LISTA CELOR 10 LUCRĂRI REPREZENTATIVE CARE SUSȚIN CONȚINUTUL TEZEI

1. **C. Muntean**, M. Bozdog, S. Duma, M. Ştefănescu, Study on the formation of $Co_{1-x}Zn_xFe_2O_4$ system using two low temperature synthesis methods, *Journal of Thermal Analysis and Calorimetry* 122 (2016) 117-126. http://link.springer.com/article/10.1007/s10973-015-4963-8
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3. **C. Muntean**, M. Stoia, P. Barvinschi, Synthesis of nanocrystalline $ZnFe_2O_4$ and its use for the removal of Congo Red from aqueous solutions, *Environmental Engineering and Management Journal* 12(5) (2013) 959-967. http://omicron.ch.tuiasi.ro/EEMJ/pdfs/vol12/no5/15_290_Muntean_13.pdf
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J Therm Anal Calorim (2016) 123:117–126
DOI 10.1007/s10973-015-4963-8

Study on the formation of $Co_{1-x}Zn_xFe_2O_4$ system using two low-temperature synthesis methods

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Received: 16 February 2015 / Accepted: 3 August 2015 / Published online: 1 September 2015

Abstract This paper deals with the synthesis of cobalt–zinc ferrite $Co_{1-x}Zn_xFe_2O_4$ ($x = 0.5$), by two different synthesis methods: thermal decomposition of carboxylate complex, and co-precipitation. The effect of temperature on the characteristics of the obtained powders was investigated by X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and magnetic measurements. Thermal analysis was used to investigate metal carboxylate complex formation and their thermal stability. The mixture of Co(II), Zn(II), and Fe(III) carboxylates (precursor) decomposed at 300 °C was annealed at 350, 500, and 1000 °C. The XRD patterns revealed that all powders consist of the spinel phase $Co_{1-x}Zn_xFe_2O_4$. As the annealing temperature increased, the crystallite size, lattice parameter, and saturation magnetization were increased. Co-precipitation method was used to synthesize samples at different temperatures: 25, 40, 60, and 80 °C. X-ray diffractometry proved that cobalt–zinc ferrite was formed starting with 25 °C, while the ferritization process was almost completed at 80 °C. The precipitate obtained at 80 °C was annealed at 500 and 1000 °C. At 80 and 500 °C, the powders have similar crystallite size (~9 nm) and similar lattice parameter ($a = 8.37$ Å) and show a super-paramagnetic behavior. Powders obtained by both methods, at 1000 °C, have close values for the saturation magnetization σ (~60 emu g^{-1}) and tend to have super-paramagnetic behavior (coercive field $H_c = 0.08$ kOe). The lattice parameter has also similar values, corresponding to the $Co_{0.5}Zn_{0.5}Fe_2O_4$ composition ($a = 8.40$ Å). Thermal decomposition of carboxylate complexes is a new method for the obtaining of $Co_{0.5}Zn_{0.5}Fe_2O_4$ ferrite. The results are comparable to those obtained by co-precipitation, starting from the same reagents (metal nitrates). The magnetic behavior makes this nanoferrite suitable for applications such as preparation of ferrofluids and hyperthermia for cancer treatment.

Keywords Cobalt–zinc ferrite · Carboxylate complex · Thermal decomposition · Co-precipitation · Thermal analysis · Magnetic properties

Introduction

Inorganic mixed oxides of ferrite type are currently the subject of interest because of their wide application in industrial as well as research areas. They are attractive because of their importance in ferrofluids, magnetic drug delivery, hyperthermia for cancer treatment, etc. [1–3]. Nanoparticle ferrites with a high surface to volume ratio have received much attention due to their useful electrical and magnetic properties. These types of nanoparticles can be produced by different wet chemical methods, such as the co-precipitation [4, 5], hydrothermal synthesis [6], and microemulsion synthesis [7]. In addition, various dry methods, including grinding [8, 9], mechanical alloying [10], and thermal plasma methods [11], have been employed. Besides these methods, several attempts have been made using auto-ignited combustion reactions [9, 12–16].

