



## Ceria associated manganese oxide nanoparticles: Synthesis, characterization and arsenic(V) sorption behavior

Kaushik Gupta<sup>a</sup>, Sayan Bhattacharya<sup>b</sup>, Dhruvajyoti Chattopadhyay<sup>c</sup>, Aniruddha Mukhopadhyay<sup>b</sup>, Harishankar Biswas<sup>d</sup>, Jagannath Dutta<sup>d</sup>, Nihar Ranjan Ray<sup>d</sup>, Uday Chand Ghosh<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Presidency University (Formerly Presidency College), Kolkata 700073, India

<sup>b</sup> Department of Environmental Science, University of Calcutta, 51/2, Hazra Road, Kolkata 700019, India

<sup>c</sup> B.C. Guha Centre for Genetic Engineering and Biotechnology, 35 Ballygunge Circular Road, Kolkata 700019, India

<sup>d</sup> Saha Institute of Nuclear Physics, Bidhannagore, Salt Lake City, India

### ARTICLE INFO

#### Article history:

Received 26 February 2011

Received in revised form 24 May 2011

Accepted 24 May 2011

#### Keywords:

Arsenic(V)

Nanoparticle

Ceria associated manganese oxide

Characterizations

Sorption

Synthesis

### ABSTRACT

Four samples of ceria incorporated manganese oxide (NCMO) were prepared by co-precipitation-calcinations and sol-gel methods, and characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, atomic force microscopy, BET surface area etc. The synthetic samples were nanoparticle agglomerates with irregular surface morphology (Ce:Mn = 1:1). The NCMO-1b sample, prepared by the calcination of metal hydroxide at 573 K for 3.0 h, was a nano-crystalline (70–90 nm) and hydrated material having high BET surface area (116.96 m<sup>2</sup> g<sup>-1</sup>). The arsenic(V)-sorption by the samples at pH 7.0 (±0.2) and 30 °C showed that the NCMO-1b is a most efficient material. Optimum pH range for the arsenic(V) sorption is 3.0–7.0 at 303 (±1.0) K. Kinetics and equilibrium data obtained (pH = 7.0 ± 0.2, T = 303 ± 1.0 K and I = 0.01 M) had described the pseudo-second order kinetics and the Freundlich isotherm models well, respectively. Thermodynamics of the sorption reaction showed that the changes of enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ), respectively, were +23.901 kJ mol<sup>-1</sup>, +0.175 kJ mol<sup>-1</sup> K<sup>-1</sup> and -25.737 to -32.753 kJ mol<sup>-1</sup> at T = 283–323 K. Estimation of the sorption energy ( $E = 17.15$  kJ mol<sup>-1</sup>) indicated that the arsenic(V) was chemisorbed on NCMO-1b. The phosphate only reduced the arsenic(V) removal efficiency of NCMO-1b.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Nanomaterials show various unique enhanced properties, which are not shown by the bulk materials, and find their application in multivariate technological fields. Materials with nanostructure have gained special attention recently in the field of solute adsorption from the liquid phase due to the small particle size, large surface area, and high in situ reactivity. Nanomaterials can be used as catalyst to react with toxic gases such as CO and NO<sub>x</sub> in automobile catalytic converter for the enhanced chemical activity. Zhang reported an overview of nano-scale iron particles for the environmental remediation [1]. Consequently, different workers [2–6] had adopted the methods such as chemical precipitation, sol-gel, vapor deposition, solvo thermal, solid state reaction, etc. for the synthesis of some mixed oxides. Among the above, the chemical precipitation method is a simple, easy to handle, cheap and mostly green technique. Like different metal oxides with nanostructure,

multi metal or doped metal oxides are also to be important for multivariate applications due to the lattice imperfections. However, the simultaneous metal hydroxide precipitate formation from an aqueous mixture containing a number of metal ions is somewhat difficult due to their differences of solubility product values and crystal structures. However, it can be manipulated by controlling the concentrations of metal ions in solution and pH for the precipitation. The difficulty encountered when nano-materials are used for the treatment of contaminated water is the separation of material from its colloidal suspension by simple filtration, but the advantage is the generation of low sludge volume which diminishes disposal problem. However, the difficulty could be overcome by using nano-particle agglomerates of the materials.

