Arsenic Removal Through Adsorption on Cobalt Nanoferrite

CORNELIU M. DAVIDESCU[1], RALUCA DUMITRU [1]*, ADINA NEGREA[1], LAVINIA LUPA[1], MIHAELA CIOPEC[1], PETRU NEGREA[1]
[1]University Politehnica Timisoara, Faculty for Industrial Chemistry and Environmental Engineering, 6 Vasile Parvan Blvd., 300223, Timisoara, Romania

This paper presents the studies regarding the synthesis, characterization and application of cobalt ferrite nanoparticles. For the synthesis of cobalt ferrite was used the thermal decomposition of $[Fe_2Co(C_2O_4)_4(OH_2)_6]$ *precursor at 500°C, an efficient route of various ferrites synthesis. The obtained cobalt ferrite was investigated by FTIR spectroscopy, X-ray diffraction, SEM coupled with EDX, investigations which showed that the obtained particles are homogeneous as shape and size. Due to the obtained nanoparticles and due to the affinity of arsenic toward iron, the obtained cobalt ferrite was applied with success as adsorbent in the removal process of arsenic from aqueous solutions. The studied material developed a maximum adsorption capacity (according to Langmuir isotherm) of 250 μg of As(V)/g of cobalt ferrite, obtaining a residual concentration of As(V) under the maximum admitted value by the World Health Organization (10μg/L).*

Keywords: cobalt nanoferrite, X-ray diffraction, adsorption, arsenic removal, Langmuir isotherm

The possibility of preparing ferrites in the form of nanoparticles has started a new and exciting research field, with revolutionary applications [1-5]. In addition, ferrites can be used as magnetic carriers to realize magnetic separation in waste water treatment for their ferromagnetic or supermagnetic properties [6-10]. The magnetic separation represents an efficient and economic method for separating magnetic particles from suspensions. Due to this important advantage in a lot of researches these ferrites were used as reusable adsorbents for the removal of various pollutants from waste waters [11-22]. In this way a few methods were developed for the spinel ferrites obtaining such as: sol-gel [23, 24], coprecipitation [25, 26], solvothermal [27], combustion [28], hydrothermal [29], etc. In the last years the thermal decomposition of solid heteropolynuclear coordination compounds, as precursors, have been widely used for synthesis of nanoferrites. It represents a versatile and predictable unconventional method, due to the possibility of controlling the quality (composition and microstructure) of the end products featuring, by selecting suitable ligands [30-32].

In the present paper we focused on the synthesis and characterization of the cobalt nanoferrite, because a few work on this compound have been reported in the literature because the experimental work which is very limited [33-37]. From this reason in this paper for the synthesis of $CoFe_2O_4$ was used the thermal decomposition of cobalt-ferrioxalate precursor. It represents an efficient route of various ferrites synthesis.

In order to determine the adsorption properties of the obtained cobalt ferrite this was used as adsorbent material in the removal process of arsenate from aqueous solutions. We took into account this pollutant because it is well known that the arsenic-contaminated drinking water is a major environmental problem, because of its toxic effects on human health and environment [38-42]. It is aspected to obtain a higher efficiency in the removal process due to the high affinity of arsenic to iron ions [43-46].

Experimental part

As starting materials, $Fe(NO_3)_3 \cdot 9H_2O$ (Merck), $Co(NO_3)_2 \cdot 6H_2O$ (Merck), 1,2-ethanediol (ethyleneglycol EG, Merck) and, 2M nitric acid (Merck) solution were employed.

An aqueous solution containing ethanediol, iron nitrate, cobalt nitrate and nitric acid (2M) in a molar ratio $x : 2 : 1 : y$ where $x \geq 3$ and $y \geq 2$ is heated in a water bath. The reaction is completed when no more gas evolving is observed. The obtained solid reaction product, purified by refluxing with an adequate acetone-water mixture, is filtered, washed with acetone and maintained in air until constant mass. The reaction yield is nearly quantitative (>90%). The coordination compound $[Fe_2Co(C_2O_4)_4(OH_2)_6]$ precursor is synthesized using 2M nitric acid solution. The oxide $CoFe_2O_4$ is obtained after heating treatment of the precursor at 500°C for one hour, with a heating rate of 5°C/min.

