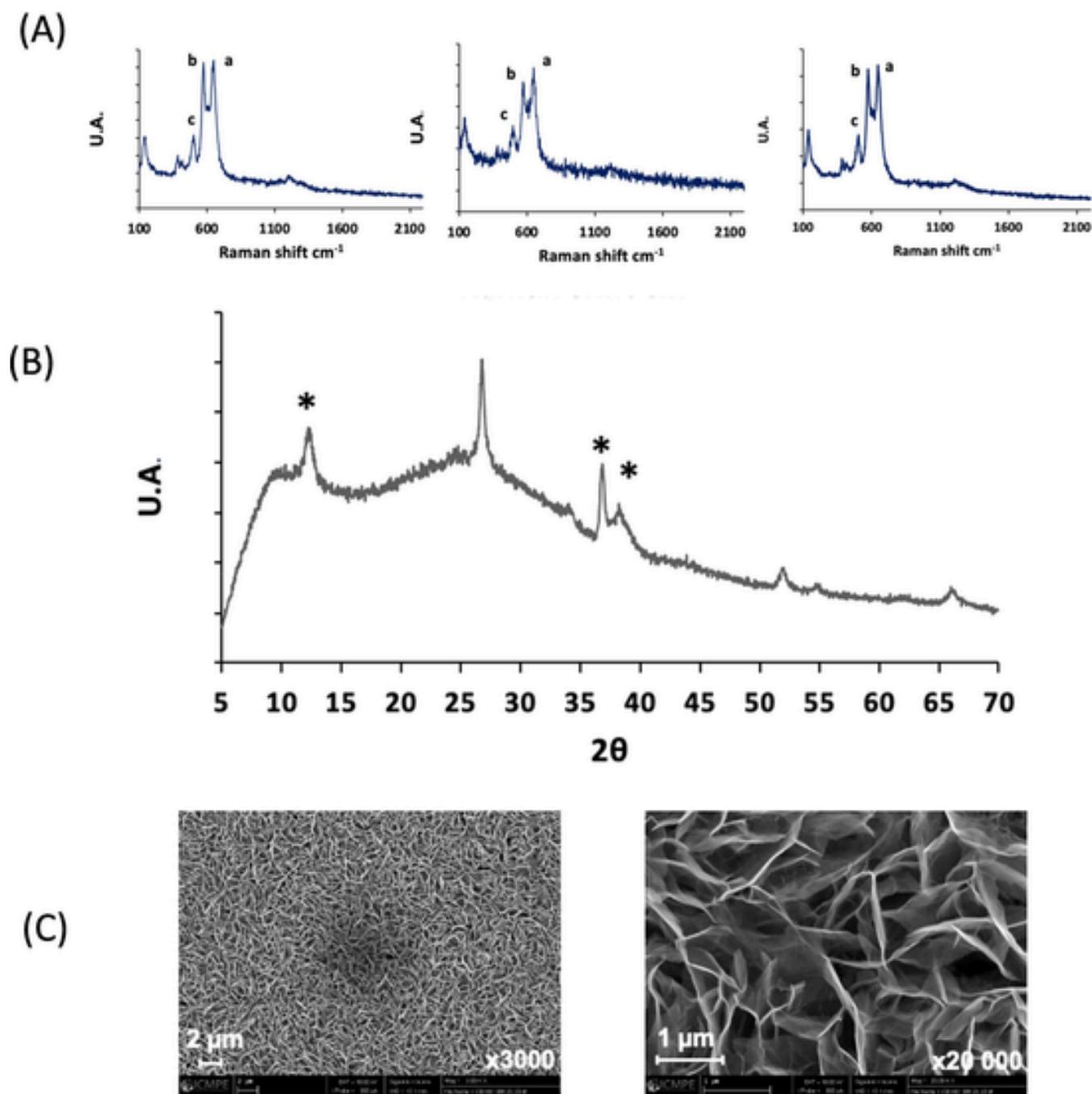


Fig. 9. (A) Raman spectra of one HB1 sample after an interaction coupled with electrochemistry during 65 h with 10 mL of MB solution at 20 mg L⁻¹, 40 mg L⁻¹ and 100 mg L⁻¹ (B) diffractogram of one HB1 sample after an interaction coupled with electrochemistry with 10 mL of MB solution at 100 mg L⁻¹ (C) SEM images of one HB1 sample after an interaction coupled with electrochemistry with 10 mL of MB solution at 100 mg L⁻¹.

3.5.1. HB4 samples: synthesis and characterization

HB4 samples were electrodeposited onto SnO₂ substrate as homogeneous brown adherent films (3 cm²), by chronoamperometry at $E = 1.0$ V at fixed electric charge equal to 0.45 C (0.15 C cm⁻²). The synthesis conditions are the same than for HB1 sample, except the duration; it only takes 15 min to synthesize HB4 samples. The experimental mass of HB4 samples is equal to $(0.27 \pm 0.10) \cdot 10^{-3}$ g, average value based on ten different samples measurements, Table 1. This value is in good concordance with the theoretical mass expected for this value of electric charge (0.26 $\cdot 10^{-3}$ g) calculated according to Eqs. (1) and (2). The Average Oxidation State of manganese (AOS) determined by the potentiometric titration method [21] is equal to 3.78 ± 0.03 , this value being almost the same that for HB1 samples.