Ferrites can be represented by the chemical formula AB_2O_4, where A and B denote metal cations on the tetrahedral (A) and octahedral (B) sites, respectively. The magnetic properties of the spinel ferrite materials originate from

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Journal of Magnetism and Magnetic Materials 393 (2015) 92–98

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Synthesis and magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ ($x=0\div1$) nanopowders by thermal decomposition of Co(II), Zn(II) and Fe(III) carboxylates

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ARTICLE INFO

Article history:
Received 18 March 2015
Received in revised form
15 May 2015
Accepted 17 May 2015
Available online 19 May 2015

Keywords:
Carboxylate
Ferrite
X-ray diffractometry
Magnetic properties
Nanoparticles

ABSTRACT

Nanoparticles of cobalt–zinc ferrite $Co_{1-x}Zn_xFe_2O_4$ with x varying from 0 to 1.0 were prepared by a new method, the thermal decomposition of carboxylates of Fe(III), Co(II) and Zn(II). The obtained carboxylate precursor was characterized by thermal analysis and FT-IR spectroscopy. The precursor was annealed at 350, 600 and 1000 °C. It was found that the spinel cobalt–zinc ferrite was formed starting at 350 °C, but in mixture with simple oxides γ-Fe_2O_3, Co_3O_4 and ZnO. At 1000 °C $Co_{1-x}Zn_xFe_2O_4$ was formed quantitatively as a single, well-crystallized phase. The saturation magnetization of the samples annealed at 1000 °C decreased significantly with increasing Zn^{2+} content from 83.93 emu/g ($x=0$) to 4.92 emu/g ($x=1.0$). At 350 and 600 °C the saturation magnetization had the same trend, even if there were contributions of other magnetic phases. Obtaining of spinel ferrite was evidenced by X-ray diffractometry and FT-IR spectrometry. Powder morphology was determined by scanning electron microscopy. Magnetic properties of the synthesized ferrites were investigated employing a conventional induction method.

1. Introduction

Ferrites continue to be remarkable magnetic materials due to their potential applications in ferro-fluids, magnetic resonance, imaging, bio-medical diagnostics, drug delivery, sensors, permanent magnets, magnetic refrigeration systems, etc. [1–3]. Experience has shown that the properties of ferrites are strongly influenced by the material composition and microstructure, which are sensitive to the preparation methodology used in the synthesis [4,5]. Choosing an optimal method is the key to getting a quality ferrite [6].

The properties of cobalt–zinc ferrite powders can be significantly improved by selecting the appropriate synthesis method. Many preparation methods have been tested until now: microwave-hydrothermal [7], sol–gel [8], co-precipitation [9] and ultrasound irradiation [10].

An increased attention has been paid to the combustion method [11]. The characteristic of this method consist in using an exothermic redox reaction to obtain the desired material. Depending on the nature of reagents (reactants) and reaction exothermicity two types of combustion can be distinguished: in solution [12] or in solid state [13].

Crystalline cobalt–zinc ferrite shows a mixed spinel configuration described by formula: $(Zn_x,Fe_{1-x})[Co_{1-x}, Fe_{1+x}]O_4$, where Zn^{2+} cations and some of the Fe^{3+} cations occupy tetrahedral positions (A), and Co^{2+} cations and the remaining Fe^{3+} cations occupy octahedral positions (B) [14,15].

In normal conditions zinc ferrite is a normal spinel (Zn^{2+} ions occupy tetrahedral voids and Fe^{3+} the octahedral voids), while cobalt ferrite is a reverse spinel. The high tendency of Co^{2+} ions to occupy octahedral voids determines cobalt–zinc ferrite to have a distribution of cations of the form: $(Zn_xFe_{1-x})[Co_{1-x}Fe_{1+x}]O_4$, but the distribution of cations depends on the particle size of ferrite, the synthesis method and the temperature [16,17]. Distribution of various ions in the octahedral and tetrahedral voids is different for ferrites obtained at low temperatures and those obtained in the form of nanoparticles [18]. These nanoferrites may present, after appropriate processing, the desired magnetic behavior.

Electrical and magnetic properties of cobalt–zinc ferrite depend very much on the distribution of cations in tetrahedral and octahedral voids, which may be different when one compares the solid material to the nanometric one. It is also known that the microstructure, particle size, chemical composition, and especially the distribution of cations varies depending on the method of preparation [9].

