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CONFERENCE**

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Jovica Sokolović

Milan Trumić

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SYNTHESIS AND CHARACTERIZATION OF COBALT FERRITE/EXPANDED VERMICULITE AS A SORBENT OF NICKEL IONS

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ABSTRACT – The minerals with unique properties such as mica minerals have promising approach in environmental and industrial sphere. In this study, cobalt ferrite/expanded vermiculite (CoFe₂O₄/EV) composite was prepared by in-situ method. Both composite and base materials are characterized by FTIR, XRD and SEM techniques, while the CEC and point of zero charge (pH_{pzc}) was also determined. The adsorption properties of CoFe₂O₄/EV and EV have been investigated in a batch system, for the Ni (II) sorption from water. Adsorption experimental results were fitted by kinetic and adsorption models, and resulted in ionic exchange mechanism with maximum adsorption capacity of 23.2 mg g⁻¹ (298 K).

Keywords: Mica Composite, Nickel Sorption, Solvothermal Deposition, Cation Exchange.

INTRODUCTION

Mineral resources already abundant in nature, such as micas possess quite interesting properties. Vermiculite, together with smectites is expandable mica mineral, intensive heating of vermiculite particles from ambient conditions up to 300 °C is method generally used for producing expanded vermiculite (EV) [1]. This, commercial readily-available material is already used as heat insulator, radiation shield [1, 2] as germination medium [3] as a matrix for phase change materials [4, 5]. Also, this material may be used as heavy metal sorbent [6, 7].

Sorption is one of the most promising methods that can be used in wastewater management. This process is simple, inexpensive and widely applicable. However, sorbent preparation and sorption management are more challenging task, since it is recommended to lead the water purification on optimal conditions with paying attention on techno economical parameters.

Sorption properties of EV towards cation species come from its moderate cation exchange capacity (CEC) from 25 to 250 cmol_{eq}/kg [8]. To utilize this material as a sorbent it is needed to improve its mechanical properties for EV is soft and brittle (longitudinal and transverse failure stress less than 30 MPa [9]).

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Such mechanical and sorption improvements could be provided decorating the surface of EV 2:1 sheets with harder minerals which would also provide its surface as a support for sorption such is cobalt ferrite.

In this study, deposition of cobalt ferrite on EV surface was done by solvothermal co-precipitation reaction. Thus, prepared composite was characterized in the manner of its sorption and physicochemical properties (pH_{PZC} , CEC, FTIR and XRD). Scanning Electron Microscopy is used to provide micro photographs of the obtained composites.

EXPERIMENTAL

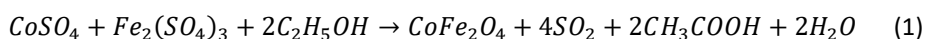
Preparing this composite is done as further described: In first step 5.0000 g of EV is measured, in order to depose 0.5000 g of cobalt ferrite on the surface of EV as it was planned. So, stoichiometric amount of cobalt sulfate heptahydrate and iron (III) sulfate monohydrate plus 10 % excess of each compound are measured. These two salts were dissolved in 5000 μ l ethanol - water mixture (volume ratio 3:1, respectively). Solution of these two salts is inserted in glass tube together with EV particles and this system is left for 1 hour on simultaneous sonicating and vacuuming with jet vacuum pump for 1 hour. After that, this system is left for 8 hours to cool down and stabilize. Stabilized sample was shut into autoclave and treated by following regime:

1 hour of preheating from ambient temperature to 180 °C

12 hours was held at 180 °C

And for 12 hours sample was cooling from 180 °C to ambient temperature

Reaction that takes place in autoclave reactor have further form (1):



Lastly sample is rinsed with ethanol and DW, after the rinsing sample is dried on atmosphere pressure on 50 °C for 4 hours. Dried sample is stored in plastic container covered with plastic caps.

Characterization of both EV and its modification included: cation exchange capacity (CEC) [10], point of zero charge (pH_{PZC}) [11], Scanning Electron Microscopy (SEM) (MIRA3 TESCAN), specific surface area (SSA) by Brunauer–Emmett–Teller (BET) technique, XRD analysis and Fourier Transform Infra-Red spectroscopy (FTIR).

Adsorption experiments were performed according to Taguchi method [12] in order to minimize the number of experiments.

RESULTS AND DISCUSSION

Summary of the CEC, pH_{PZC} and SSA results obtained from BET isotherm are given in Table 1. Values of CEC of $CoFe_2O_4$ modification and native EV sample is comparable, however $CoFe_2O_4$ /EV has a little higher CEC. This is due to contribution of Co^{2+} ions which sustained in interlayer due to low yield of $CoFe_2O_4$ particles.

