



# Cesium and cobalt adsorption on synthetic nano manganese oxide: A two dimensional infra-red correlation spectroscopic investigation



Abdul G. Al Lafi<sup>a,\*</sup>, Jamal Al Abdullah<sup>b</sup>

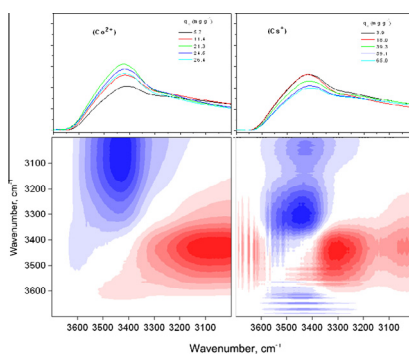
<sup>a</sup> Department of Chemistry, Atomic Energy Commission, Damascus, P.O. Box 6091, Syrian Arab Republic

<sup>b</sup> Department of Protection and Safety, Atomic Energy Commission, Damascus, P.O. Box 6091, Syrian Arab Republic

## HIGHLIGHTS

- Two-dimensional Infrared spectroscopy is used to analyze Cs<sup>+</sup> and Co<sup>2+</sup> adsorption.
- An intensity increase in the 3100 cm<sup>-1</sup> band indicates an ion-exchange reaction.
- New O–O and M–O bands at 1100, 1160 and 510 cm<sup>-1</sup> indicate Inner-sphere complexation.
- Splitting of the 565 cm<sup>-1</sup> band indicates the coupled vibrations of M–O and Mn–O.
- Splitting of the 875 cm<sup>-1</sup> band indicates two different O–O bond lengths species.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 11 December 2014

Received in revised form 1 February 2015

Accepted 17 March 2015

Available online 24 March 2015

### Keywords:

Cesium

Cobalt

Nano manganese oxide

Infra-red spectroscopy

Two-dimensional correlation spectroscopy

## ABSTRACT

Molecular scale information is of prime importance to understand ions coordination to mineral surfaces and consequently to aid in the design of improved ion exchange materials. This paper reports on the use of two-dimensional correlation infra-red spectroscopy (2D-COS-IR) to investigate the time dependent adsorptions of cesium and cobalt ions onto nano manganese oxide (NMO). The metal ions uptake was driven mainly by inner-sphere complex formation as demonstrated by the production of new absorption bands at 1160, 1100, 585 and 525 cm<sup>-1</sup>, which were assigned to the O–O bond vibration and the coupled vibrations of M–O and Mn–O bonds. The progressive development of the 3100 cm<sup>-1</sup> band, which is attributed to the stretching vibration of the lattice–OH group, indicates an M<sup>n</sup>/H<sup>+</sup> ion-exchange reaction. The new bands at 700 and 755 cm<sup>-1</sup> in the case of cobalt ion adsorption and at 800 and 810 cm<sup>-1</sup> in the case of cesium ion adsorption, and the splitting of other bands at 1135 and 875 cm<sup>-1</sup> indicate the presence of different O–O bond lengths. This suggests different coordination of the two metal ions with oxygen. The infrared spectroscopy combined with 2D-COS provides a powerful tool to investigate the mechanism of interaction between heavy metals and manganese oxide.

© 2015 Elsevier B.V. All rights reserved.

## Introduction

Separation of radionuclides from aqueous streams is an important issue to either recover metal ions or reduce their

concentration in waste water to low levels of toxicity. Selective separation of low concentration levels of Cs<sup>+</sup> and Co<sup>2+</sup> has attracted the attention of many researchers, because of its importance in nuclear industry and environment protection [1–3].

Manganese oxides with different structures have been prepared, and extensively investigated as one of the best sorbent with high affinity for metal ions. The basic building block for the structural frameworks of Mn-oxides is the MnO<sub>6</sub> octahedral units

\* Corresponding author. Tel.: +963 11 213 2580; fax: +963 11 611 2289.