The diffractogram of HB4 sample reports the main peaks of H-birnessite at 12.33°, 36.26° and 38.01°, but the intensity was low certainly due to the very few amounts of birnessite ($< < 10^{-3}$ g), Fig. 12A. The crystallite size equal to 9.17 nm is comparable to HB1 samples, Table 1. The SEM observation reports the homogeneous and stable structure with well-defined nanosheets typical of H-birnessite, Fig. 12B, with crystal size smaller than for an HB1 sample (about 1 μm × 10 nm) Table 1. The Raman spectrum is similar and superimposable to the spectrum of a HB1 sample with the characteristic bands of birnessite, Fig. 12C. This is consistent with the similar Mn oxidation degree within the material. In conclusion, both sample have nearly the same properties, except that HB4 has four times less material than HB1, Table 1.

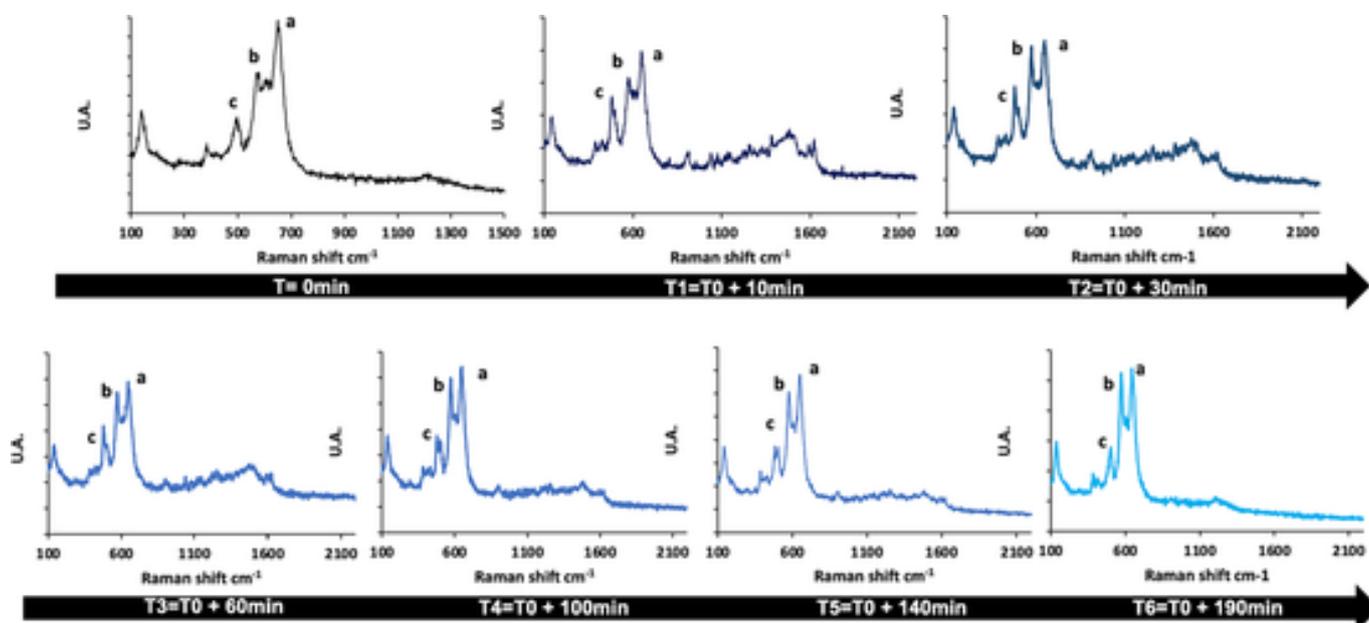


Fig. 10. Characterization by Raman spectroscopy of one HB1 sample during the interaction coupled to electrochemistry with 10 mL of a MB solution at 100 mg L^{-1} , and the associated electrochemistry curves. Measurements after 10 min, 30 min, 60 min, 100 min, 140 min and 190 min in comparison to the initial Raman spectrum of the HB1 sample before interaction.

3.5.2. Studies of the HB4 sample reactivity used as electrode material by *in situ* UV-visible spectroscopy measurements on the solution in real time: comparison to HB1 sample

The *in situ* measurement coupled to electrochemistry was performed with one HB4 sample ($3.95 \cdot 10^{-7}$ mol of birnessite) put in an optical cell ($l = 1 \text{ cm}$) containing 3.5 mL of MB solution at 10 mg L^{-1} ($1.09 \cdot 10^{-7}$ mol of BM). The total interaction duration was equal to 3 h 10, but after only 2 h, a total discoloration of the BM solution was reached without the production of intermediary species (no azures and/or thionin), Fig. 13A, as already observed for an equivalent interaction with one HB1 sample, Fig. 6D. In addition, the intensity of the current was very low (inferior to 10^{-5} A) (inset Fig. 13A) with a final electric charge very small and comparable to experiments performed with one HB1 sample (0.26 C for HB4 and 0.33 C for HB1 respectively).

Moreover, the kinetics of degradation, which is a pseudo-order 1, are similar for HB1 and HB4 samples, Fig. 13B. This order of reaction is the same that reported in our previous studies focused on the spontaneous degradation of MB with birnessite thin films [9]. However, this pseudo-order 1 was largely reported in the literature for the elimination and/or degradation of MB by different methods [1–3].