Several authors who studied the obtaining of ferrite $Co_{1-x}Zn_xFe_2O_4$ by different synthesis methods reported the same

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http://dx.doi.org/10.1016/j.jmmm.2015.05.048
0304-8853/

Environmental Engineering and Management Journal *May 2013, Vol.12, No. 5, 959-967*
http://omicron.ch.tuiasi.ro/EEMJ/

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SYNTHESIS OF NANOCRYSTALLINE $ZnFe_2O_4$ AND ITS USE FOR THE REMOVAL OF CONGO RED FROM AQUEOUS SOLUTIONS

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Abstract

The paper describes the synthesis of nanocrystalline zinc ferrite starting from 1,4-butanediol and a mixture of zinc and iron nitrates. During the heating of the obtained solution, a redox reaction takes place with emission of brown nitrogen oxides and formation of a solid powder. This powder was characterized by thermal analysis and FT-IR spectrometry, techniques that confirmed the formation of a mixture of zinc and iron carboxylates. This mixture was further used as precursor for zinc ferrite. By thermal decomposition at 350 °C and annealing at different temperatures, nanocrystalline zinc ferrite powders have been obtained, as evidenced by X-ray diffractometry. The adsorption performance of nanocrystalline zinc ferrite was examined in the process of Congo red removal from aqueous solutions. The influence of various experimental parameters like the amount of adsorbent, initial concentration and contact time was evaluated in batch experiments. The equilibrium adsorption data were analyzed using the Langmuir and Freundlich isotherm equations. The experimental data were well described by the Langmuir model. The maximum adsorption capacity of the material was of 97.6 mg Congo red/g. The experimental data were fitted to conventional kinetic models: the pseudo-first-order model and the pseudo-second-order model. The kinetics of the adsorption process was best described by the pseudo-second-order kinetic equation.

Key words: adsorption, Congo red, isotherm, kinetic, nanocrystalline zinc ferrite, organic precursor

Received: January 2013; Revised final: May, 2013; Accepted: May, 2013

1. Introduction

Spinel ferrites (MFe_2O_4) are very important magnetic materials that show great potential for many important technological applications, ranging from the information storage to the medical diagnostics and drug deliver. The applications of the spinel ferrites are greatly related to their magnetic properties. For high-performance applications in biomedicine, the magnetic nanocrystals are required to possess a narrow size distribution, a uniform spherical shape, and superparamagnetic properties. Most importantly, it is necessary to find an economical and efficient process for the synthesis of ferrite nanocrystals (Hu et al., 2008).

Zinc ferrite ($ZnFe_2O_4$) has a normal spinel structure with tetrahedral A-sites occupied by Zn^{2+} ions and octahedral B-sites by Fe^{3+} ions (Yang et al., 2004). It is well known that the morphology of zinc ferrite strongly affects its main properties by the reason of size-quantization effect and specific shape (Zhao et al., 2007). The preparation of zinc ferrite nanoparticles often uses physical methods, chemical reactions and sophisticated equipment, such as mechanosynthesis, aerogel, sol–gel, hydrothermal and ball milling (Yu and Yoshimura, 2000; Yuan and Zhang, 2001). These methods have difficulties in improving the dispersity and controlling the shape of the product because two reactants are used, are involved in complex reaction processes and need sophisticated apparatus.

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Environmental Engineering and Management Journal

June 2015, Vol.14, No. 6, 1247-1259
http://omicron.ch.tuiasi.ro/EEMJ/

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PREPARATION, CHARACTERIZATION AND ADSORPTION PROPERTIES OF MFe_2O_4 (M = Ni, Co, Cu) NANOPOWDERS

