Applied Surface Science 282 (2013) 46–51

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Selective adsorption and determination of iron(III): Mn_3O_4/TiO_2 composite nanosheets as marker of iron for environmental applications

Sher Bahadar Khan[a,b,*], Mohammed M. Rahman[a,b], Hadi M. Marwani[a,b], Abdullah M. Asiri[a,b], Khalid A. Alamry[b], Malik Abdul Rub[a,b]

[a] Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia
[b] Chemistry Department, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:
Received 11 January 2013
Received in revised form 12 March 2013
Accepted 13 March 2013
Available online 23 May 2013

Keywords:
Mn_3O_4/TiO_2
Composite
Nanosheets
Structural properties
Fe^{3+} uptake
Environmental application

ABSTRACT

Mn_3O_4/TiO_2 composite nanosheets have been synthesized by simple and low temperature magnetic stirring method and applied for water treatment application. The synthesized Mn_3O_4/TiO_2 composite nanosheets were characterized by using field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The spectroscopic techniques agreed that synthesized product is well crystalline nanosheets composed of Mn_3O_4/TiO_2. The analytical potential of synthesized Mn_3O_4/TiO_2 composite nanosheets was studied for a selective separation of Fe^{3+} prior to its determination by inductively coupled plasma-optical emission spectrometry. The selectivity of Mn_3O_4/TiO_2 composite nanosheets toward different metal ions, including Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Pd^{2+} and Zn^{2+} was investigated. Results of the selectivity study demonstrated that Mn_3O_4/TiO_2 composite nanosheets were the most selective toward Fe^{3+}. The adsorption capacity of Fe^{3+} was found to be 69.80 mg g^{-1}. Moreover, adsorption isotherm data also provided that the adsorption process was mainly monolayer on a homogeneous adsorbent surface.

1. Introduction

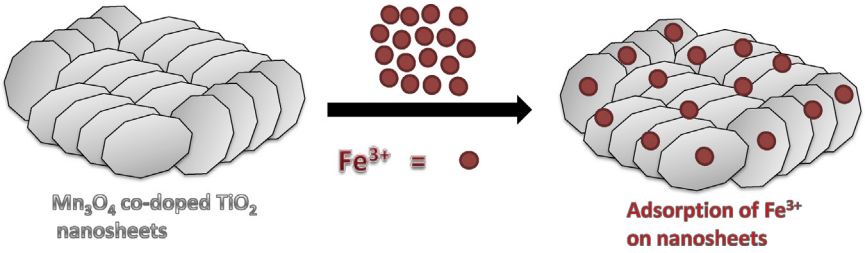
Nanomaterials possess unique properties along with distinctive performance and numerous applications concerning human health and environmental importance [1,2]. Nanomaterials contribute significantly toward medicine, environment and energy [3,4]. The reasons for major contribution of nanomaterials are their particular shape, small size, high active surface to volume ratio, and high surface activity [5,6]. Nanomaterials display capability to adsorb metal ion which is scarcely expected for the conventional systems [7,8]. Titanium oxide is versatile nanomaterial due to its wide range of applications but the features of titanium oxide still need to be modified in order to increase its various properties to meet different applications in a range of fields. The modification features include the doping process i.e. doping materials in the parent system as it shows excellent properties in various sectors [9].

Semiconductor materials are used as host material for transition doped materials and have involved insightful research effort due to their excellent properties and multidimensional applications [10,11]. Nowadays, an extensive investigation has been made on the progression of doped nanomaterials by basic sciences and potential classy technologies. Dopants can improve the surface area of metal oxide nanostructure. These dopants have the property for alleviation of surface and it also encourages the decrease in size as well as changes the orientation, shapes and morphologies of the nanomaterials. Doping of nanomaterials also helps in improving their other properties such as resistivity, diffuse reflectivity and chemical sensing. Doped nanomaterials, large band-gap material, are conductive in nature due to the formation of oxygen vacancies and interstitials in nanomaterials. These oxygen vacancies and interstitials formed readily in nanomaterials due to its low energy formation and result in the conductivity of doped nanomaterials. These dopants can develop the conductivity, electrical, sensing and catalytic performance of the nanomaterials which has a fundamental role in environmental uses which has also favorable effects on human health [12,13].

In addition, the development of simple, rapid and efficient methods has become of interest for monitoring metal ions in the environment. Several analytical methods have been applied to analyze metal ions in aqueous solutions, such as atomic absorption spectrometry [14], inductively coupled plasma-optical emission spectrometry (ICP-OES) [15], anodic stripping voltammetry [16], and ion chromatography [17]. However, analytical methods cannot

* Corresponding author at: Center of Excellence for Advanced Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia.
E-mail address: drkhanmarwat@gmail.com (S.B. Khan).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.03.180



Scheme 1. Schematic view of adsorption process of Fe^{3+} on Mn_3O_4/TiO_2 composite nanosheets.

directly measure metal ions, in particular at ultra-trace concentration, in aqueous systems due to the lack of sensitivity and selectivity of these methods. Therefore, an efficient separation procedure is usually required prior to the determination of noble metals for sensitive, accurate and interference-free determination of noble metals [18].