In complement, the HB4 sample was characterized by Raman spectroscopy after interaction, and the spectrum is equivalent to a sample before interaction with no adsorption of organic compound onto the surface, exactly like a HB1 sample, Fig. 13C. In conclusion, despite the lower matter amount of HB4, the two samples have quite similar reactivity and degrading power, when birnessite was in excess (low concentration of dye, $\leq 10 \text{ mg L}^{-1}$).

3.5.3. Preliminary results of HB4 samples used as electrode towards higher MB concentrations

To test the efficiency of HB4 sample used as electrode, higher BM concentrations (from 20 to 60 mg L^{-1}) were studied. In all cases, BM was in excess in comparison to the amount of birnessite containing in one HB4 sample, Fig. 11.

➤ Discoloration rates

As previously, UV-Visible spectroscopy measurements were performed after 6 h, 24 h and 65 h for determining the rates of discoloration at $\lambda = 664 \text{ nm}$.

After 6 h, the rate of discoloration slightly decreases with the increasing of the initial concentration; however, it stays around to 74 % even for the highest initial concentration. This value is directly comparable to the % discoloration of a MB solution after 6 h of interaction with one HB1 sample. Again, this proves the efficiency of the HB4 samples, even in presence of an excess of BM, Fig. 14A. For these all concentrations, MB is in excess compared to the amount of birnessite, and small amounts of azures as mixture were observed in solution after 6 h.

Therefore, it appears that the sample HB4 behaves like the sample HB1, as soon as the quantity of MB is higher than the quantity of birnessite, intermediate by-products are detected in solution during its degradation. However, one HB4 sample can degrade 100 % up to 60 mg L^{-1} of a MB solution in 65 h. The example of the case at 60 mg L^{-1} , with the initial and final UV-visible spectra, is given on Fig. 14B: there is no longer any trace of MB in solution, which demonstrates the effectiveness of the sample despite its low quantity of matter.

➤ Analysis by ion chromatography

The ion chromatography analyses of the decolorized MB solutions after 65 h and containing initially different concentrations (from 20 to 60 mg L^{-1}) report the detection of the same organic acids (e.g. formate, acetate, oxalate, maleate ions) in addition to chloride, nitrate and sulfate ions. In complement, there is no Mn (II) in solution; this once again supports the fact that there is a continuous regeneration of the material, hence the interest of electrochemistry.

➤ Characterization of the solids after interaction

Thin films were characterized after interaction by XRD, SEM and Raman spectroscopy (Fig. 15A, B and C). On the diffractogram, the main peaks of birnessite were always present in addition to the SnO_2 peak, Fig. 15A. Moreover, there is no change into nanosheets, as observed on the SEM images, which stayed stable and robust after interaction coupling to electrochemistry, Fig. 15B. In addition, there is no adsorption of organic compounds onto the surface of the HB4 sample at the end of the reaction regardless of the BM concentration from