The FTIR spectrum (KBr pellets) of the ferrite was recorded on a Vertex 70 BRUKER-FTIR spectrophotometer in the range 400–4000 cm^{-1}. The oxide was characterized by X-Ray diffraction (XRD) analysis. The powder X-Ray diffraction pattern of the obtained oxide was recorded at room temperature with a XRD using a Rigaku Ultima IV diffractometer, using Cu K_α radiation (λ = 1.5418A°). SEM image was recorded using a Quanta FEG 250 microscope, equipped with an EDAX ZAF quantifier.

For the adsorption experiments a well quantity of cobalt ferrite (0.05 g) was used for the treatment of 25 mL of As(V) solutions containing various concentrations (50, 100, 300, 500 and 700 μg/L). The samples were shacked for 2 h using a Julabo SW 23 shacker. Atfer the time elapsed the samples were magnetically separated and in the resulted solutions was determined the residual concentration of As(V) through atomic absorption spectrometry using a Varian SpectrAA 110 atomic absorption spectrometer with a Varian VGA 77 hydride generation system. The adsorption performance of the studied material was expressed as arsenic metal uptake (μg/g) eq.1. [1-5]:

---

* *email: raluca.voda@upt.ro; ralucadumitru2002@yahoo.com*
Tel.: (+40) 0740785104

$$q_e = \frac{(C_0 - C_e)\cdot V}{m} \qquad (1)$$

where: C_0 and C_e are the concentrations of arsenate (mg/L) in the solution, initially (t=0) and at equilibrium, respectively, V is the volume of the solution and m is the mass of adsorbent.

In all the adsorption experiments the used solid – liquid ratio was 0.1 g of adsorbent in 25 mL of arsenic containing aqueous solutions, and the *p*H of the solutions was kept around 9. The stock solution of arsenic was prepared by diluting an appropriate amount of H_3AsO_4 in 0.5 M HNO_3 solution (Merck Standard Solutions). Other solutions of As(V) ions were prepared from the stock solution by appropriate dilution. All other chemicals used for experiments were of analytical reagent grade, and were used without further purification. Distilled water was used in all experiments.

The equilibrium studies were conducted in order to determine the maximum adsorption capacities of the studied material in the removal process of As(V) from aqueous solutions as a function of its surface properties. In order to determine the relationship between the amount of As(V) ions adsorbed by the cobalt ferrite and the maximum adsorption capacity of the studied material the experimental data were fitted with the well known Freundlich and Langmuir isotherms [38-46].

The linear form of the Freundlich isotherm equation can be written as:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (2)$$

where q_e is the quantity of As(V) adsorbed per gram of adsorbent and C_e is the equilibrium concentration of the adsorbate after adsorption (μg/L). K_F and 1/n are characteristic constants which can be associated with the relative adsorption capacity of the adsorbent material (μg/g), respective with the intensity of adsorption.

The linear form of the Langmuir isotherm is expressed as the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \qquad (3)$$

where: q_m is the maximum adsorption capacity (μg/g) and K_L is the Langmuir constant associated with the affinity between the adsorbent and adsorbate (L/μg). The other terms have the same meaning as described above.

Results and discussions

Mixed oxide obtaining and characterization

The obtaining of the coordination compound, as precursor, is based on the redox reaction between 1,2-ethanediol and nitrate ion [32]:

$$12C_2H_4(OH)_2 + 6([Fe(OH_2)_6]^{3+} + 3NO_3^-) + 3([Co(OH_2)_6]^{2+} +$$
$$+ 2NO_3^-) + 8(H^+ + NO_3^-) \xrightarrow{\Delta t^\circ}$$
$$3Fe_2Co(C_2O_4)_4\cdot 6H_2O_{(s)} + 32NO_{(g)} + 76H_2O_{(g)}$$
$$(NO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow NO_{2(g)})$$

The cobalt ferrite was obtained after the calcination of the coordination compound at 500°C. The ferrite were identified by IR (fig. 1) and XRD (fig. 2).