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Abstract

MFe_2O_4 nanopowders (M = Ni, Co, Cu) were prepared using the precursor technique, starting from the corresponding metal nitrates and poly(vinyl alcohol)-PVA. During the heating of metal nitrates- PVA solution, a redox reaction takes place around 150 °C, leading to the formation of M(II) and Fe(III) carboxylates. These compounds were used as precursors for the ferrites nanopowders. The desired ferrites were obtained by thermal decomposition of the carboxylates; the obtained powders were characterized by means of Fourier Transform Infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) specific surface area measurements. According to the results, $CoFe_2O_4$ and $NiFe_2O_4$ were obtained at 500 °C, while $CuFe_2O_4$ was contaminated with simple oxides. All powders consisted in micrometric aggregates of nanometric particles. Magnetic measurements evidenced that all powders obtained at 500 °C exhibited ferrimagnetic behavior. MFe_2O_4 nanopowders were used as adsorbents for Congo red removal from aqueous solutions. The influence of various experimental parameters (pH value, amount of adsorbent, initial concentration and contact time) was evaluated in batch experiments. The experimental data were analyzed using the pseudo-first-order, the pseudo-second-order and the intra-particle diffusion kinetic models. The pseudo-second-order model best described the kinetics of the adsorption process. The equilibrium adsorption data were fitted to Langmuir, Freundlich and Sips isotherm models. The experimental data were well described by the Sips model.

Key words: adsorption, Congo red, kinetic, nanocrystalline ferrite, poly(vinyl alcohol)

Received: December, 2014; Revised final: June, 2015; Accepted: June, 2015

1. Introduction

Dye-contaminated effluents result worldwide in large quantities from many industries like paper, tannery, paint and textile industries. The release of colored wastewater from these industries induces an eco-toxic hazard. Congo red [1-naphthalene sulfonic acid, 3,30-(4,40-biphenylenebis (azo)) bis (4-amino) disodium salt] is a benzidine-based anionic disazo dye and is one of the most used dyes in the textile industry.

Congo red (CR) is toxic and hazardous to many organisms. Despite its toxicity (a human carcinogen), CR is still widely consumed in several countries. Synthetic dyes, such as CR, are difficult to decompose due to their physicochemical, thermal and optical stability. The use of CR as sodium salt, with very good water solubility, makes the treatment of CR contaminated wastewater difficult (Afkhami and Moosavi, 2010; Rahimi et al., 2011; Smaranda et al., 2010).

For the removal of dyes from aqueous environment several methods such as coagulation, oxidation, photocatalysis, adsorption, nanofiltration, micellar-enhanced ultrafiltration were studied. Adsorption technology is one of the methods extensively applied for dyes removal from aqueous solutions being an effective, economic and simple-

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Thermochimica Acta 621 (2015) 61–67

Contents lists available at ScienceDirect

Thermochimica Acta

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

Obtaining of γ-Fe_2O_3 nanoparticles by thermal decomposition of polyethyleneglycol–iron nitrate mixtures

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 7 October 2015
Accepted 14 October 2015
Available online 19 October 2015

Keywords:
γ-Fe_2O_3
Polyethylene glycol
Iron nitrate
Magnetic nanoparticles
Thermal decomposition

ABSTRACT

γ-Fe_2O_3 nanoparticles with magnetic properties can be obtained by thermal decomposition in air of iron nitrate–polyethylene glycol (PEG) mixtures. In this paper we report a study regarding the obtaining of the single phase, well crystallized γ-Fe_2O_3 spinel, that takes place directly by thermal decomposition at ~300 °C without other thermal treatments. PEG acts as a reducing and coating agent of iron oxide and limits the agglomeration of γ-Fe_2O_3 nanoparticles. We studied the obtaining of γ-Fe_2O_3 by thermal decomposition of PEG–iron nitrate mixtures by thermal analysis and Fourier transform infrared spectroscopy. From the thermal behavior of the samples prepared using different PEG–iron nitrate ratios, we have established 300 °C as annealing temperature. The obtained powders were characterized by X-ray diffractometry, Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis and magnetic measurements. It was established that the obtaining of γ-Fe_2O_3 at 300 °C as single phase requires a minimum PEG–iron nitrate molar ratio of 0.25:100. The resulting γ-Fe_2O_3 particles had a spherical shape and an average size smaller than 10 nm, in agreement with the average crystallite size calculated from XRD patterns. The obtained γ-Fe_2O_3 powders presented magnetic properties, which are influenced by the molar ratio of the reactants.

