Interaction of ammonium with birnessite: Evidence of a chemical and structural transformation in alkaline aqueous medium

Hella Boumaiza[a,b,c], Romain Coustel[b], Christelle Despas[b], Christian Ruby[b], Latifa Bergaoui[a,c,*]

[a] Laboratoire de Chimie des Matériaux et Catalyse, Faculté des Sciences de Tunis, Université Tunis El Manar, Tunisia
[b] Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME)-UMR 7564, CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, France
[c] Département de Génie Biologique et Chimique, Institut National des Sciences Appliquées et de Technologies (INSAT), Université de Carthage, Tunis, Tunisia
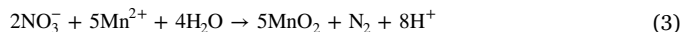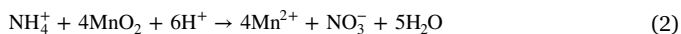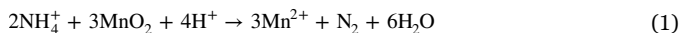
ARTICLE INFO

ABSTRACT

The ammonium cation interaction with Na-birnessite in aqueous alkaline medium was studied. Solution and solid analysis give evidence that birnessite is not only acting as a cationic exchanger toward NH_4^+. The surface analysis performed by XPS showed that N1s spectra are characterized by the existence of two different environments: one assignable to an interlayer NH_4^+ and the second to a chemisorbed N-species. Structural and chemical transformations were observed on birnessite with nitrogen mass balance deficit. The monitoring of NH_4^+, Na^+, Mn^{2+}, NO_3^- and NO_2^- and solid changes (average oxidation state of Mn, cation exchange capacity, solid nitrogen content and symmetry evolution identified by XRD and FTIR) indicate unambiguously that NH_4^+ reacts chemically with the birnessite.

1. Introduction

In marine and sediments, the conversion of combined nitrogen to dinitrogen is traditionally assumed to take place via the coupled bacterial nitrification-denitrification process or through the anaerobic ammonium oxidation (anammox). Bacterial nitrification-denitrification is a two-step process: ammonia is first oxidized aerobically to nitrate by nitrifying bacteria followed by the anaerobically nitrate reduction into N_2 by denitrifying bacteria [1–3]. The anammox reaction is the oxidation of N-NH_4^+ by N-NO_2^- leading to N_2 gas [4–6]. However, in Mn-rich media, some studies suggest the existence of an alternative abiotic pathway that may take place via chemical process [7–11].

In conditions as those found in marine pore waters, Luther et al. [12] and Hulth et al. [13] suggest that two major mechanisms would be involved: 1) Organic N and N-NH_4^+ could be oxidized by Mn(IV) oxides to produce N_2 (Eqs. (1)), or 2) N-NH_4^+ would be oxidized to NO_3^- (Eq. (2)) followed by denitrification (Eq. (3)) to produce N_2. The reduced Mn(II) would then be recycled into MnO_2 (Eq. (3)). This catalytic cycle would consequently affect the marine nitrogen cycle.

$$2NH_4^+ + 3MnO_2 + 4H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O \qquad (1)$$

$$NH_4^+ + 4MnO_2 + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O \qquad (2)$$

$$2NO_3^- + 5Mn^{2+} + 4H_2O \rightarrow 5MnO_2 + N_2 + 8H^+ \qquad (3)$$

Even if this process has been suggested in many field experiments to explain the low ammonium concentrations observed in the Mn-oxide rich sediments and for annamox process [13–22], its existence remains under debate [23].

Among manganese oxides, birnessite was found to be the most existing form in soils and sediments [24,25]. It is a lamellar compound consisting of layers of edge shared MnO_6 octahedra. These layers are negatively charged and are stacked together with an interlayer space containing charge-compensating cations. Depending on the synthesis conditions, the birnessite symmetry differs. When prepared in alkaline medium, birnessite presents triclinic symmetry. It is characterized by vacancy-free layers containing high amounts of Mn(III) due to a partial substitution of Mn(IV) which results in negatively charged layers. The layers consist of an alternation of one Mn(III)O_6 octahedral chain and two Mn(IV)O_6 ones [26]. The Mn(III) octahedra distorted by Jahn-Teller effect are responsible of the triclinic symmetry [27]. The hexagonal homologue is obtained either by $KMnO_4$ reduction in acidic medium [28] or by stabilization of the triclinic one at low pH [27,29,30]. In hexagonal birnessite, Mn is predominantly present in the +IV oxidation state and the octahedral vacancies represent the major source of layer charge deficit [27]. For both structures, the negatively charged layers are compensated with hydrated interlayers

---

cations providing a cation exchange capacity to these solids [31]. The ion exchange is assumed to take place through a diffusion mechanism in the interlamellar space [32–34] that should consequently not influence the birnessite symmetry.