The FTIR (absorption bands at 584 cm^{-1} and 400 cm^{-1}) [47] and XRD (diffraction lines in accordance with JCPDS 22-1086, fig. 1) of the oxide obtained at 500° C indentify only the presence of cubic cobalt ferrite of $CoFe_2O_4$. These results are superior that the ones obtained through the thermolysis of a physical mixture $CoC_2O_4\cdot 2H_2O$-$2FeC_2O_4\cdot 2H_2O$, where after a similar heating treatment only a mixture simple oxides such as Co_3O_4 and α-Fe_2O_3 was obtained [48].

In figure 2 is presented the XRD pattern of the product obtained after an independent calcination in the furnace at 500°C in static air atmosphere. The XRD pattern shows the presence of the characteristic peaks of pure cobalt ferrite was identified in using JCPDS 22-1086 (8.392A°). The average crystallites size was evaluated using Scherrer's formula [49]: $d_{XRD} = [0.91\lambda/(\beta\cos\theta)] \times 57.32$, where d_{XRD} is the crystallite size, λ the wave length (Cu K_α), β the corrected half-width obtained using α quartz as reference and the Waren formula and θ is the diffraction angle of the most intense diffraction peak.

The mean crystallite size evaluated using Scherrer's formula is 20 nm and the lattice parameter from XRD analysis is 8.3855A°.

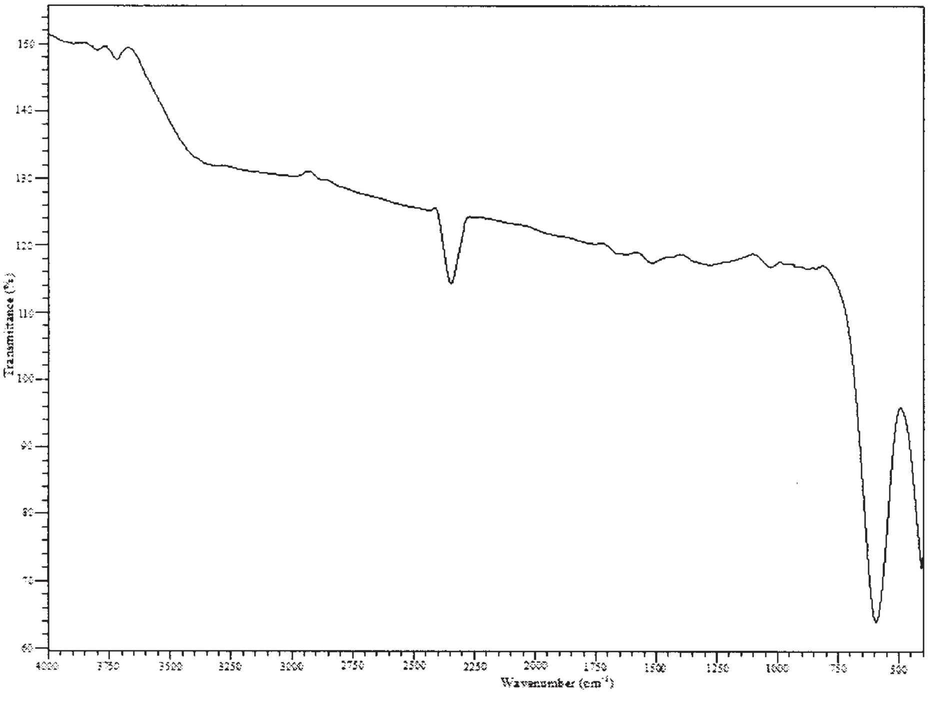

Fig. 1. FTIR spectrum of $CoFe_2O_4$ ferrite obtained after the calcination at 500p C for 1h of the coordination compound