Several analytical methods can be used for separation of analyte of interest, including liquid–liquid extraction [19], ion exchange [20], coprecipitation [21], cloud point extraction [22] and solid phase extraction (SPE) [23]. SPE is considered to be one of the most powerful techniques because it minimizes solvent usage and exposure, disposal costs, and extraction time for sample preparation. Several adsorbents have appeared because of the popularity of SPE for selective extraction of analytes, such as alumina [24], C18 [25], molecular imprinted polymers [15], cellulose [26], silica gel [27,28], activated carbon [29,30] and carbon nanotubes [31,32].

In this contribution, Mn_3O_4/TiO_2 composite nanosheets were synthesized by simply low-temperature magnetic stirring method and characterized by XRD, FESEM, FTIR, and XPS. In accordance, the objective of this study was to investigate the analytical potential of Mn_3O_4/TiO_2 composite nanosheets as an adsorbent on the selectivity and adsorption capacity of Fe^{3+} prior to its determination by ICP-OES. The selectivity of Mn_3O_4/TiO_2 composite nanosheets toward different metal ions, including Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Pd^{2+} and Zn^{2+} was investigated in order to study the effectiveness of Mn_3O_4/TiO_2 composite nanosheets on the adsorption of selected metal ions. Based on the selectivity study, it was concluded that the selectivity of Mn_3O_4/TiO_2 composite nanosheets phase was the most toward Fe^{3+}. The static uptake capacity for Fe^{3+} was determined to be 69.80 mg g^{-1}. Results of adsorption isotherm also confirmed that the adsorption process was mainly monolayer on a homogeneous adsorbent surface. Adsorption data of Fe^{3+} were well fit with the Langmuir classical adsorption isotherm.

2. Experimental

2.1. Chemicals and reagents

Stock standard solutions of 1000 mg L^{-1} Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Pd^{2+} and Zn^{2+} were purchased from Sigma–Aldrich (Milwaukee, WI, USA). All reagents used were of analytical and spectral purity grade. Doubly distilled deionized water was also used throughout experimental studies.

2.2. Synthesis of Mn_3O_4/TiO_2 composite nanosheets

Equi-molar aqueous solutions of TiO_2 and manganese nitrate tetrahydrate were mixed together and titrated by NH_4OH solution till pH reached above 10.0. This ensuing high basic solution was stirred at 60.0 °C for overnight and the resulting product was washed with 1:1 mixture of distilled water and ethanol. The product was then dried at room temperature and further calcined at 400.0 °C for 5 h.

2.3. Samples preparation and procedure

Stock solutions of Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Pd^{2+} and Zn^{2+} were prepared in 18.2 MΩ cm distilled deionized water and stored in the dark at 4 °C. For selectivity study, standard solutions of 1 mg L^{-1} of each metal ion were prepared and adjusted to pH value of 5.0 with acetate buffer. Then, each standard solution was individually mixed with 25 mg Mn_3O_4/TiO_2 composite nanosheets. In this study, a fixed pH value of 5.0 was chosen for all metal ions in order to avoid any precipitation of other species, in particular for Fe^{3+}. For example, Fe^{3+} usually forms a precipitation of $Fe(OH)_3$ with buffer solutions at pH value greater than 5.0. For the study of Fe^{3+} static adsorption capacity, standard solutions of 0, 5, 10, 15, 20, 25, 30, 50, 75, 125 and 150 mg L^{-1} were prepared as above, adjusted to the optimum pH value of 5.0 and individually mixed with 25 mg Mn_3O_4/TiO_2 composite nanosheets. All mixtures were mechanically shaken for 1 h at room temperature.

2.4. Characterization

The morphology of the synthesized product was studied at 15 kV using a JEOL Scanning Electron Microscope (JSM-7600F, Japan). X-ray diffraction patterns (XRD) were taken with a computer controlled RINT 2000, Rigaku diffractometer using the Ni-filtered Cu-K_α radiation (λ = 0.15405 nm). FT-IR spectrum was recorded in the range of 400–4000 cm^{-1} on Perkin Elmer (spectrum 100) FT-IR spectrometer. XPS spectrum was recorded in the range of 0–1350 eV by using Thermo Scientific K-Alpha KA1066 spectrometer (Germany). ICP-OES measurements were acquired by use of a Perkin Elmer ICP-OES model Optima 4100 DV, USA. The ICP-OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min^{-1}; auxiliary gas (Ar) flow, 0.2 L min^{-1}; nebulizer gas (Ar) flow, 0.8 L min^{-1}; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min^{-1}; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. Selected metal ions were measured at wavelengths of 267.60 nm for Au^{3+}, 228.80 nm for Cd^{2+}, 238.90 nm for Co^{2+}, 267.72 nm for Cr^{3+}, 259.94 nm for Fe^{3+}, 340.46 nm for Pd^{2+} and 206.20 nm for Zn^{2+} (Scheme 1).

3. Results and discussion

3.1. Physiochemical characterization of Mn_3O_4/TiO_2 composite nanosheets

The morphology of Mn_3O_4/TiO_2 composite was investigated by using FESEM which gives information about the surface features of the sample (i.e. how it looks, its texture) and morphology (i.e. the shape and size of the particles making up the sample). The low and high magnifications of FESEM images are shown in Fig. 1(a)–(c). FESEM clearly shows that the synthesized product is composed of