Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.852135

53 (2015) 1031–1036
January

Taylor & Francis
Taylor & Francis Group

Chemical transformation of ferrihydrite coating into green rust followed by Raman and X-ray photoelectron spectroscopies

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Received 28 May 2013; Accepted 25 September 2013

ABSTRACT

This study describes the mineralogical transformation of ferrihydrite (Fh) coated on grains of pozzolana into mixed Fe^{II}–Fe^{III} sulphated green rust $\{GR(SO_4^{2-})\}$. The formed $GR(SO_4^{2-})$ coating is intended to be used for the reduction of nitrate in batch and column experiments. Raman and X-ray photoelectron spectroscopies (XPS) are used to characterize the pozzolana substrate and the coatings and proved that in the presence of sulphated anions and Fe^{II} cations, Fh is transformed into chemically stable sulphated green rust. The Raman spectra exhibit the presence of characteristic bands of sulphated green rust, spectra on which we rely on to interpret the O 1s XPS high resolution spectra which are characterized by a major contribution located around 531.5 eV, in good agreement with the formation of OH^- coordinated to Fe^{II} and Fe^{III} ions in brucite-like layers of GR. The reduction of nitrate by GR (SO_4^{2-}) coatings is then investigated from combined solution and solid phases analyses. In agreement with previous studies carried out on bulk mineral, $GR(SO_4^{2-})$ coating reduces nitrate into ammonium and is mainly transformed into magnetite.

Keywords: Ferrihydrite; Green rust; Nitrate; X-ray photoelectron spectroscopy; Raman spectroscopy

1. Introduction

Nitrates (NO_3^-) are naturally present in groundwater. These species are formed during the natural cycle of degradation of organic matter. However, the introduction of NO_3^- due to agricultural (fertilizers and livestock), industrial and domestic (untreated waste) activities remains paramount and the increase of nitrate concentration constitutes a serious environmental problem, especially where groundwater is a source of drinking water. Therefore, the nitrate removal has been the centre of interest of many studies and different methods have been proposed such as biological denitrification [1], adsorption [2], electrochemical reduction [3] and reverse osmosis [4]. Iron compounds are abundant in the environment and are able to buffer the redox potential of the aqueous medium in soils [5]. They are also able to adsorb many poisonous and harmful species such as inorganic phosphates, polycyclic aromatic

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Presented at the International Joint CB-WR-MED Conference / 2nd AOP'Tunisia Conference for Sustainable Water Management, 24–27 April 2013, Tunis, Tunisia hydrocarbons, metals (Mn, Cd, Pb, …), etc. [6]. In soils, iron minerals are commonly found as ferric oxides like ferrihydrite (Fh) and goethite (α-FeOOH), or as mixed Fe^{II}–Fe^{III} compounds such as magnetite ($Fe^{II}Fe_2^{III}O_4$) and fougerite, the layered double hydroxides mineral counterpart of Fe^{II}–Fe^{III} green rust [7]. Among the compounds containing iron, green rusts are particularly interesting because of the presence of Fe^{II} cations in their structure which provides them a high reactivity. The structure of GR consists of positively charged hydroxide layers containing Fe^{II} and Fe^{III} cations and hydrated anionic layers. The presence of trivalent cations induces a positive charge which is compensated by the solvated anions A^{n-} entering into the interlayer space. Green rusts are characterized by the general formula $[Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2]^{x+} \cdot [(x/n)A^{n-} \cdot mH_2O]^{x-}$ where A^{n-} are the intercalated anions (A^{n-} = Cl^-, SO_4^{2-}, CO_3^{2-}, …) and x is the Fe^{III} molar fraction [8,9]. Besides, previous studies have shown that freshly precipitated Fe oxyhydroxide [10] and green rust [9,11,12] are reducing agents for NO_3^-. In this study, we develop a new method to synthesize green rust coated onto pozzolana by mineralogical tranformations of ferrihydrite. In each reaction step, Raman spectroscopy has been performed to monitor the mineralogical transformations, and X-ray photoelectron spectroscopy (XPS) has been used to highlight the changes in surface properties.