Table 1 CEC, pH_{PZC} and SSA of EV and EV based adsorbents

	CEC*/cmol _c kg ⁻¹	pH _{PZC}	SSA/ m ² g
EV	40.9	6.42	3.28
CoFe ₂ O ₄ /EV	42.7	6.30	8.47

*CEC values were determined measuring ion-exchange equilibrium concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺ and Fe³⁺ ions for both samples, however Co²⁺ contribution to CEC is measured only for CoFe₂O₄/EV sample

Such low yield may be explained with low temperature applied in autoclave reactor (only 180 °C). However, presence of these particles increased SSA more than double. CoFe₂O₄ nanoparticles can be observed on the SEM images. On the Figure 1 are shown appropriate SEM images of start material (EV) and its modification with cobalt ferrite.

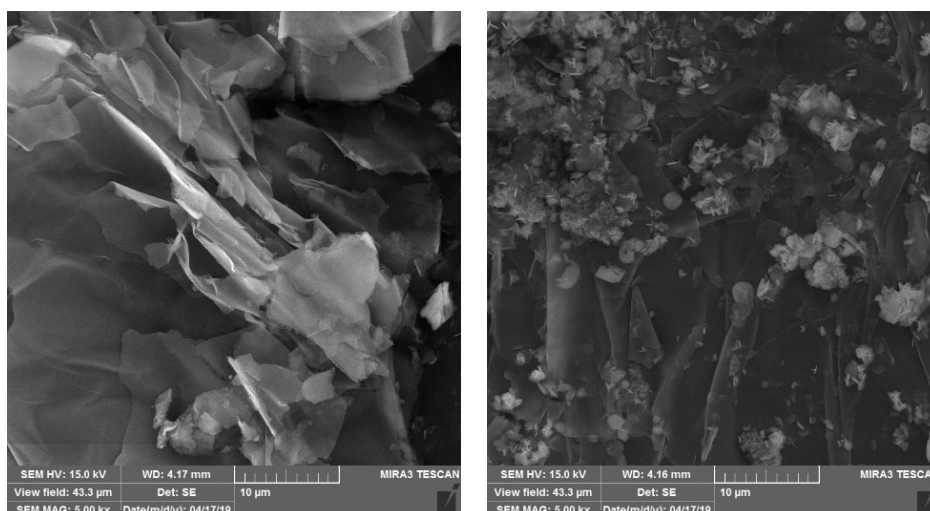


Figure 1 SEM images of EV (a) and CoFe₂O₄/EV (b)

At the Figure 1a can be seen sheet structure of vermiculite, at the Figure 1b can be seen CoFe₂O₄ nanoparticles on these sheets, dimensions of CoFe₂O₄ agglomerates are less than 3 μm while single particle is less than 0.3 μm.

Diffraction pattern of CoFe₂O₄/EV didn't have peaks corresponding to CoFe₂O₄ due to low content of these particles with regard to mass of EV carrier. However, modified mica composite (CoFe₂O₄/EV) possess peaks of both biotite vermiculite and vermiculite due to solvothermal action. At Figure 2 are shown diffraction patterns of both EV and its modification. Intensity of diffracted rays are arbitrary, for that reason, are not shown on y-axis label.

FTIR spectra of EV and CoFe₂O₄/EV are given at Figure 3, while the interpretations of the spectra are given within Figure itself.

Adsorption experiments results provided enough data to determine various parameters correlated to adsorption phenomena. Results of equilibrium adsorption were fitted by adsorption isotherms (Langmuir and Freundlich) and corresponding isotherm parameters were obtained (Table 2).