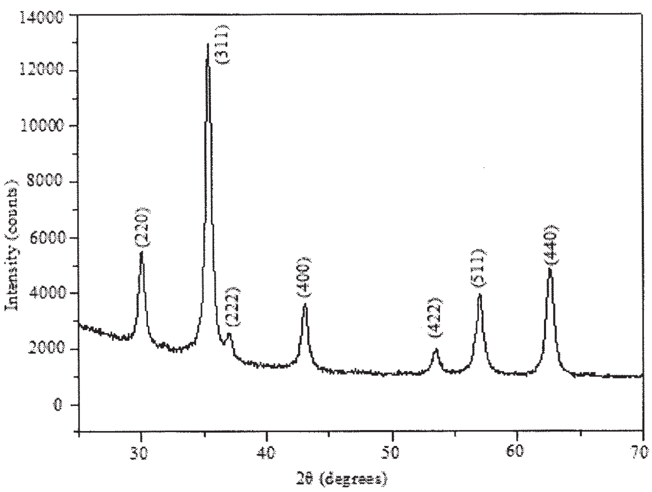

Fig. 2. The XRD of $CoFe_2O_4$ derived from $[Fe_2Co(C_2O_4)_4\,(OH_2)_6]$ compound obtained by an independent pyrolysis at 500°C

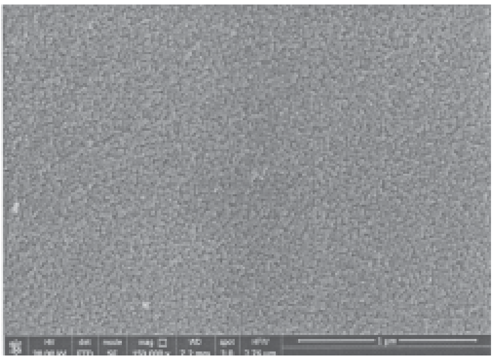

Fig. 3. SEM image of $CoFe_2O_4$ powder prepared from $Fe_2Co(C_2O_4)_4(OH_2)_6$ compound thermally treated at 500°C

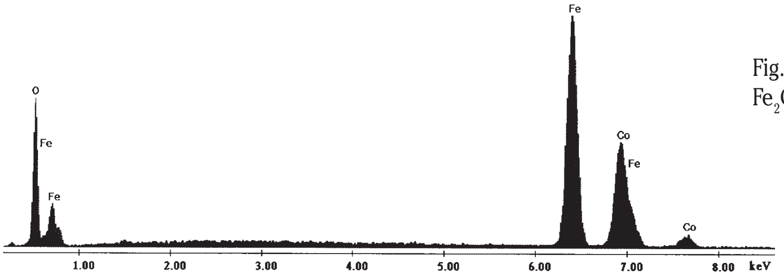

Fig. 4. EDX spectrum of $CoFe_2O_4$ powder prepared from $Fe_2Co(C_2O_4)_4(OH_2)_6$ compound thermally treated at 500°C

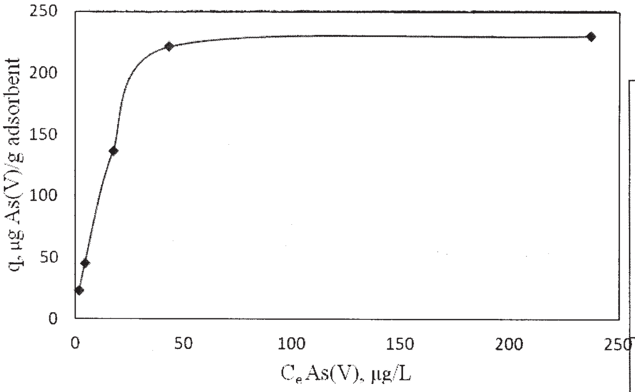

Fig. 5. As(V) adsorption isotherm onto the cobalt ferrite

Table 1
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERMS FOR As(V) ADSORPTION ONTO THE COBALT FERRITE

$q_{m,\,exp}$ (μg/g)	Adsorption isotherm Freundlich			Adsorption isotherm Langmuir		
	K_F (μg/g)	1/n	R^2	K_L (L/μg)	$q_{m,\,calc}$ (μg/g)	R^2
230	22.2	0.5051	0.8626	0.0654	250	0.9963

The SEM image (fig. 3) at high magnification (x150 000) shows for the cobalt ferrite obtained at 500°C is compased of very small particles, almost homogeneous as shape and size.

The size of the nanoparticles evaluated from SEM image was found to be in the range of 20-50nm, which is in good agreement with the particle size calculated using XRD data.