2. Methods

2.1. Chemicals

All reagents, i.e. iron(III) nitrate nonahydrate ($Fe(NO_3)_2 \cdot 9H_2O$, Merck, EMSURE®), iron(II) sulfate heptahydrate, ($FeSO_4 \cdot 7H_2O$, Sigma–Aldrich, 99 + %), sodium nitrate ($NaNO_3$, Prolabo®, 99.5–100%) and sodium hydroxide (NaOH, Carlo Erba, >99%), were of analytical grade.

2.2. Fh preparation

The two-line Fh was synthesized according to the method of Cornell and Schwertmann [13]. 100 g of $Fe(NO_3)_2 \cdot 9H_2O$ was dissolved in 500 mL of distilled water and neutralized with 4.5 M NaOH solution to obtain a pH ~7.5.

2.3. Synthetic route for the coating

In order to synthesize coated pozzolana, a dry contact method was used [14]. This method consists of mixing in dry state the pozzolana and the Fh prepared by the method outlined in Section 2.2. This mixture was shaken in dry mode for about 12 h using a Reax 20/8 overhead shaker (Heidolph Instruments GmbH & Co., Germany). The coated pozzolana was then subjected to the separation of free particles of Fh by sieving. The amount of Fh deposited on pozzolana was determined by the difference of weight between the uncoated pozzolana and the coated one.

2.4. Transformations of Fh coatings into green rust

Appropriate amounts of NaOH and $FeSO_4 \cdot 7H_2O$ were added to Fh coating in order to study the potential transformation into sulphated green rust $GR(SO_4^{2-})$ of formula $Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 \cdot 3H_2O$. Stoichiometric GR is characterized by a Fe^{II}:Fe^{III} ratio of 2:1, so the quantities were taken accordingly. An appropriate amount of NaOH (1 M) was then added to the mixture (Fe^{II}/Fe^{III}-pozzolana) to provide the ratio $[OH^-]/[Fe^{III}] = 3$. This ratio ($[OH^-]/[Fe^{III}] = 3$) is required to obtain stoichiometric GR.

2.5. Nitrate reduction experiment

Coated grains of pozzolana, initially in suspension, were washed with distilled water (18 mΩ cm at 293 K), filtered and added in a solution of $NaNO_3$. The concentration of nitrate was in default compared to the total iron present in the green rust, in a ratio NO_3^-:Fe = 1/3 to maximize the percentage of nitrates that may be reduced. The nitrate reduction has been monitored by the measurement of nitrate concentration in solution by ion chromatography. Ammonium concentration was measured according to the method of Baethgen and Alley [15] and iron concentration in solution by the method of Viollier et al. [16]. At the end of the chemical reaction between GR and nitrate, the pozzolana grains were analysed by Raman spectroscopy to identify the newly formed solid compounds.

2.6. Coatings characterization with Raman and XPS

XPS spectra were obtained using a KRATOS Axis Ultra X-ray photoelectron spectrometer with a monochromatized AlKα X-ray ($h\nu$ = 1486.6 eV) operated at 150 W and using a charge neutralizer. The samples were pressed onto a Cu tape inside a glovebox and transferred into the spectrometer through a second small glovebox mounted on the preparation chamber. The base pressure in the analytical chamber was ~10^{-9} mbar. The incident beam was focused on a 0.7 mm × 0.3 mm area of the surface of the sample. They were acquired with an analyser pass energy of 160 eV.

Narrow region electron spectra were used to determine chemical state information. They were acquired with an analyser pass energy of 20 eV (instrumental resolution better than 0.5 eV) and a sample analysis. Sample charging effects on the measured binding energy positions were corrected by setting the lowest binding energy component of the C 1s spectral envelope to 284.6 eV, i.e. the value generally accepted for adventitious carbon surface contamination. Spectra for oxygen were fitted using a Shirley background and a Gaussian G (70%) Lorentzian L (30%) peak model. The Raman analyses were performed on a Jobin Yvon T64000 equipped with a charged coupled device detector and a motorized XYZ stage. The samples were placed on a glass and mounted in the focal plane of an Olympus X50 objective (N.A. = 0.55). Radiation was used with a power lower than 1 mW to prevent sample degradation. The spectral resolution was about 4 cm^{-1} and the precision on the wavenumber was lower than 1 cm^{-1}.