The occurrence of arsenic (+3 and +5), which is a carcinogenic element in groundwater much exceeding the tolerance limit (10 µg L<sup>-1</sup>) is a well known global problem, and poses an ever-increasing degree of health hazard. The Bengal Delta Basin (West Bengal in India and Bangladesh) has become infested with this menace, and in some pockets of this region it has assumed life-threatening, causing deaths of a good number of inhabitants because rural people of those areas are still consuming groundwater as the source of drinking water. Therefore, the removal excess

\* Corresponding author at: Department of Chemistry, Presidency University (Formerly Presidency College), Kolkata-700073, India. Tel.: +91 33 2241 3893.

E-mail address: [ucghosh@yahoo.co.in](mailto:ucghosh@yahoo.co.in) (U.C. Ghosh).

arsenic from the contaminated ground water is an urgent need. Among the available different technologies, adsorption is the best one due to its easy handling, high efficiency, and way to develop a filter for house hold purpose.

All these encouraged the workers to synthesis nanoparticle agglomerates of mixed oxides such as iron–cerium [7], iron–manganese [8–11] iron–zirconium [12], iron–titanium [13] and iron–chromium [14] for the arsenic sorption from aqueous solutions. Literatures showed that the synthesis of cerium–manganese mixed oxide had gained special attention for a number of applications such as cerium incorporated porous manganese oxide OMS-2 as catalyst [15], cerium–manganese mixed oxide for the removal of H<sub>2</sub>S at high temperature [16], MnO<sub>x</sub>–CeO<sub>2</sub> mixed oxide for complete catalytic oxidation of formaldehyde [17], Mn(III)/(IV)–cerium(IV) oxide [18], cerium–manganese mixed oxides as oxidation catalysis [19], etc. Multiple activities of this mixed oxide [15–26] had encouraged us in taking attempt to synthesis cerium–manganese mixed oxide of nano-dimension for scavenging undesired solutes such as arsenic and fluoride from the contaminated groundwater.

This manuscript reports herein the synthesis and characterization of nano-structured ceria associated manganese oxide (NCMO-1 and NCMO-2) samples with arsenic(V) sorption behavior from the aqueous solution.

## 2. Experimental

### 2.1. Chemicals

Ammonium ceric nitrate (ACN), manganous chloride, sodium bicarbonate, tartaric acid used for synthesis of the NCMO samples were laboratory reagent (LR) grade, which were procured from E. Merck, Mumbai (India). Disodium hydrogen arsenate (99.99%), which was used for the preparation of stock arsenic(V) solution, was Analar Reagent (A. R.) grade (BDH, England). Sodium chloride used for the ionic strength adjustment was A. R (BDH, England) grade. All other chemicals used were of LR grade (E. Merck, Mumbai, India).

### 2.2. Synthesis of NCMO-1 samples

The solutions of ACN (0.1 M in 0.1 M HNO<sub>3</sub>) and manganous chloride (0.1 M in 0.01 M HCl) were warmed separately at 80 °C. Hot ACN solution was dropped from a separatory funnel slowly into an equal volume of agitating (speed: 300 rpm) hot manganous chloride. To the above agitating mixture, 0.1 M NaHCO<sub>3</sub> solution was dropped from the separating funnel till the solution pH rose to ~8.0. The precipitate including mother liquid was kept for 24 h at room temperature for aging. After filtering the precipitate, jell-like mass was washed with distilled water to make carbonate free and dried at 50–60 °C inside an air oven. Dry solid mass was divided into the three fractions, and incinerated for 3.0 h separately at 373, 573 and 773 K which were marked as NCMO-1a, NCMO-1b and NCMO-1c samples, respectively. In addition, manganese oxide and cerium oxide samples were also separately prepared. Here, 0.1 M manganous chloride solution was hydrolyzed with 0.1 M sodium bicarbonate. The basic metal carbonate obtained was ignited at 773 K inside a muffle furnace for 3.0 h for the manganese oxide. The pure ceria was also prepared by cerium oxalate precipitation from 0.1 M ACN solution with 0.1 M oxalic acid. The cerium oxalate precipitate was ignited at 773 K inside a muffle furnace for the cerium oxide for 3.0 h.