The EDX spectrum of $CoFe_2O_4$ is presented in figure 4. Qualitative and quantitative EDX analyzes showed a high purity and corresponding stoichiometry of the cobalt ferrite analyzed.

Adsorption experiments

The adsorption isotherm of As(V) removal by the studied material is presented in figure 5. It can be observed that the initial removal of As(V) is fast and at higher equilibrium concentration the adsorption capacity achieve a constant value.

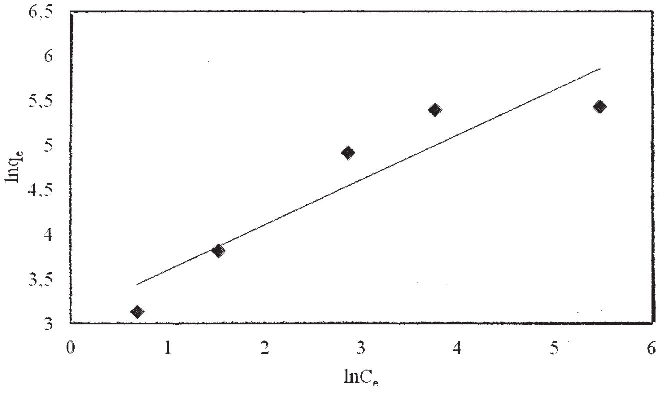

Fig. 6. Freundlich isotherm of As(V) adsorption onto the cobalt ferrite

The linear plot for the Freundlich isotherm was obtained through the graphical representation of $\ln q_e$ function of $\ln C_e$ (fig. 6). From the plot and intercept values were calculated 1/n and KF parameters. The values of q_m and K_L were determined from the graphical representation of C_e/q_e versus C_e (fig. 7).

The isotherms parameters, as well as the correlation coefficients (R^2) for As(V) adsorption onto the cobalt ferrite are presented in table 1.

The Freundlich isotherm presents a lower regression coefficient suggesting a restriction in its use. The constants K_F can be defined as an adsorption coefficient which

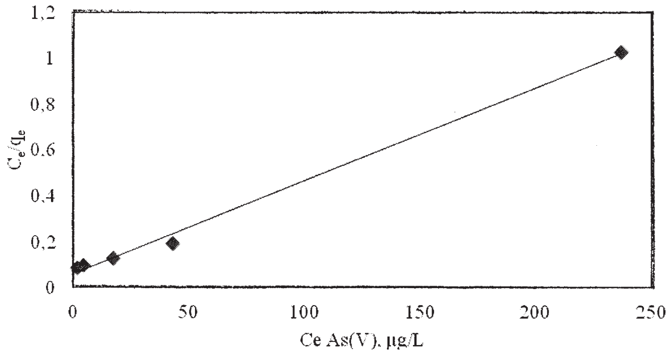

Fig. 7. Langmuir isotherm of As(V) adsorption onto the cobalt ferrite

represent the quantity of As(V) ions adsorbed for an unitary equilibrium concentration. The slope 1/n is a measure of the adsorption intensity. Because the value of 1/n is lower than 1 this shows that the As(V) adsorption onto cobalt ferrite is favorable (table 1). The Langmuir model effectively describes the adsorption of As(V) onto the cobalt ferrite on the entire concentration range studied. Moreover the maximum adsorption capacity obtained from the Langmuir isotherm is closed with those experimental determined.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, R_L expressed as in the following equation:

$$R_L = \frac{1}{1+K_L C_0} \qquad (4)$$

where K_L is the Langmuir constant and C_0 is the initial concentration of As(V) ions. The value of separation parameter R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$). The R_L was found to be between 0 and 1 for the entire concentration range, which indicates the favourable adsorption of As(V) onto the studied material.

The experimental data confirm the fact that the obtained cobalt ferrite can be successfully used in the removal process of As(V) from aqueous solutions, the maximum adsorption capacity being of 250 244 µg/g.

Conclusions

Cobalt nanoferrite with spinel structure was obtained after the calcination of cobalt ferrioxalate coordination compound at 500°C. The ferrite was identified by IR and XRD. The average particle size of oxide was in the range of 20-50 nm, as revealed by XRD and SEM techniques.