3. Results and discussion

3.1. Characterization of the pouzzolana substrate

The pozzolana was first characterized with Raman and XPS spectroscopies in order to better identify the future surface transformations. The Raman spectrum of the uncoated pozzolana (Fig. 1) is characterized by the presence of vibrational bands characteristic of hematite (α-Fe_2O_3), magnetite ($Fe^{II}Fe_2^{III}O_4$) [17] and sulphate (SO_4^{2-}) located at about 1,000 cm^{-1}.

Characteristic XPS survey spectrum of pozzolana (Fig. 2(a)) allows highlighting the presence of various elements, such as sodium, oxygen, iron, titanium, calcium, magnesium, carbon, aluminum and silicon. Besides, the quantitative analysis shows an atomic concentration of Fe of ~1.4%. The decomposition of the O 1s spectrum (Fig. 2(b)) has been performed in a classical way, using three components located at 529.6, 531.6 and 532.9 eV corresponding to oxygen atoms in three chemical environments namely oxide, hydroxyl and absorbed H_2O, respectively. It appears clearly that the oxide and water contribution are rather weak and the O 1s spectrum is dominated by the hydroxyl component.

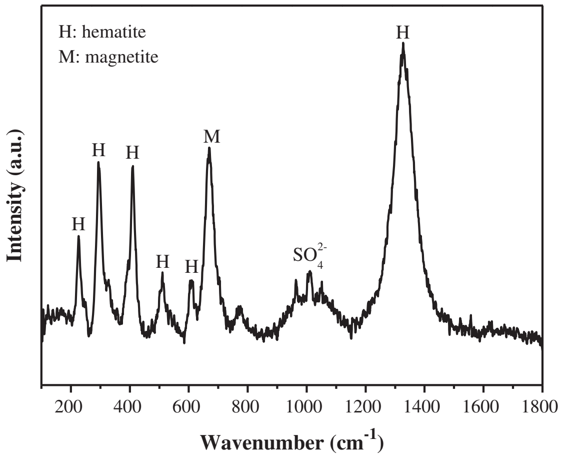

Fig. 1. Raman spectrum of uncoated pozzolana.

3.2. Characterization of pozzolana coated with Fh

The Raman analysis of the pozzolana coated with Fh (Fig. 3) exhibits the presence of characteristic vibrational bands of Fh [18] and the absence of vibrational signal of pozzolana, i.e. hematite and magnetite (Fig. 1), indicating that the thickness of the deposited layer is larger than the depth of analysis of Raman beam (of the order of 1 μm).

The XPS survey spectrum (Fig. 4(a)) exhibits a strong decrease or even an almost complete disappearance of many characteristic peaks of pozzolana