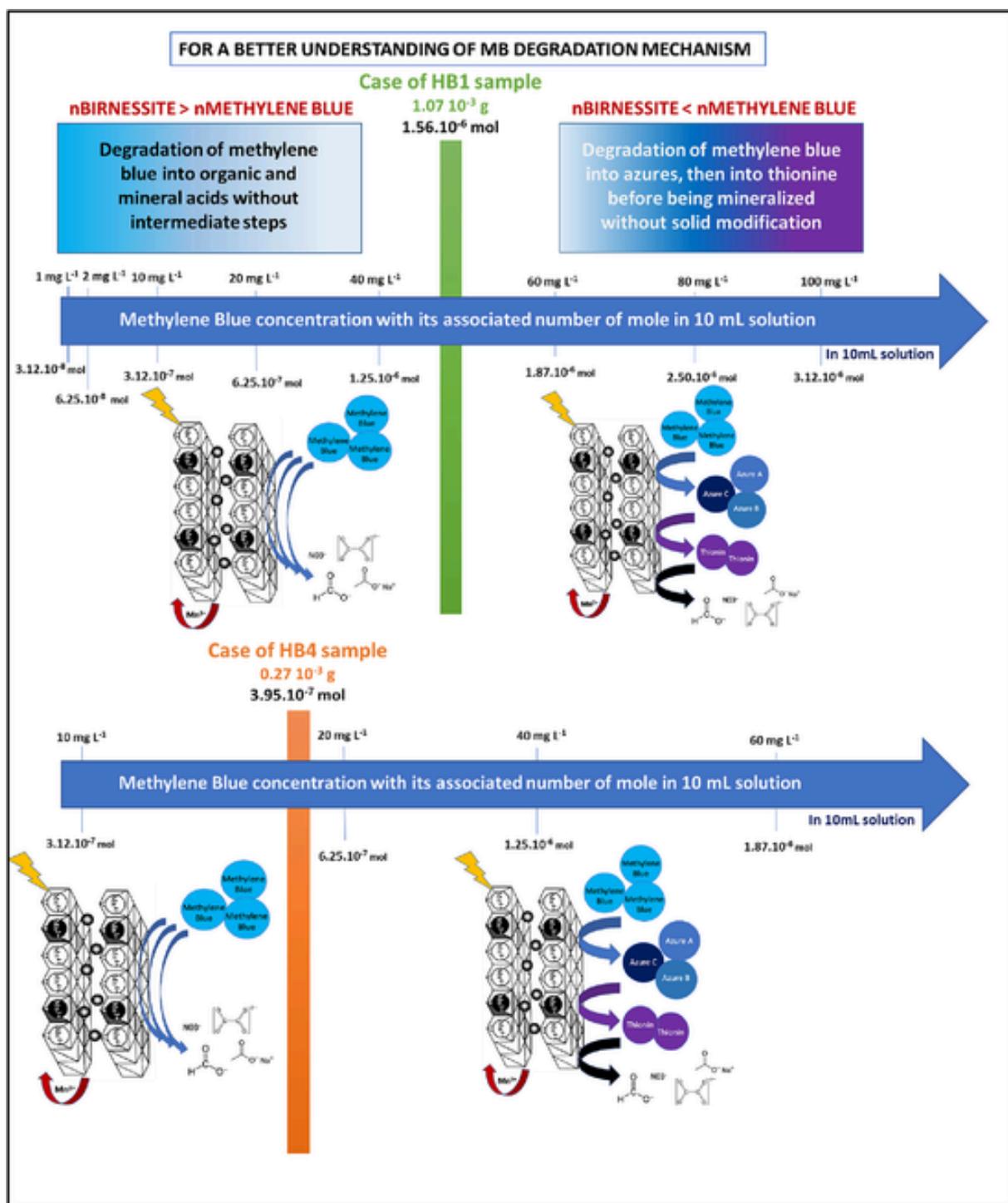


Fig. 11. Comparison of the amount of birnessite, contained in one HB1 or HB4 sample, to the amount of MB present in 10 mL of solution for different initial concentrations, with the direct consequences on the interfacial degradation mechanism of MB when the interactions are coupled to electrochemistry.

20 mg L⁻¹ to 60 mg L⁻¹, as shown by the Raman spectrum for the initial concentration of 40 mg L⁻¹, Fig. 15C.

According to these results, it appears that one HB4 sample used as an electrode material is able to totally discolored and degraded 0.60 mg of MB containing initially in 10 mL of solution with an initial concentration equal to 60 mg L⁻¹, which corresponds to a capacity equal to 2222 mg of MB per gram of HB4 material, Eq. (7). These results are very promising since they confirm the possible degradation of phenothiazine molecules such as MB even with nanostructured birnessite thin films electrodeposited with very low amount of material, in addition to

the fact that such samples are sufficient robust for the treatment of high amounts of pollutant present in excess.

3.6. Opening to applications?

3.6.1. Calculation of energy costs

It is always important to quantify the energy costs for new method before application because energy consumption becomes a crucial problem nowadays. The total energy consumed for removing MB with birnessite thin films can be calculated as follows, Eqs. (8) and (9) [27]:

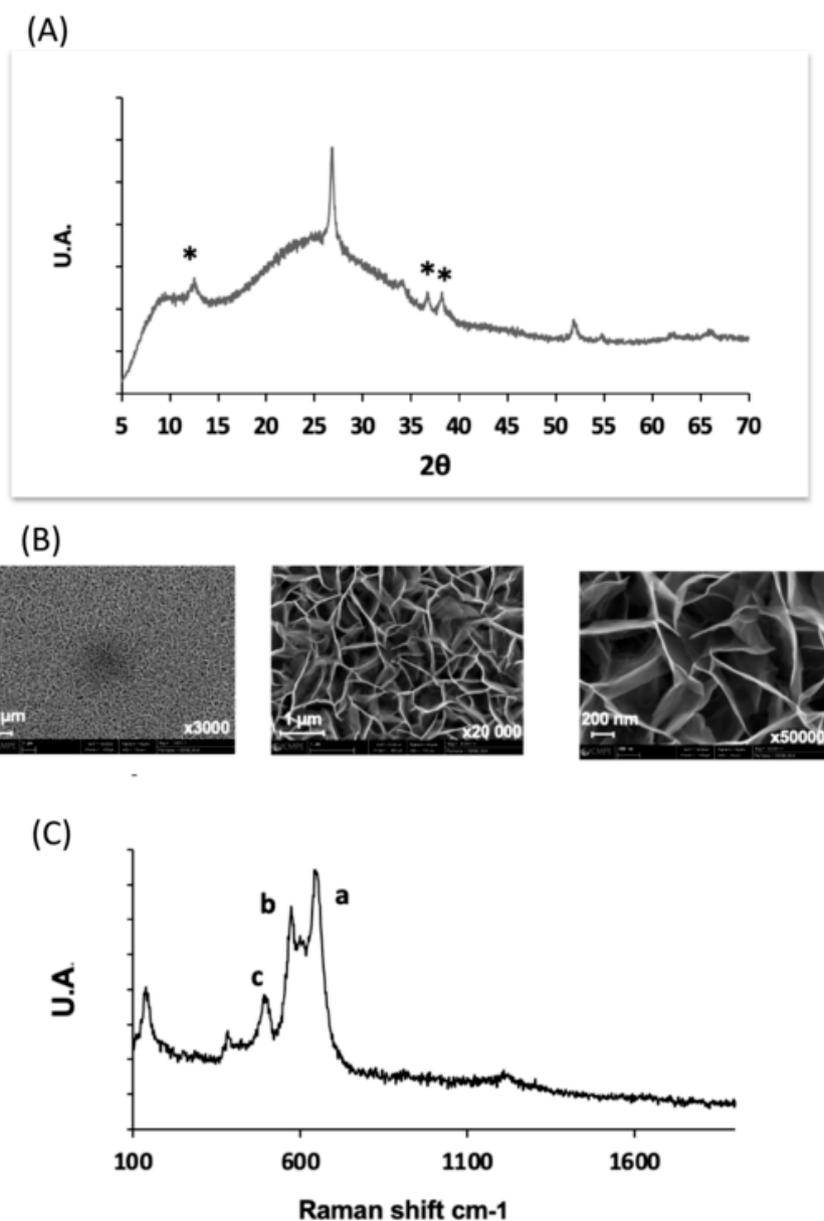


Fig. 12. Characterization of one HB4 sample with (A) a typical XRD diffractogram, (B) typical SEM images at different magnifications, and (C) the typical Raman spectrum with the main bands of birnessite.