The triclinic Na-birnessite selectivity towards monovalent cations (M^+) has been previously studied and the amount of retained M^+ by the solid was deduced by experimentally analyzing the released sodium cation in the solution [35]. For Na-birnessite, the monovalent cations selectivity decreases in the following order: $Cs^+ > K^+ \geq NH_4^+ > Na^+ > Li^+$ where there was an implicit understanding that the interaction between Na-birnessite and NH_4^+ does not involve any chemical transformations in the solid and is only based on a cation exchange mechanism.

Moreover, it has been proved that birnessite possesses a strong oxidizing capacity as it can oxidize several elements: As(III) to As(V) [36], Se(IV) to Se(VI) [37], Co(II) to Co(III) [38] and Cr(III) to Cr(VI) [39]. Birnessite also oxidizes organic molecules and inorganic complexes such as glyphosate [40], ferrocyanide [41], phenolic mixtures [42], Cu-citrate [43] or dye molecules [44,45]. Thereby, the possible coupling between the Mn and N cycles, the potential role of the Mn(IV)/Mn(III) couple in theses cycles, the cationic exchange and the oxidative capacities of birnessite led us to consider the Na-birnessite/NH_4^+ system for this work. Despite the existence of many studies on the interaction of birnessite with organic ammonium compound [46–48] and to the very best of our knowledge, no study focused on the reactivity of birnessite with NH_4^+ by monitoring the modifications of both solid and liquid phases.

To this end, a kinetic study of the reactivity of triclinic Na-birnessite toward NH_4^+ is performed for ammonium concentration in the range 5–50 mmol L^{-1}. The monitoring of the reaction is realized by 1) quantifying aqueous species: the remaining NH_4^+, the released Na^+ and eventually Mn^{2+}, NO_3^- and NO_2^-, 2) analyzing the amount of retained nitrogen by elemental analysis and 3) following the structural and chemical transformation of birnessite by X-ray diffraction, Infrared and X-ray Photo-electron spectroscopies and also by measuring the evolution of the average oxidation state (AOS) of the manganese in the birnessite and the cation exchange capacity (CEC) of the solid.

2. Materials and method

2.1. Chemicals

All chemicals were purchased from Sigma-Aldrich. Manganese(II) chloride tetrahydrate ($MnCl_2,4H_2O$, ACS reagent, $\geq$ 98%), sodium permanganate monohydrate ($NaMnO_4,H_2O$, ACS reagent $\geq$ 97%) and sodium hydroxide (NaOH BioXtra, $\geq$ 98% pellets anhydrous) were used for birnessite synthesis. Ammonium sulfate ((NH_4)$_2SO_4$ (BioXtra, $\geq$ 99.0%) was used as NH_4^+ supplier. Sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$, ACS reagent, 98.0–102.0%), potassium sodium tartrate tetrahydrate ($C_4H_4KNaO_6$, $4H_2O$, ACS reagent, 99%), sodium salicylate ($C_7H_5NaO_3$, ReagentPlus®, $\geq$ 99.5%), salicylate nitroprusside ($Na_2Fe(CN)_5NO \cdot 2H_2O$, ACS reagent, $\geq$ 99%) and sodium hypochlorite solution (NaOCl, reagent grade, available chlorine 10–15%) were used for the UV–visible determination of NH_4^+. Mohr salt ((NH_4)$_2Fe(SO_4)_2 \cdot 6H_2O$, ACS reagent, 99%), sodium pyrophosphate dibasic ($Na_2H_2P_2O_7$, practical grade) and potassium permanganate ($KMnO_4$, ACS reagent, $\geq$99.0%) were used for the determination of the Mn AOS in birnessite. Na_2CO_3 (Sigma-Aldrich, 99.5+%) and $NaHCO_3$ (Sigma-Aldrich, 99.7+%) were used as mobile phase for the ionic chromatography determination of nitrates and nitrites. Double distilled water (DDW, 18.2 MΩ cm) was used for all the experiments.