### 2.3. Synthesis of NCMO-2

The NCMO-2 sample was prepared by the sol–gel method. Here, 0.1 M ACN and 0.1 M manganous chloride (1:1, v/v) were mixed

together. To this mixture, tartaric acid was mixed (10 times in mole proportion) with mechanical stirring, and placed on a boiling water bath for slow evaporation. The yellow gel formed was calcined at 773 K for 6 h. Here, the gel was converted to grey powder via floppy mass with black color, which was washed with distilled water and dried.

### 2.4. Analytical tools used for characterizations of NCMO samples

X-ray diffraction (XRD) patterns of the samples were taken by an X-ray powder diffractometer (Philips Analytical PW-1710) with Cu K $\alpha$  radiation. The potential current and voltage applied were 30 mA and 40 kV, respectively. Atomic Force Microscopic (AFM) images for surface topography of the samples were taken in non-contact mode by multimode scanning probe microscope (Agilent AFM 5500 series, USA) having multi purpose small scanner with low coherence laser (1 mW power, 670 nm wavelength, coherence length (<50  $\mu$ m), scan range: XY: 0–10  $\mu$ m; Z: 0–2  $\mu$ m, noise level: XY < 0.1 nm RMS, Z < 0.02 nm RMS). Fourier Transform Infrared (FTIR) spectra of the mixed oxide samples and the pure oxides were recorded using Perkin Elmer (U.S.) system 2000 spectrophotometer with a resolution of 2 cm<sup>-1</sup>. Transmission electron micrographic (TEM) images were recorded on a H800 transmission electron micrograph (Hitachi, Japan) operating at 200 kV. Scanning electron microscopic (SEM) images with EDS (Tescan Vega, U.K.; model LSU+) spectra were recorded spraying the sample on a carbon tape. The surface area and pore width distributions were analyzed by Quatachrome Autosorb-1C surface analyzer. The pH of each solution was analyzed by pH-meter of model: LI-127 (ELICO, India).

### 2.5. Arsenic analysis

Arsenic samples were analyzed using atomic absorption spectrophotometer with hydride generator assembly attachment (Perkin Elmer AAnalyst 200) and UV-VIS spectrophotometer (Hitachi model U-3210) using the methods described in 'Standard Methods for the Examination of Water and Wastewater' [27].

### 2.6. Arsenic(V) solutions

2.08 g of Na<sub>2</sub>HAsO<sub>4</sub> (99.99%) was dissolved in 1.0 L of arsenic free distilled water. The concentration of arsenic(V) was found to be 1000 ( $\pm$ 1) mg L<sup>-1</sup>. Arsenic(V) solution of any desired concentration to be used in the experiments was made by diluting the stock with 0.2% (v/v) HCl. Each arsenic(V) solution was analyzed for the concentration [27] before using in the experiments. The stock solution was prepared fresh after every 15 days.

### 2.7. Batch experiments

#### 2.7.1. Effect of pH

For the effect of initial pH (pH<sub>i</sub>), 50 mg of NCMO was mixed with 50 mL of arsenic(V) solutions of C<sub>0</sub> (initial concentration, mg L<sup>-1</sup> = 5.0 and 10.0) with ionic strength (I) = 0.01 M and pH<sub>i</sub> adjusted separately at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0 separately into polyethylene tetra phthalate (PET) bottles (each capacity = 250 mL), agitated (speed, S<sub>T</sub> = 280  $\pm$  5 rpm) for a duration of 2.0 h at temperature (T) = 300 ( $\pm$ 1) K. The equilibrium solution pH (pH<sub>f</sub>) value of each mixture was recorded immediately after 2 h of agitation and centrifuged to separate the solid NCMO particles. Each centrifuged solution was analyzed [27] for the remaining arsenic concentration (C<sub>R</sub>, mg L<sup>-1</sup>).

Download English Version:

<https://daneshyari.com/en/article/151045>

Download Persian Version:

<https://daneshyari.com/article/151045>

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