$$E_T = E_{\text{electrodeposition}} + E_{\text{interaction}} \quad (8)$$

With: E_T , the total energy consumed (kWh); $E_{\text{electrodeposition}}$, the energy consumed to electrodeposit birnessite as thin films (kWh); $E_{\text{interaction}}$, the energy consumed to remove MB during interaction with birnessite used as electrode (kWh).

$$E_{\text{electrodeposition or interaction}} = IVt \quad (9)$$

With V , the applied potential (V); I , the current (A), t , the duration (h) for the electrodeposition or the interaction coupled to electrochemistry.

In the best conditions, the degradation capacity of one HB1 sample is equal to 934 mg g⁻¹ (10 mL at 100 mg L⁻¹). In the optimal conditions, the total energy consumed to remove 1 g of MB with such samples at the laboratory scale was estimated to be equal to 7.63 10⁻³ kWh, by using the maximal intensity of current and not the mean value. The

values used for the calculations were regrouped in Table 3. 1 kWh being equal to 0.18 euros (in France), the degradation of 1 kg of MB costs 1.37 euros.

Concerning HB4 sample, in the best conditions, the degradation capacity of one HB4 sample is equal to 2222 mg g⁻¹ (10 mL at 60 mg L⁻¹). In the optimal conditions, the total energy consumed to remove 1 g of MB with such samples at the laboratory scale is estimated to be equal to 3.73 10⁻³ kWh, Table 3. Therefore, to degrade 1 kg of MB (3.73 kWh), it costs 0.67 euros, even better and cheaper than with one HB1 sample.

According to these values, the use of such nanostructured birnessite thin films, an eco-friendly non-toxic material based on abundant element, in an electrochemical treatment seems very interesting and cheaper in comparison to other methods applied to the degradation of dyes present in aqueous solutions. Indeed, organic dyes can be degraded by electro-oxidation with active chlorine of selected dyes such as Reactive Black 5B or Acid Blue 113 (160 mg L⁻¹) in chloride solu-

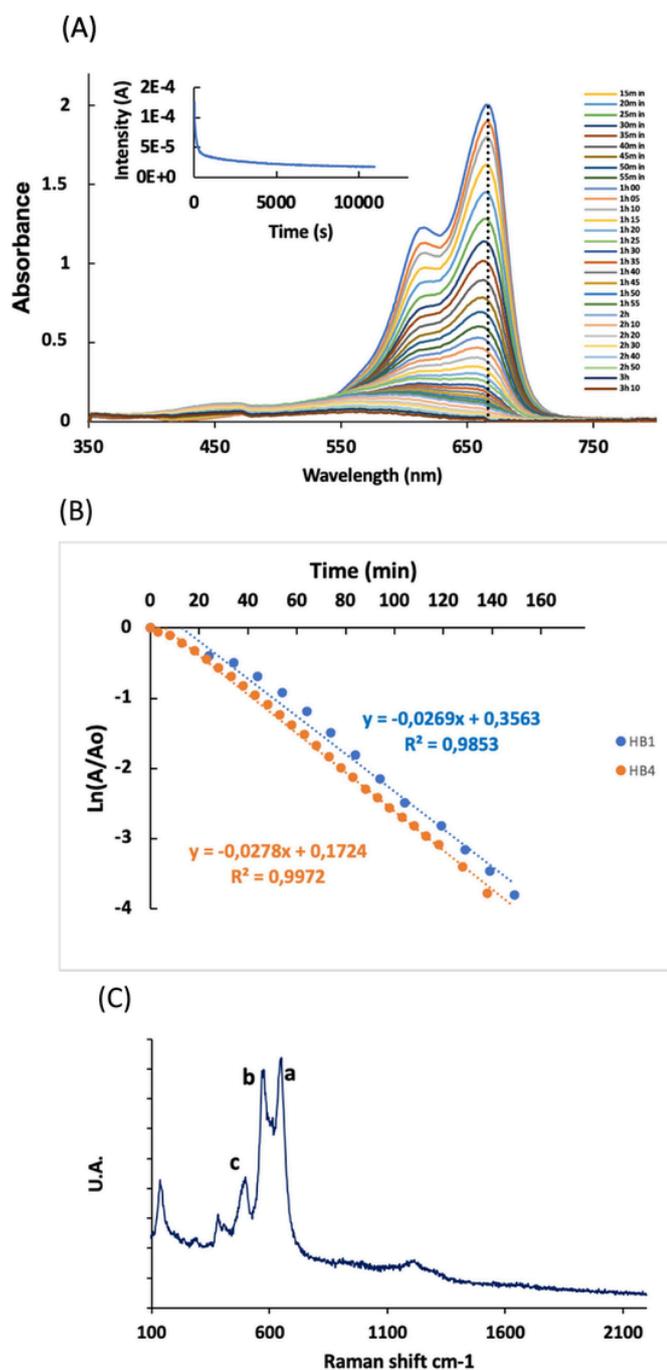


Fig. 13. (A) UV-Visible spectrum measured *in situ* and in real time during the interaction of one HB4 sample used as electrode with 3.5 mL of MB solution at 10 mg L^{-1} under stirring at 250 rpm with a 3-electrodes system (reference: Ag/AgCl homemade, working: one HB4 sample, CE: Pt wire) (B) kinetics of interaction reactions coupled with electrochemistry with 10 mg L^{-1} MB solutions for one HB1 sample and one HB4 sample (C) Raman spectrum of one HB4 sample after the interaction coupling to electrochemistry with 10 mL of MB solution at 10 mg L^{-1} .