The cobalt ferrite obtained shows a good adsorptive properties based on particles size. The obtained ferrite was investigated for As(V) adsorption from aqueous solutions containing arsenic concentration from 50 to 700 mg/L. The adsorption behaviours were thoroughly studied by Langmuir and Freundlich isotherms. The studied material can be effectively used in the removal process of As(V) from aqueous solutions containing trace concentration of arsenic (the most often found concentrations in the real underground waters) and obtaining a residual concentration under the maximum admitted value by the World Health Organization.

Aknowledgments: This work was partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectoral Operational Programme Human Resources Development 2007-2013.”

References

1. SUGIMOTO M., J. Am. Ceram. Soc., **82**, 1999, p. 269.
2. BUENO A.R., GREGORI M.L., NÓBREGA M.C., J. Magn. Magn. Mater., **320**, 2008, p. 864.
3. ARIAS J.L., RUI M.A., GALLARDO V., J. Controlled Release, **125**, 2008, p. 50.
4. MORAIS P.C., J. Alloy. Compd., **483**, 2009, p. 544.
5. YAN A.G., QIU G.Z., LIU X.H., SHI R.R., ZHANG H.N., YI R., LI Y.B., GAO G.H., Chem. J. Chinese Universities, **29(1),** 2008, p. 23.
6. LÜ S., CHEN X., YE Y., YIN S.H., CHENG J.P., XIA M.S., J. Hazard Mater., **171**, 2009, p. 634.
7. ZHAO X.L., SHI Y.L., CAI Y.Q., MOU S.F., Environ. Sci. Technol., **42,** 2008, p. 1201.
8. REN Y.M., WEI X.Z., ZHANG M.L., J. Hazard Mater., **158(1)**, 2008, p. 14.
9. LIU X.Q., GUAN Y.P., MA Z.Y., LIU H.G., Langmuir, **20(23)**, 2004, p. 10278.
10. YUAN J., LÜ Y.K., LI Y., LI J.P., Chem. Res. Chinese Universities, **26(2)**, 2010, p. 278.
11. ZHANG S.X., NIU H.Y., CAI Y.Q., SHI Y.L., Chem. Eng. J., **158(3)**, 2010, p. 599.
12. PARSONS J.G., LOPEZ M.L., PERALTA-VIDEA J.R., GARDEA-TORRESDEY J.L., Microchem. J., **91,** 2009, p. 100.
13. HU J., LO I.M.C., CHEN G., Sep. Purif. Technol., **56**, 2007, p. 249.
14. GAO Z., CUI F.M., ZENG S.Z., GUO L.M., SHI J.L., Microporous and Mesoporous Mater., **132(1/2)**, 2010, p. 188.
15. VÎRLAN C., CIOCÂRLAN R.G., ROMAN T., GHERCA D., CORNEI N., PUI A., Acta Chemica Iasi, **21**, 2013, p. 19.
16. WANG L., LI J., WANG Y., ZHAO L., JIANG Q., Chem. Eng. J., **181-182**, 2012, p. 72.
17. HOU X.-yu, FENG J., LIU X.-han, ZHANG M.-lin, Chem. Res. Chinese Universities, **27(4)**, 2011, p. 543.
18. MAYO J.T., YAVUZ C., YEAN S., CONG L., SHIPLEY H., YU W., FALKNER J., KAN A., TOMSON M., COLVIN V.L., Sci. Technol. Adv. Mater., **8**, 2007, p. 71.
19. LIU Q., WANG L., XIAO A., GAO J., DING W., YU H., HUO J., ERICSON M., J. Hazard. Mater., **181**, 2010, p. 586.
20. ZHOU L., GAO C., XU W., ACS Appl. Mater. Interface, **2**, 2010, p. 1483.
21. ZARGAR B., PARHAM H., HATAMIE A., Chemosphere, **76**, 2009, p. 554.
22. ZHANG S.X., NIU H.Y., CAI Y.Q., ZHAO X., SHI Y.L., Chem. Eng. J., **158**, 2010, p. 599.
23. GATELYTË A., JASAITIS D., BEGANSKIENË A., KAREIVA A., Mater. Sci., **17(3)** 2011, p. 302.
24. YIN Y., WANG X., Adv. Mater. Res, **79-82**, 2009, p. 305.
25. YASENEVA P., BOWKER M., HUTCHINGS G., Phys. Chem. Chem. Phys., **13(41)**, 2011, p. 18609.
26. MAAZ K., KARIM S., MUMTAZ A., HASANAIN S.K., LIU J., DUAN J.L., J. Magn. Magn. Mater., **321(12)**, 2009, p. 1838.
27. MOHAPATRA S., ROUT S.R., PANDA A.B., Colloids Surf A. Physicochem. Eng. Aspects, **384**, 2011, p. 453.
28. RANDHAWA B.S., GUPTA M., DOSANJH H.S., KUMAR N., Ceram. Int., **37(7)**, 2011, p. 2207.
29. AHNIYAZ A., FUJIWARA T., SONG S.W., YOSHIMURA M., Solid State Ionics, **151(1-4)**, 2002, p. 419.
30. PAULUS M., Preparation methods of ferrites, Eds. P. Hagenmüller, Academic Press, 1972, p. 487.
31. L. PATRON, I. MÎNDRU, G. MARINESCU, in: SCHWARZ J.A., CONTESCU C.I., PUTYERA K., Magnetic Nanomaterials: Nonconventional Synthesis and Chemical Design, Dekker