1. Introduction

Nowadays, systems of oxidic nanoparticles are much studied due to their magnetic, electrical, optical and catalytic properties, very different from those of bulk material, as well as due to their potential applications in electronics, catalysis, biology, medicine, environmental [1,2]. The research in this field proved that nanomaterials must have some morpho-functional and structural characteristics: a certain chemical composition, purity, crystal structure, shape of nanoparticles, volume and dimensional distribution, important for both theoretical studies and applications [3–9].

The oxide systems can be synthesized by conventional and unconventional methods. The conventional methods are increasingly losing ground to the unconventional ones because of some major disadvantages: high temperature, long time of obtaining, waste of material and contamination. The unconventional methods assure synthesis at lower temperatures, a homogenous distribution of the components at molecular level (condition of maximum reactivity), a high specific surface of the obtained oxides and amorphous or slightly crystallized oxidic phases (due to the low preparation temperature).

The obtaining of oxidic systems with certain morphological characteristics, impose the selection of suitable methods. Thus, the dimension and the shape of the nanoparticles, which determine certain properties of the system, are decisive in choosing the synthesis method. The distribution of diameters and the interactions between nanoparticles are also important parameters. The possibility of perfect isolation of the nanoparticles and their immobilization, as well as the possibility to control the nanoparticles dimensions in the preparation phase, open new directions of knowledge and practical applications [10,11].

From the variety of simple and mixed oxidic systems that have been studied in the literature, Fe–O systems offer a wide field of fundamental and applied research, due to their remarkable properties, having applications in different fields such as ferrofluids, catalysts, magnetic data stocking, magnetic resonance imaging for diagnostic, magnetic drug release and control [12–14].

Polyethylene glycol (PEG) is widely used as a coating agent for magnetic nanoparticles, with potential applications in medicine

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http://dx.doi.org/10.1016/j.tca.2015.10.010
0040-6031/

J Therm Anal Calorim
DOI 10.1007/s10973-017-6268-6

Synthesis and characterization of $ZnAl_2O_4$ spinel from Zn(II) and Al(III) carboxylates

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Received: 29 July 2016 / Accepted: 6 March 2017

Abstract In this paper, zinc aluminate ($ZnAl_2O_4$) nanoparticles were obtained by a new synthesis method, thermal decomposition of Zn(II) and Al(III) carboxylates mixture. Complex combinations were obtained in the redox reaction between $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and 1,3-propanediol at 130 °C. The mechanism of Zn(II) and Al(III) carboxylates formation and decomposition was observed by thermal analysis and Fourier transform infrared spectroscopy. Zn(II) carboxylate, Al(III) carboxylate, and Zn(II) and Al(III) carboxylates mixture were annealed at different temperatures. Metal oxides synthesized from carboxylates precursors in single metal systems crystallized very well at 400 °C (ZnO) and weak at 800 °C (Al_2O_3), as shown by X-ray powder diffractometry. Homogenous mixture of Zn(II) and Al(III) carboxylates heated at 400 °C has led to a mixture of amorphous ZnO and Al_2O_3, which reacted forming at 600 °C well-crystallized $ZnAl_2O_4$, with mean crystallites size of 14.2 nm. The decomposition of carboxylates precursors is an appropriate method to obtain $ZnAl_2O_4$ spinel as well-crystallized single phase at low temperatures.

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Keywords Zinc aluminate · Thermal analysis · Nanoparticles · Carboxylate · Spinel

Introduction

Zinc aluminate ($ZnAl_2O_4$), also named gahnite, is a spinel-type oxide, with high chemical and thermal stability, high mechanical resistance, low surface acidity [1], and low sintering temperature [2]. It is suitable for a large range of applications, as optical coating or host matrix, ceramic materials for high temperatures, and catalyst support [3]. Lately, $ZnAl_2O_4$ spinel was largely used as catalyst in reactions like gaseous toluene degradation, vegetal oil transesterification, and isobutene combustion [4].

Zinc aluminate is also a semiconductor material suitable for photo electronic applications in ultraviolet, due to its wide band gap (3.8 eV) [5]. Recent investigations showed that this system could also be used as transparent and electroconductive material. The optical band gap of polycrystalline $ZnAl_2O_4$ indicates that the material is transparent for light with wavelength >320 nm. Thus, it can be used for photo electronic devices in UV [6]. Recently, $ZnO/ZnAl_2O_4$ nanocomposite was used for the photodegradation of methyl orange dye under artificial UV irradiation [7]. Foletto et al. [8] observed the satisfactory photocatalytic activity of $ZnAl_2O_4$ particles for the degradation of red Procion dye from aqueous solution.