tions, with Ti/RuO₂ anode. For these examples, costs are between $16.3 \text{ kWh (g COD)}^{-1}$ and $61.3 \text{ kWh (kg COD)}^{-1}$. For other type of electrodes and dyes, these electrical inputs can cost up to $450 \text{ kWh (kg COD)}^{-1}$ [30], which is very high compared to our eco-friendly electrochemical process, which requires very low energy inputs.

3.6.2. Effects of chemical species and/or media on the reactivity?

Preliminary tests with HB1 samples

Until now, studies were performed in model solutions with only MB and Na₂SO₄ at $10^{-5} \text{ mol L}^{-1}$ as electrolyte. However, it was important to validate if the reactivity of the samples could be modified in presence of different organic or inorganic chemical species. For that, equivalent experiments were made during the degradation of MB (initial concentration fixed to 10 or 20 mg L^{-1}) with HB1 samples used as electrodes in presence of significant amounts of formate ($0.25 \cdot 10^{-3} \text{ mol L}^{-1}$ equivalent to 11.25 mg L^{-1}) or acetate ions ($0.10 \cdot 10^{-3} \text{ mol L}^{-1}$ equivalent to 6.25 mg L^{-1}), as representative of organic species, and MnSO₄ ($1.6 \cdot 10^{-3} \text{ M}$) or NaCl (0.1 mol L^{-1}) as representative of inorganic species. In all cases, the results were very similar with (i) a total discoloration after 24 h, without intermediary products in solution (azures or thionin), (ii) equivalent current intensities, (iii) the same amounts of produced species quantified by ion chromatography, and (iv) no modification of the solids. In addition, some tests with methylene blue diluted with spring water or even tap water were carried out with results like those with MB in Milli-Q water.

Finally, robustness tests of the samples were carried out with a repeatability of four uses without no loss of their degradation capacity. For these tests, a solution of MB at 20 mg L^{-1} was chosen with interaction times of 24 h. Not only is the sample efficient, but it is also reusable, as the level of Mn (IV) remains stable within the material, and Raman spectroscopy measurements performed between each use confirm that there is no adsorption of organic compounds onto the surface of the material. These all results are very promising for future applications.

4. Conclusion

Birnessite thin film used as electrode for the treatment of aqueous solutions containing dyes is very successful. In comparison to the spontaneous reactions, blocked to the significant production of azures in solution, the imposition of a potential during interaction significantly increases the reaction with one birnessite thin films (HB1 or HB4 samples). Indeed, in this case, 100 % of dye disappears after 6 h for an initial concentration of MB equal to 10 mg L^{-1} in classical conditions (room temperature, no deaeration, classical cell).

The degradation of MB is very fast with no intermediate dye organic compound in solution and/or adsorbed onto birnessite surface, when birnessite is in excess. However, it appears that the quantity of birnessite compared to the quantity of MB plays a key role in the presence or not of intermediary compounds during the degradation of the pollutant. When the pollutant is present in excess in solution, the degradation of methylene blue exhibits the azure and thionin steps *via N*-demethylation oxidative reaction in solution, however at the end of the experiments, the reaction stays total with a full regeneration of the solid without adsorption of organic compound onto the surface.

These new electrodes are very promising due to a good efficiency and low energy needs with degradation capacities equal to 934 mg g^{-1} of HB1 and 2222 mg g^{-1} of HB4. These results are engaging for future eco-friendly applications to degrade such organic pollutants due to the very good efficiency of these types of samples, the simplicity of the processes and conditions, in addition to the very low energy needs for their synthesis and uses. In fact, no chlorine is used in solution during interactions, so there is no production of toxic organochlorine products. Moreover, the current during synthesis or interactions is very low with no addition of toxic reagents. In addition, there is no production of waste as with other techniques, in particular electro flocculation. Finally, our material is particularly robust due to a very efficient regeneration in continuous without any treatment, with possible multiple reuses without loss of reactivity. These all results are very promising for future applications for degrading methylene blue but also other organic molecules.