E-mail addresses: [cscientific9@aec.org.sy](mailto:cscientific9@aec.org.sy) (A.G. Al Lafi), [prscience@aec.org.sy](mailto:prscience@aec.org.sy) (J. Al Abdullah).

shared by corners and/or edges. In Mn-oxides with tunnel structures Mn octahedral share both edges and corners, while in Mn-oxides with layered structures, Mn octahedral are arranged in sheets by sharing edges [4,5].

To the best of our knowledge, X-ray powder diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and extended X-ray absorption fine structure (EXAFS) are the most useful techniques to provide information of manganese oxides in relation to their structure and the adsorption mechanism of metal ions. However, it has been reported that the Infrared (IR) spectroscopy reveals more complexes than the EXAFS [6,7]. Infrared spectroscopy can be used to analyze both metal oxides, and their adsorption mechanism due to its sensitivity to amorphous regions and those with short-range and/or long-range order [5,8,9]. However, the scope of this work is to utilize recent development in the field of IR analysis namely, two dimensional correlation spectroscopy to investigate the adsorption mechanism of different metal ions (cesium and cobalt) onto a synthetic manganese oxide. 2D correlation spectroscopy (2D-COS) has been introduced to vibrational spectroscopy by Noda [10], and subsequently has been applied to wide range of other analytical spectroscopies [11–15]. The use of 2D-COS simplifies the complex spectra and improves spectral resolution by means of spreading the peaks over a second dimension. In addition, the use of 2D-COS enables the determination of specific sequential order of spectral intensity changes [10,13,16,17].

In this work, IR spectra were measured during the adsorption processes of metal ions ( $\text{Cs}^+$  and  $\text{Co}^{2+}$ ) onto NMO. 2D-COS analysis was applied to investigate the mechanism of adsorption. The nature of complexes formed on adsorption of different metal ions were discussed, and correlated to the chemical and physical properties of the synthetic manganese oxide.

## Materials and methods

### Synthesis and characterization of NMO

NMO was prepared by the reduction of  $\text{KMnO}_4$  by HCl. As a typical synthesis, 15 ml of HCl,  $4.0 \text{ mol L}^{-1}$  was added drop-wise to 600 ml of  $\text{KMnO}_4$ ,  $0.02 \text{ mol L}^{-1}$ , under fume cupboard. After stirring for 20 min, the obtained solution was heated to  $80^\circ\text{C}$  for 3 h. After cooling, NMO was collected by centrifugation, and subsequently washed three times with ultra pure water to remove any impurities, then with  $\text{HNO}_3$ ,  $1.0 \text{ mol L}^{-1}$ , and finally dried in air at  $80^\circ\text{C}$  for 12 h. The powder X-ray diffraction (XRD) patterns of NMO before and after metal sorption were recorded using a transmission diffractometer (STADI-P STOE, Darmstadt, Germany), with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) and a germanium monochromator operated at 50 kV and 30 mA.

The specific surface area of NMO was measured using an  $\text{N}_2$  adsorption and desorption test at 77 K (Quantachrome NOVA 2200 pore structure analyzer, Florida, USA).

IR spectra of NMO particles before and after metal sorption were recorded by the KBr method (Thermo Scientific Nicolet 6700 FT-IR Spectrometer, Madison, USA). All IR spectra were measured from  $400$  to  $4000 \text{ cm}^{-1}$  at a resolution of  $4 \text{ cm}^{-1}$  and a total of 64 scans. A separate background spectrum was subtracted in each data acquisition.

The morphology of NMO before and after adsorption process was investigated by a scanning electron microscope (Tescan Vega II XMU, USA) operated at 20 kV.