Zinc aluminate is commonly prepared by high-temperature calcination of aluminum and zinc oxides mixtures. Lately, $ZnAl_2O_4$ was obtained by several methods: co-precipitation [6, 9], sol–gel method [10], hydrothermal [11], solvothermal [1], citrate precursor method [12], combustion method [2]. By thermal decomposition of metallic carboxylates, Ştefănescu et al. obtained spinel-

Published online: 15 March 2017

Materials Chemistry and Physics 186 (2017) 399–406

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

$ZnO-SiO_2$ based nanocomposites prepared by a modified sol-gel method

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HIGHLIGHTS

- By modified sol-gel method, ZnO/SiO_2 and Zn_2SiO_4/SiO_2 nanocomposites were obtained.
- ZnO dispersed in silica matrix results from zinc carboxylate thermal decomposition.
- Zinc carboxylate was synthesized in situ in hybrid silica gels via redox reaction.
- Evolution of ZnO in SiO_2 matrix depends on temperature and system composition.

ARTICLE INFO

Article history:
Received 29 June 2016
Received in revised form
10 October 2016
Accepted 3 November 2016
Available online 4 November 2016

Keywords:
Composite materials
Sol-gel
Heat treatment
X-ray powder diffraction
Transmission electron microscopy

ABSTRACT

This paper presents a study on nanocomposites formation in $ZnO-SiO_2$ systems with different $ZnO:SiO_2$ molar ratios (1:4, 1:1, and 4:1), prepared employing a sol-gel method modified by an original procedure. The evolution of $ZnO-SiO_2$ systems depending on the composition and temperature was studied by thermal analysis, Fourier transform infrared spectroscopy, X-ray diffractometry and transmission electron microscopy. Zn(II) carboxylate was synthesized in situ in hybrid silica gels by redox reaction between zinc nitrate and 1,3-propanediol. Its thermal decomposition at low temperatures led to ZnO dispersed in the pores of silica matrix. Only for the 4:1 system, at 400 and 600 °C, ZnO nanocrystallites (average size ~9 nm) embedded in the amorphous silica matrix were obtained, the other systems being amorphous. Whatever the mixture composition is, above 600 °C, ZnO reacts with SiO_2 to form zinc silicate. At 800 °C, for both 1:4 and 1:1 systems, poor crystallized β-Zn_2SiO_4 and α-Zn_2SiO_4 phases embedded in silica matrix were formed. Increasing the temperature, at 1000 °C, only for 1:1 system, β-Zn_2SiO_4 phase turned into single phase α-Zn_2SiO_4 (average crystallites size 28.3 nm). For 4:1 composition, at 800 and 1000 °C, systems consisting of ZnO and α-Zn_2SiO_4 nanocrystallites dispersed in silica were obtained.

1. Introduction

Oxide semiconductors have attracted considerable attention in scientific research and technological applications due to their use in optoelectronic devices and as sensors [1–3]. Zinc oxide (ZnO) is an n-II-IV type semiconductor material, with a wide band gap of 3.3 eV [4], high chemical and thermal stability, high exciton binding energy [5], and high electrical conductivity [6]. Zinc oxide and other similar materials have become promising candidates in recent years for various applications such as materials filter for emitting UV light, catalysts, varistors, gas sensing, solar cells [4,7], optoelectronic or magneto-electronic devices [8,9].