Encyclopedia of Nanoscience and Nanotechnology, Dekker, New York, 2004, p. 1683.
32. DUMITRU R., PAPA F., BALINT I., CULITA D., MUNTEANU C., STANICA N., IANCULESCU A., DIAMANDESCU L., CARP O., Appl. Catal. A: General, **467**, 2013, p. 178.
33. FERREIA T.A.S., WAERENBORGH J.C., MENDONCA M.H.R.M., NUNES M.R., COSTA F.M., Solid State Sci., **5**, 2003, p. 383.
34. KAWANO S., ACHIWA N., YAMAMOTO N., HIGASHI S., Mat. Res. Bull., **11**, 1976, p. 911.
35. MURRAY P.J., LINNETT J.W., J. Phys. Chem. Solids, **37**, 1976, p. 1041.
36. SMITH P.A., SPENCER C.D., STILLWELL R.P., J. Phys. Chem. Solids, **39**, 1978, p. 107.
37. TAKAHASHI M., FINE M.E., J. Appl. Phys., **43**, 1972, p. 4205.
38. KUNDU S., GUPTA A.K., Sep. Purif. Technol., **51**, 2006, p. 165.
39. BORAH D., SATOKAWA S., KATO S., KOJIMA T., J. Colloid Interface Sci., **319**, 2008, p. 53.
40. BORAH D., SATOKAWA S., KATO S., KOJIMA T., J. Hazard. Mater., **162**, 2009, p. 1269.
41. NEGREA A., LUPA L., CIOPEC M., LAZAU R., MUNTEAN C., NEGREA P., Adsorpt. Sci. Technol., **28**, 2010, p. 467.
42. **NEGREA A.**, MUNTEAN C., BOTNARESCU I., CIOPEC M., MOTOC M., Rev. Chim. (Bucharest), **64**, no. 4, 2013, p. 397.
43. NEGREA A., LUPA L., LAZAU R., CIOPEC M., POP O., MOTOC M., Rev. Chim. (Bucharest), **64**, no. 5, 2013, p. 487.
44. GUPTA K., GHOSH U.C., J. Hazard. Mater., **161**, 2009, p. 884.
45. PARTEY F., NORMAN D., NDUR S., NARTEY R., J. Colloid Interface Sci., **321**, 2008, p. 493.
46. BILICI BASKAN M., PALA A., J. Hazard. Mater., **166**, 2009, p. 796.
47. GILLOT B., JEMMALI F., ROUSSET A., J. Solid State Chem., **50**, 1983, p. 138.
48. GABAL M.A., EL-BELLIHI A. A., ATA-ALLAH S. S., Mater. Chem Phys., **81**, 2003, p. 84.
49. SURYANARAYANA C., NORTON M.G., X-Ray Diffraction A Practical Approach, Plenum Press, New York, 2008, p. 207

Manuscript received: 30.09.2014