2.2. Synthesis of birnessite and reactivity towards NH_4^+

The sodium birnessite (Na-Bir) was synthesized by the alkaline method followed by Boumaiza et al. [49] in which 125 mL of NaOH (8.8 mol L^{-1}) were added dropwise during 2 h into a mixture of 250 mL $NaMnO_4$ (0.1 mol L^{-1}) and 125 mL $MnCl_2$ (0.6 mol L^{-1}). The reaction mixture was then stirred for another 30 min and aged at 60 °C for 14 h. The product was finally centrifuged and washed until the pH of the solution was between 9 and 10 and dried at 60 °C during 16 h. The obtained Na-birnessite was fully characterized by XRD and FTIR analyses. It consisted on triclinic Na-birnessite [30] with an Mn AOS equal to 3.65 ± 0.02 and a CEC = (230 ± 10) mmol/100 g which give a general formula corresponding to $[Mn^{III}_{0.35} Mn^{IV}_{0.65} O_2][Na^+_{0.35} 0.7H_2O]$. Thermal gravimetric analysis was used to determine the amount of water.

To study the rate of ammonium retention on Na-Bir (6 g L^{-1}), different initial NH_4^+ concentrations were used (5.0, 15.0 or 50.0 mmol L^{-1}). The natural pH was found to be 8.0. Samples at different contact times were collected and filtered through 0.22 μm syringe filter. Reference sample of hexagonal birnessite was also synthesized using 1.5 g of Na-Bir that were dispersed in 250 mL of an acidic solution at pH = 3.0 during 24 h, centrifuged and washed with distilled water until pH = 6.0 and finally dried at 60 °C during 16 h.

2.3. Chemical analysis of the solutions

Analysis of NH_4^+ in the solution was achieved by UV–visible spectroscopy [50]. A 0.5 mL sample of filtered solution was mixed with 1.375 mL of buffer solution (0.1 M Na_2HPO_4, 5% K-Na tartrate, 5.4% NaOH), 1 mL of Na-salicylate/Na-nitroprusside solution (15% – 0.03%) and 0.5 mL of Na-hypochlorite (0.315%). After a rest period of 15 min at 37 °C, the absorbance of the reacting mixture was determined at 650 nm using UV–visible spectrophotometer (Agilent, Cary 60). Total contents of manganese and sodium released in solution were determined using Inductive Coupled Plasma Atomic Emission Spectroscopy ICP-AES (JobinYvon-Horiba, Ultima). Nitrate and nitrite ions in solution were determined by ionic chromatography (IC) with a Metrohm 882 Compact IC plus instrument equipped with a high pressure pump, sequential (Metrohm CO_2 suppressor MCS) and chemical (Metrohm suppressor MSM II for chemical) suppression modules and a conductivity detector. The separation was performed on a Metrosep A Supp 5–250 column packed with polyvinyl alcohol particles functionalized with quaternary ammonium group (5 μm particles diameter) and preceded by a guard column (Metrosep A supp 4/5 guard). The mobile phase consisted of a solution of Na_2CO_3 (3.2 mmol L^{-1}) and $NaHCO_3$ (1 mmol L^{-1}) in ultrapure water (18.2 MΩ cm at 293 K). The flow rate was 0.7 mL min^{-1} and the sample loop volume was 20 μL. The MagIC Net™ 2.3 Professional chromatography software controlled the 882 Compact IC plus instrument and its peripherals. It also allowed data acquisition, evaluation and monitoring as well as report generation for IC analyses.

2.4. Chemical analysis of the solids

The Mn AOS in the different samples was measured by potentiometric titration using Mohr salt, potassium permanganate and sodium pyrophosphate dibasic [51,52]. This method was chosen because of its precision compared to other existing methods [53]. The N content in the birnessite after reaction with ammonium was measured using a CE instruments Flash EA 1112 (Thermofinnigan). The procedure consists on heating the solid at 940 °C followed by reactions with different catalysts to reduce the NO_x (WO_3, and/or V_2O_5 and Cu) under helium flow. The separation and analysis is realized by gas chromatography using a catharometer as detector.

The Cation Exchange Capacity (CEC) was determined following the cobalt-hexamine method [54] in which 150 mg of birnessite were put in 20 mL of 16.67 M $Co(NH_3)_6Cl_3$ solution. The mixture was shaken for 2 h without temperature regulation and then microfiltered. The cobalt-hexamine concentrations before and after contact with the birnessite