For ZnO synthesis several methods were used: solvothermal [10], hydrothermal [4], sol-gel [8,11–13], self-assembly method [1], ultrasonic spray [12], decomposition of carboxylate combinations [14]. In recent years, sol-gel method won increasingly more importance in materials science [15], due to the high purity,

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http://dx.doi.org/10.1016/j.matchemphys.2016.11.011
0254-0584/

Journal of chemical & engineering data

Article

pubs.acs.org/jced

Lanthanum Separation from Aqueous Solutions Using Magnesium Silicate Functionalized with Tetrabutylammonium Dihydrogen Phosphate

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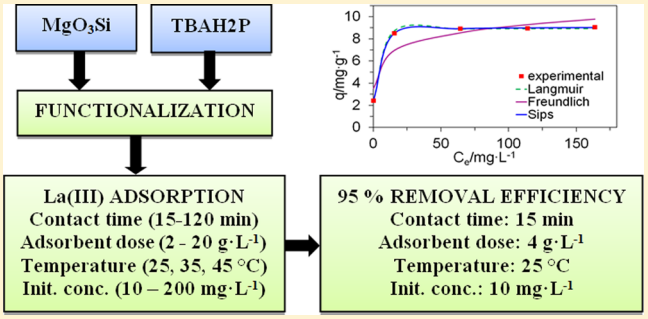
ABSTRACT: Magnesium silicate functionalized with tetrabutyl ammonium dihydrogen phosphate was developed as a new adsorbent for La(III) removal from aqueous solutions. The functionalized material was characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, and determination of the specific surface area (194 $m^2 \cdot g^{-1}$). The influence of several experimental parameters (amount of adsorbent, contact time, temperature,and initial concentration of lanthanum ions) on the adsorption process was examined. The optimum dose of adsorbent was established as 4 $g \cdot L^{-1}$. The optimum contact time of 15 min ensured a ~95% La(III) removal efficiency at 298.15 K. The pseudo-second-order kinetic model was the best fit of the experimental data. The positive value of activation energy (10.7 $kJ \cdot mol^{-1}$) suggested that the adsorption process was endothermic and the mechanism was chemisorption. Thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) showed that the adsorption process was endothermic and spontaneous. Nonlinear regression analysis of the equilibrium data showed that the experimental data were well described by the Sips model. The maximum adsorption capacity was 9.13 $mg \cdot g^{-1}$. The obtained results demonstrated that magnesium silicate functionalized with tetrabutyl ammonium dihydrogen phosphate is suitable for use as adsorbent for the removal of La(III) ions from aqueous solutions.



1. INTRODUCTION

Lanthanum belongs to a set of 17 chemical elements named rare earth elements (REE). This group contains the 15 lanthanides plus scandium and yttrium,[1] and is further divided into light rare earth elements (lanthanum, cerium, praseodymium, neodymium, promethium, and samarium) and heavy rare earth elements containing the rest of the lanthanides elements with yttrium.[2] These elements can be found in the Earth's crust in many deposits across 34 countries.[3] They can be naturally found mixed and scattered in minerals, which makes their separation from each other difficult because of the very similar physicochemical properties.[2] REEs are used in many industries due to their metallurgical, optical, and electronic properties, but also in agriculture, in very small amounts, or in fertilizers with phosphorus.[3] REEs have been used in China as fertilizers in low concentrations for a long period of time. This led to a bioaccumulation in the environment.[4]

Lanthanum represents about 30% of the total amount of REEs used. China is the largest consumer of lanthanum and lanthanides, using them in manufacturing of electronic products.

Lanthanum is used in petroleum refining and automobile catalytic converters. It is also added to glass and alloys to improve specific properties. Lanthanum is used in applications that require the production of colored light. In large amounts lanthanum is used in rechargeable nickel−metal-hydride batteries to store hydrogen.[5] In the pharmaceutical industry, lanthanum can be used as lanthanum carbonate for renal failure, reducing the phosphorus adsorption with 45%.[6,7] A group of Chinese researchers discovered that lanthanum is accumulated in cereals, vegetables, seafood, meat, and eggs up to 30 $\mu g \cdot kg^{-1}$.[8] It was also found in drinking water up to 10 $\mu g \cdot L^{-1}$.

Received: August 12, 2015
Accepted: December 7, 2015
Published: December 21, 2015

DOI: 10.1021/acs.jced.5b00687
J. Chem. Eng. Data 2016, 61, 535−542

Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20173

63 (2017) 124–134
February

Magnesium silicate doped with environmentally friendly extractants used for rare earth elements adsorption

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Received 15 May 2016; Accepted 13 August 2016

ABSTRACT

New adsorbent materials using different doping methods were obtained. Magnesium silicate was doped with environmentally friendly extractants like sodium β-glycerophosphate, tetraethylammonium bromide, and thiourea. The methods used were the dry method, the ultrasound unconventional method, and a new method, the pellicular vacuum solvent vaporization. The doped materials were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and determination of the specific surface area (BET). The usefulness of these materials and their performances were studied on the adsorption of rare earth elements Eu(III), Nd(III), and La(III). The best adsorption capacity of 16 mg/g was obtained for Eu(III) on magnesium silicate doped with thiourea. Nonlinear regression analysis of adsorption data was made employing Langmuir, Freundlich and Sips models.