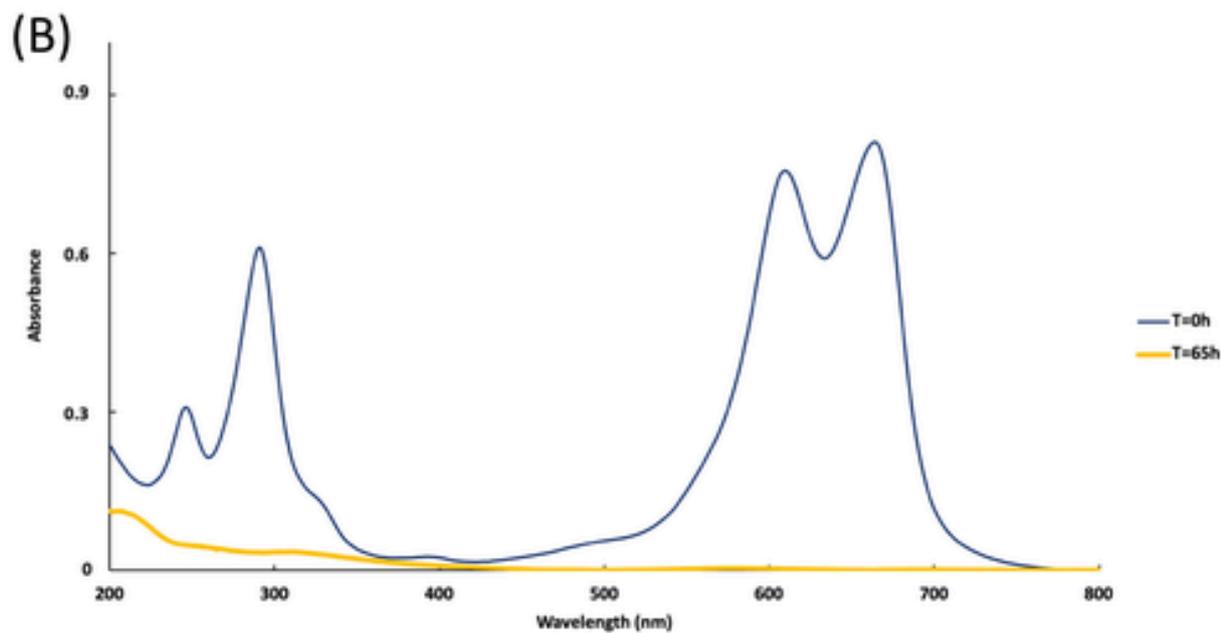
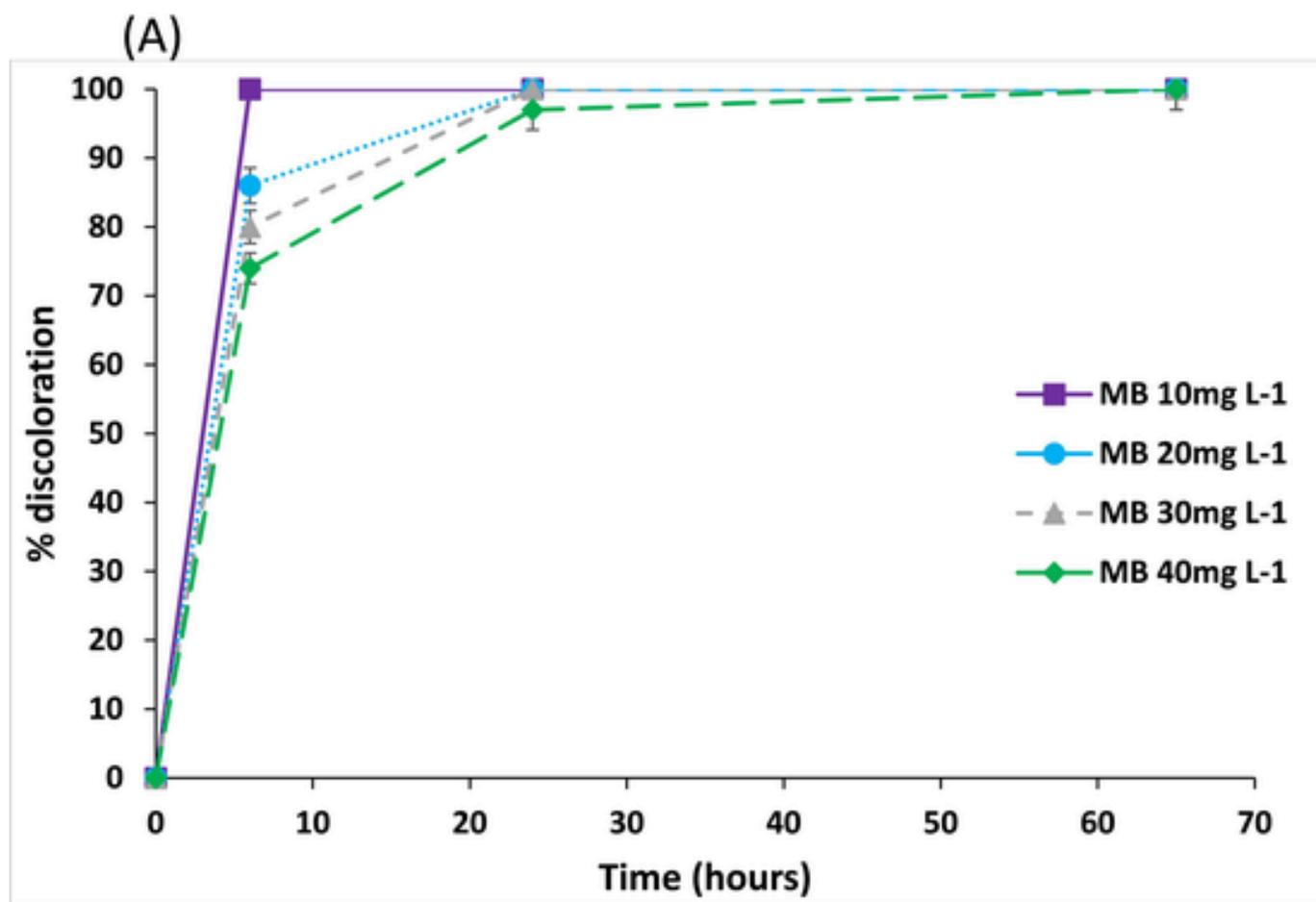


Fig. 14. (A) % of degradation for different durations at $\lambda = 664 \text{ nm}$ for different initial concentration of MB in interaction with one HB4 sample used as electrode. B) UV-vis spectrum of the initial MB solution at 60 mg L^{-1} and after 65 h in interaction with one HB4 sample used as electrode, both measurements realized into a 0.1 cm quartz cell.