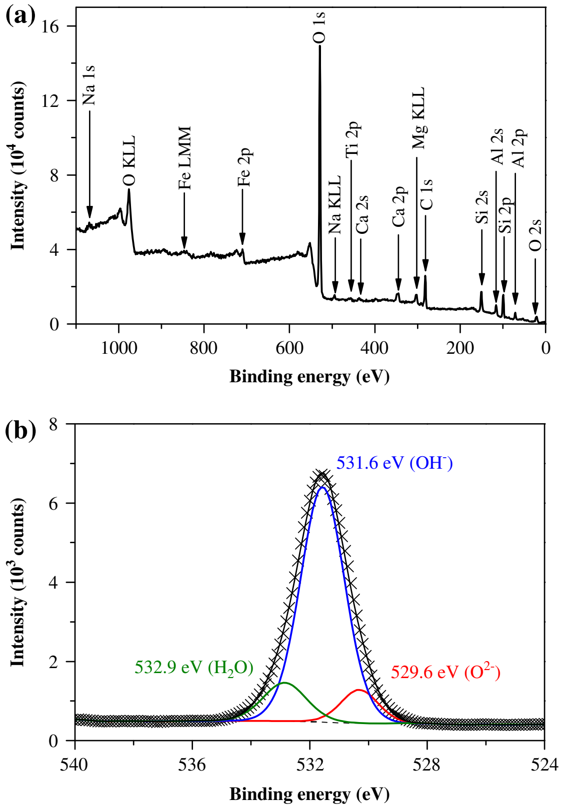

Fig. 2. (a) Wide scan energy and (b) O1s high resolution spectra of uncoated pozzolana.

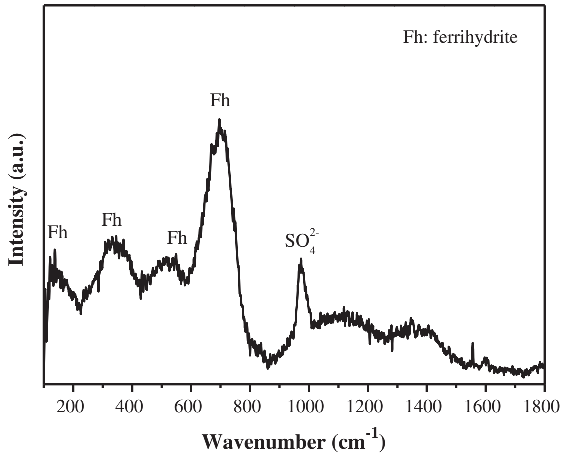

Fig. 3. Raman spectrum of pozzolana coated with Fh.

(Fig. 2(a)), concomitant to a strong increase of those of iron, which confirms the covering of the grain surface by ferrihydrite. In fact, the surface atomic concentration of Fe increases from ~1.4 to ~9% in agreement with the presence of an iron coating. Typical O 1s spectrum (Fig. 4(b)) reveals that the distribution of oxide and hydroxyl species at the surface strongly differs from that previously observed for the pozzolana support. The increase in the oxide component is in good agreement with the presence of ferrihydrite.

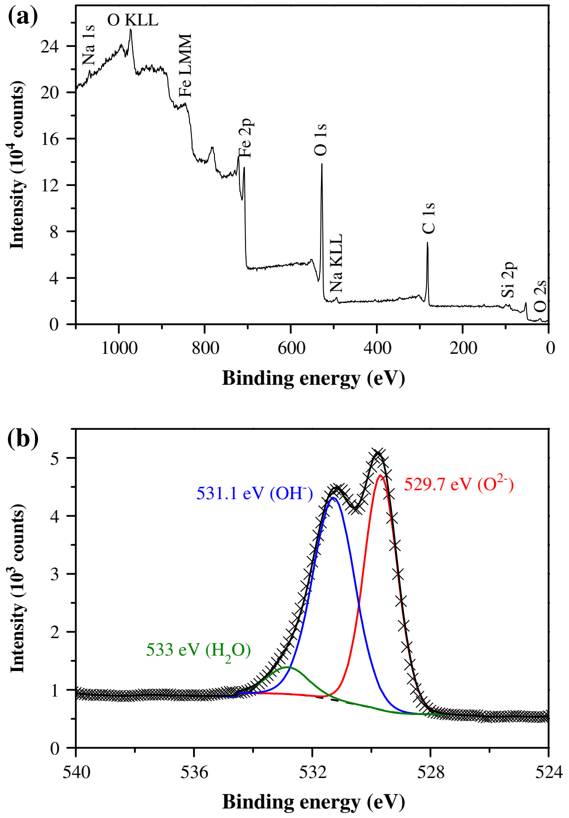

Fig. 4. (a) Wide scan energy and (b) O 1s high resolution spectra of the Fh coating.

3.3. Characterization of the green rust coating

After chemical reaction of Fh-coated pouzzolana, the Raman spectrum (Fig. 5) shows the presence of vibrational signals characteristic of sulphated green rust [19]. In addition, the most intense vibrational bands of Fh located at 720 cm^{-1} are not detected anymore, indicating a complete transformation of Fh initially present at the interface of the pozzolana into sulphated green rust.