Keywords: Rare earth elements; Magnesium silicate; Extractant; Adsorption; Adsorption isotherm

1. Introduction

Numerous studies highlight that rare earth elements (REEs) are being used in high technology applications [1]. This includes catalyst, glassmaking, lighting and metallurgy, battery alloys, ceramics, and permanent magnets [2]. REEs are found in earth's crust with many reserves in about 34 countries [1]. It is also known that REEs can be used as fertilizers in agriculture [3] and as reagents in magnetic resonance imaging (MRI), in the medical field [4].

REEs can be removed from wastewater through traditional methods such as precipitation with chemical reagents, ion exchange [1], liquid-liquid extraction [3], biosorption [5], and adsorption [6]. Some methods such as alkaline precipitation have disadvantages like low efficiency, high consumption of chemical reagents, and high costs. Adsorption is known as an advanced method for treatment of wastewater with REEs, featuring a number of advantages, namely: high efficiency, high adsorption capacity, the possibility of regeneration and use of adsorbents in multiple adsorption-desorption cycles, and selectivity for rare metals [6].

It is known that magnesium silicate possesses adsorption properties. Various studies revealed it in adsorption of dyes [7], phenols [8], and metals [9].

In order to improve the adsorption properties of inorganic supports, doping with various functional groups

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Conference paper

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Sorption properties of Amberlite XAD 7 functionalized with sodium β-glycerophosphate

DOI 10.1515/pac-2016-0806

Abstract: This paper presents the sorption properties of a new adsorbent material prepared by impregnating Amberlite XAD 7 polymer with sodium β-glycerophosphate. For impregnation, the pellicular vacuum solvent vaporization method was employed. The functionalization was evidenced by energy dispersive X-ray analysis. The usefulness of this material and its performances were studied for the adsorption of the rare earth element La(III) in batch experiments. The influence of various parameters affecting the adsorption of lanthanum like contact time, initial concentration, pH value, and temperature was studied. The kinetic of the adsorption process was best described by the pseudo-second-order model. Sips isotherm was found to be the best fit of the equilibrium data. The maximum adsorption capacity of the functionalized material was of 33.8 mg La(III)/g. The values of thermodynamic parameters (ΔG^o, ΔH^o, ΔS^o) showed that the adsorption process was endothermic and spontaneous. The results proved that Amberlite XAD 7 functionalized with sodium β-glycerophosphate is an efficient adsorbent for the removal of La(III) ions from aqueous solutions. Quantum chemistry was performed using Spartan software.

Keywords: Amberlite XAD 7; functionalization; lanthanum; POC-16; sodium β-glycerophosphate.

Introduction

Rare earth elements, including lanthanum, are found in the earth's crust and finding them where they can lead to an economic gain is a challenge. China is considered the country with the largest amount of exploited lanthanum (95 %) [1].

Lanthanum can deliver long-term toxic effects on humans due to accumulation, causing cancer by inhalation. Lanthanum can also be gradually accumulated in soil and groundwater presenting negative effects on humans and animals.

Due to the presence of lanthanum in household equipment such as color TV sets, fluorescent lamps, energy saving lamps and bottles, in industries such as manufacturing of optical glass, catalysts, polish glass, but also in the pharmaceutical industry in form of lanthanum carbonate, lanthanum has to be removed or recovered through different methods [2, 3].

Due to the increased demand of lanthanum separation, several physical-chemical methods such as extraction, ion exchange, co-precipitation and adsorption were developed [4–6]. One of the most convenient

Article note: A collection of invited papers based on presentations at the 16th International Conference on Polymers and Organic Chemistry (POC-16), Hersonissos (near Heraklion), Crete, Greece, 13–16 June 2016.

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