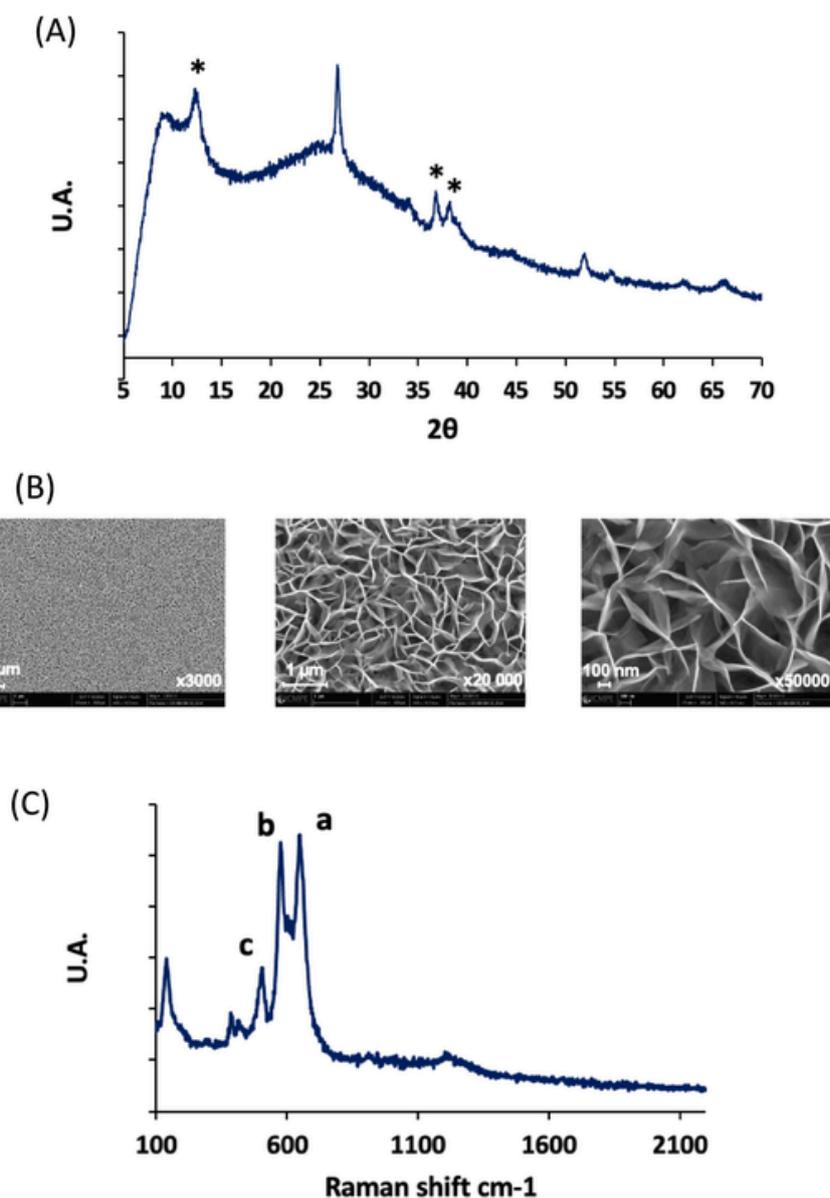


Fig. 15. Characterization of one HB4 sample after interaction with 10 mL of MB solution at 40 mg L⁻¹: (A) typical diffractogram (B) typical SEM images for x 3000, x 20.000 and x 50.000 (C) Raman spectrum with the typical bands of birnessite.

Table 3

Energy consumed under optimal conditions with the maximum degradation capacities by coupling to electrochemistry.

Conditions	Electrodeposition of one HB1 sample	Electrodeposition of one HB4 sample	Interaction between one HB1 and 10 mL of MB at 100 mg L ⁻¹	Interaction between one HB4 and 10 mL of MB at 60 mg L ⁻¹
I _{max} (A)	6.5 10 ⁻⁴	6.5 10 ⁻⁴	1 10 ⁻⁴	5 10 ⁻⁵
V(V)	1	1	1.1	1.1
T (h)	0.75	0.25	65	65
E (kWh)	4.87 10 ⁻⁷	1.62 10 ⁻⁷	7.15 10 ⁻⁶	3.57 10 ⁻⁶
Et (kWh)	4.87 10 ⁻⁷	1.62 10 ⁻⁷	7.63 10 ⁻⁶	3.73 10 ⁻⁶
Et (kWh/g of MB)			7.63 10 ⁻³	3.73 10 ⁻³

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jwpe.2023.104024>.

Declaration of competing interest

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.

Data availability

No data was used for the research described in the article.

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