### Adsorption experiments

Batch adsorption experiments were carried out using 0.2 mg of NMO added to solutions containing various concentrations of the

metal ions at a temperature of  $22 \pm 2^\circ\text{C}$ . The value of solid/liquid was  $0.1 \text{ g L}^{-1}$ . The initial pH of the working solutions was adjusted at 4.0. NMO was separated from the solution by filtration after adsorption equilibrium was reached (after 2 h), and subsequently the concentration of the free ions in the filtrate was determined. Each experiment was repeated three times, and the concentration values were averaged.

### 2D correlation analysis

All IR spectra were baseline corrected using OMNIC software package, and smoothed with a Savitzky–Golay smoothing method using a second order polynomial function with 13 points as the number of the points of the convolution weights. Finally, all spectra were normalized based on the  $540 \text{ cm}^{-1}$  band. The high intensity  $540 \text{ cm}^{-1}$  band is one of the Mn–O lattice vibration bands. This band is only affected by the phase structure and composition of NMO [5,18], and it has been observed both in the absence and presence of adsorbed ions [19]. As the absorption processes occurs without changing the phase structure of  $\text{MnO}_6$  so this band could be used as an internal reference (i.e. a band intensity that is not selectively affected by the perturbation) [20]. The subsequent 2D correlation analysis was performed using the algorithm developed by Noda [10,17], and calculated using the 2DShige software version 1.3 software (Shigeaki Morita, Kwansai-Gakuin University, 2004–2005). The spectral intensity of each sample was corrected by subtraction of a reference spectrum taken as the spectrum corresponding to NMO with maximum metal ions adsorption [14]. The dynamic spectra were then used to develop the 2D correlation spectra (synchronous and asynchronous) based on a discrete Hilbert transform algorithm. The 2D correlation spectra consist of positive (shown in white/red areas) and negative (shown in gray/blue areas) cross-peaks in both synchronous and asynchronous maps, and they are interpreted according to Noda's rule [17].

## Results and discussions

### Characterization of NMO

The surface area of NMO was found to be  $165 \text{ m}^2 \text{ g}^{-1}$ , and this was consistent with the value reported in literature [21,22]. The diffraction peaks of the XRD pattern for NMO are shown in Fig. 1(a). Despite well defined yet low-intensity and broad peaks, i.e. matching the pattern of the  $\alpha\text{-MnO}_2$ , the XRD patterns reveal that the synthesized NMO was in poor crystalline state with a short-range crystal form. This may be responsible for the high surface area of NMO [23,24].

The infrared spectrum of manganese dioxide consists of three informative regions. These are the region  $4000\text{--}3000 \text{ cm}^{-1}$  which yields information on the constitutional water present in the sample; the region  $1200\text{--}800 \text{ cm}^{-1}$  which reveals the interactions between manganese and the constituent species; and the region  $800\text{--}400 \text{ cm}^{-1}$  which can be used to examine the octahedral structure of  $\text{MnO}_6$  [18].

Fig. 1(b) shows the characteristic FT-IR spectrum of NMO. Several absorption bands were observed at  $3400$ ,  $1622$ ,  $880$ ,  $580$ ,  $540$ ,  $520$ ,  $470$ , and a weak band at  $710 \text{ cm}^{-1}$ . It has been reported that the  $3400$  and the  $1622 \text{ cm}^{-1}$  bands are attributed to the O–H stretching vibration and the O–H bending vibration combined with Mn atoms respectively. [3,23] The other bands at  $570$ ,  $520$ ,  $470$  and  $710 \text{ cm}^{-1}$  have been reported to be characteristic bands of the  $\alpha$ ,  $\gamma$  and  $\delta$  oxide. The absence of a band at  $665 \text{ cm}^{-1}$  is indicative of the absence of  $\beta$  oxide [25,26]. The morphology of NMO was determined by SEM. As shown in Fig. 1(c), it is composed of uniform

Download English Version:

<https://daneshyari.com/en/article/1404845>

Download Persian Version:

<https://daneshyari.com/article/1404845>

[Daneshyari.com](https://daneshyari.com)