Typical O 1s spectrum (Fig. 6) reveals that the distribution of the oxide and hydroxyl species at the surface strongly differs from previously observed for the Fh coating. In fact, after mineralogical transformation, the hydroxyl peak becomes more intense than the oxide one, suggesting a strong hydroxylation of the surface.

3.4. Nitrate reduction experiment

3.4.1. Analysis of NO_3^-, NH_4^+ and Fe soluble species

The concentrations of nitrate and ammonium are represented herein as a function of time (Fig. 7). Nitrate reduction generates thus ammonium ions whose concentration increases as the nitrate decreases. Indeed, starting from an initial concentration of nitrates equal to ~1.13 mmol L^{-1}, the concentration of nitrate decreases to 0.634 mmol L^{-1} after 7 days, generating total concentration of ammonium equals to

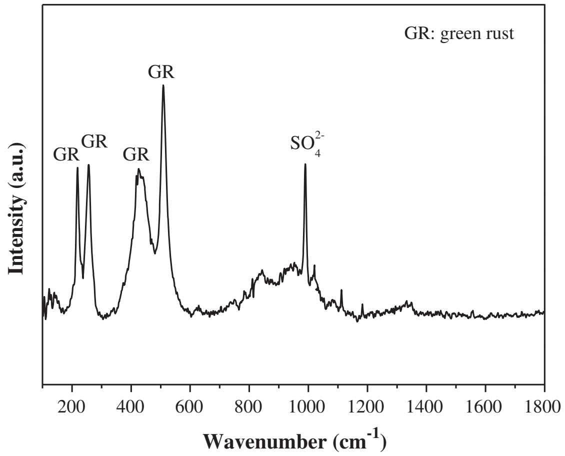

Fig. 5. Raman spectrum of pozzolana coated with Fh after mineralogical transformation.

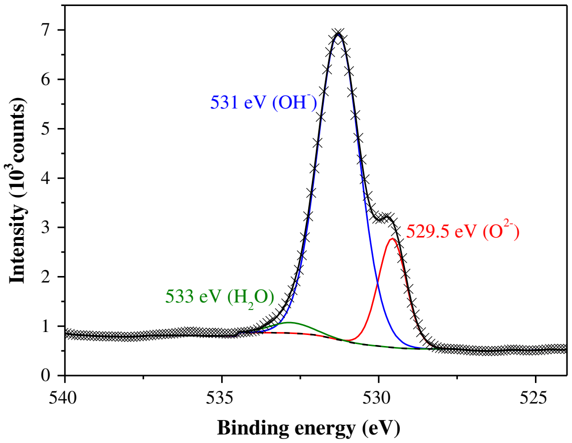

Fig. 6. O 1s high resolution spectrum of the pozzolana coated with Fh after mineralogical transformation.

~0.496 mmol L^{-1}. Therefore, at the end of reaction, 44% of nitrate initially present is converted into ammonium and the final reaction balance shows that there are no formation of other product, as the sum of the final concentrations of ammonium and nitrate is equal to the initial concentration of nitrates introduced. The monitoring of the concentration of total iron in solution shows that the latter increases as the reaction time increases (Fig. 8), but still remains negligible compared with the initial concentration deposited on the support. Indeed, for a concentration of iron deposited onto the pozzolana grains equal to ~ 19.7 mmol L^{-1}, the total iron concentration measured in solution after 7 days is ~0.036 mmol L^{-1}. This shows that nitrate reduction by green rust occurs at the pozzolana/solution interface almost with negligible release of iron soluble species in solution.

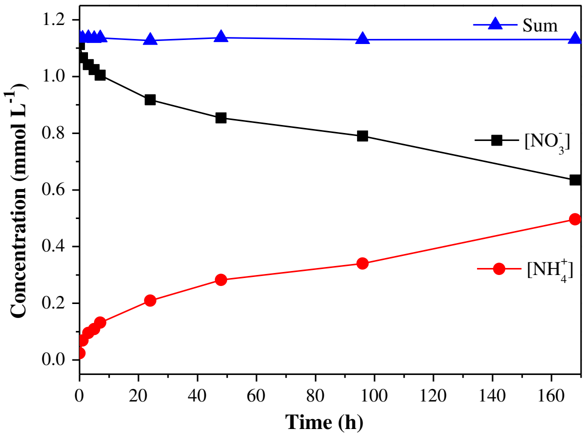

Fig. 7. Effect of time on nitrate reduction using GR-coated pozzolana.

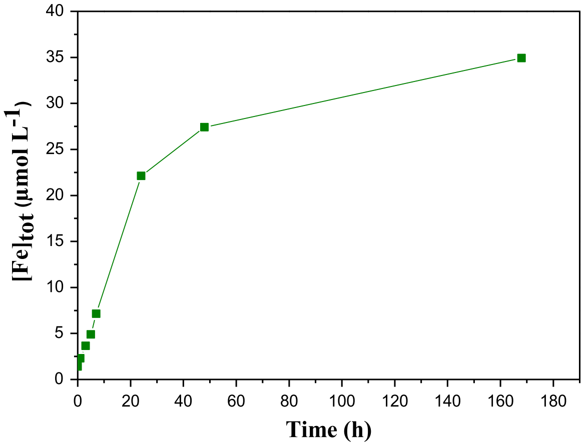

Fig. 8. Total iron release in solution during nitrate reduction experiment.

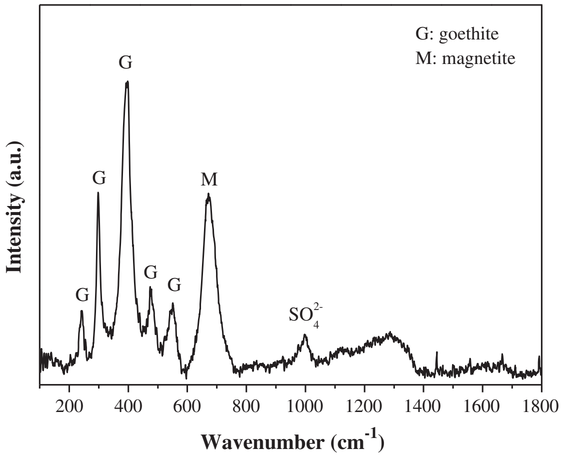

Fig. 9. Raman spectrum of coated pozzolana after the nitrate reduction experiment.

3.4.2. Nature of the GR oxidation products

The analysis of the pozzolana grains at the end of reaction with Raman spectroscopy (Fig. 9) shows the presence of vibrational bands characteristic of goethite and magnetite [20], and the presence of minor bands of sulfate. This indicates that the sulphated ferrous-ferric green rust is partially oxidized into a mixture of goethite and magnetite but the characteristic bands of the GR(SO_4^{2-}) are probably concealed by those of goethite. These results coupled with the analysis of iron in solution indicate that the GR(SO_4^{2-}) is not dissolved during the nitrate reduction to ammonium and the GR(SO_4^{2-}) oxidation products, i.e. magnetite and goethite, are more likely lying on the pozzolana substrate.

4. Conclusion

The present study demonstrates that mixed Fe^{II}–Fe^{III} green rust coatings can be formed by the mineralogical transformation of Fh deposited onto pozzolana. Raman spectroscopy confirms that the transformations have occurred and demonstrates the presence of sulphated green rust. In addition, the modification at the samples' surface agrees well with the deposition of sulphated green rust $\{GR(SO_4^{2-})\}$ onto the support. The coated $GR(SO_4^{2-})$ support remains stable for a period of time higher than a month and is characterized by a high reactivity and can be used to reduce nitrates anions to ammonium, generating goethite and magnetite without release of iron particles in solution.

Acknowledgements

The Agence Nationale de la Recherche (ECOTECH2009 – N0994C0103) is gratefully acknowledged for financial support.

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