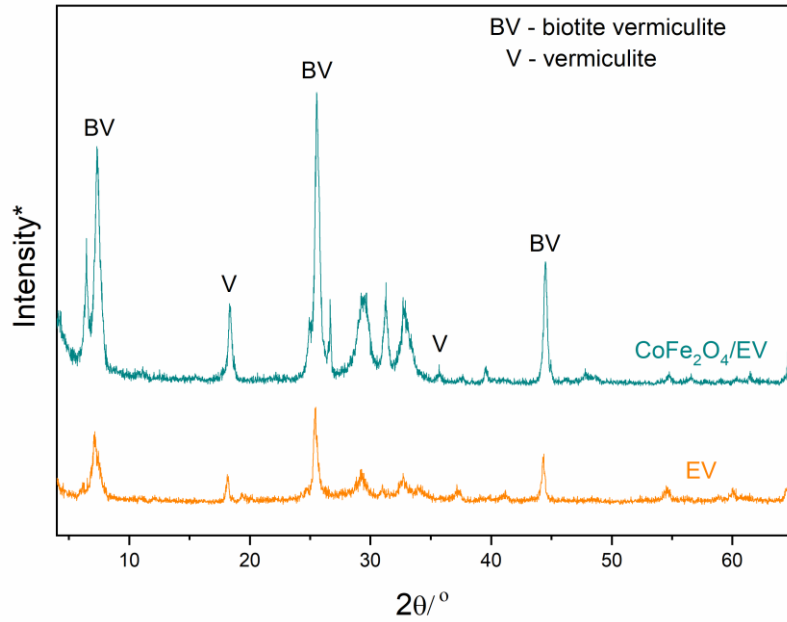


Figure 2 XRD of EV and its modification with CoFe_2O_4

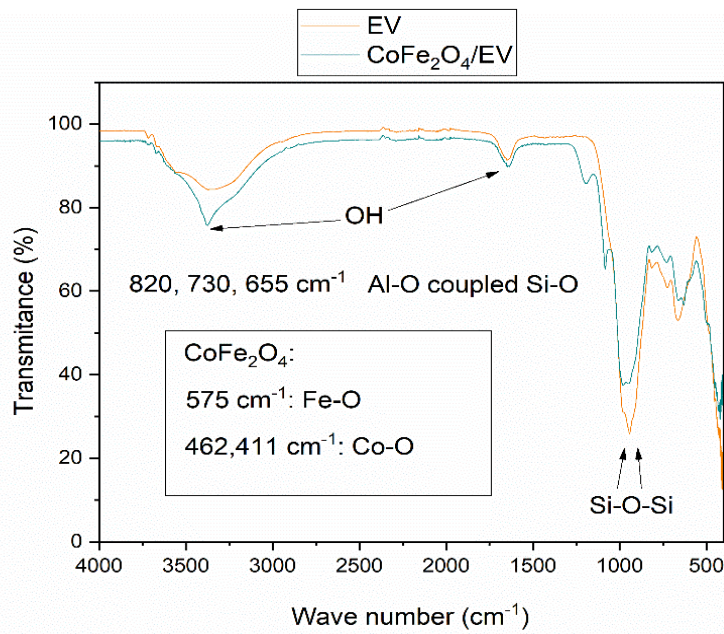


Figure 3 FTIR spectra of EV and $\text{CoFe}_2\text{O}_4/\text{EV}$ with most important peaks position

Table 2 Results of nickel adsorption on EV and its modification with CoFe₂O₄ fitted with Langmuir and Freundlich isotherm models

			Temperature/ K		
			298	308	318
EV	Langmuir	$q_m/ \text{mg g}^{-1}$	18.89	21.95	24.82
		$K_L/ \text{L mg}^{-1}$	0.734	0.738	0.762
	Freundlich	$K_F/ \text{mg g}^{-1} (\text{Lmg}^{-1})^{1/n}$	8.372	9.397	10.547
		$1/n$	0.358	0.375	0.385
CoFe ₂ O ₄ /EV	Langmuir	$q_m/ \text{mg g}^{-1}$	23.20	27.08	29.53
		$K_L/ \text{L mg}^{-1}$	0.434	0.547	0.741
	Freundlich	$K_F/ \text{mg g}^{-1} (\text{Lmg}^{-1})^{1/n}$	7.097	9.243	11.804
		$1/n$	0.467	0.442	0.408

From the Table 2 it can be observed that the samples modified with CoFe₂O₄ possess higher maximum adsorption capacity as well as 1/n values, which means that presence of ferrite particles improves overall adsorption properties of EV surface.

Function between contact time and adsorption capacity towards nickel ions of the EV samples and CoFe₂O₄/EV samples were fitted by both kinetic and diffusion models. The best fitting goodness were obtained for pseudo second order (PSO) kinetic model and for Webber – Morris diffusion model. Determined parameters are presented in Table 3.

Table 3 Kinetic parameters for adsorption of Ni ions on EV and CoFe₂O₄/EV

Sample	Webber-Morris diffusion model			PSO	
	$k_{id1}/ \text{mg g}^{-1} \text{min}^{-0.5}$	$C/ \text{mg g}^{-1}$	$k_{id2}/ \text{mg g}^{-1} \text{min}^{-0.5}$	$q_{max}/ \text{mg g}^{-1}$	$k_2/ \text{g} (\text{min mg})^{-1}$
EV	1.70	5.98	0.18	19.280	0.008162
CoFe ₂ O ₄ /EV	2.21	2.68	0.26	20.588	0.008324

From the results given in Table 3 can be concluded that both diffusion rates are increased (see k_{id1} and k_{id2} values) for modified mica sample. Although, intercept capacity is lowered, overall positive effect of CoFe₂O₄ nanoparticle presence can be noticed from both PSO parameters. These particles give extra surface for Ni ions adsorption, as well as solvothermal action offered an increase in CEC value of mica composite (Table 1).

CONCLUSION

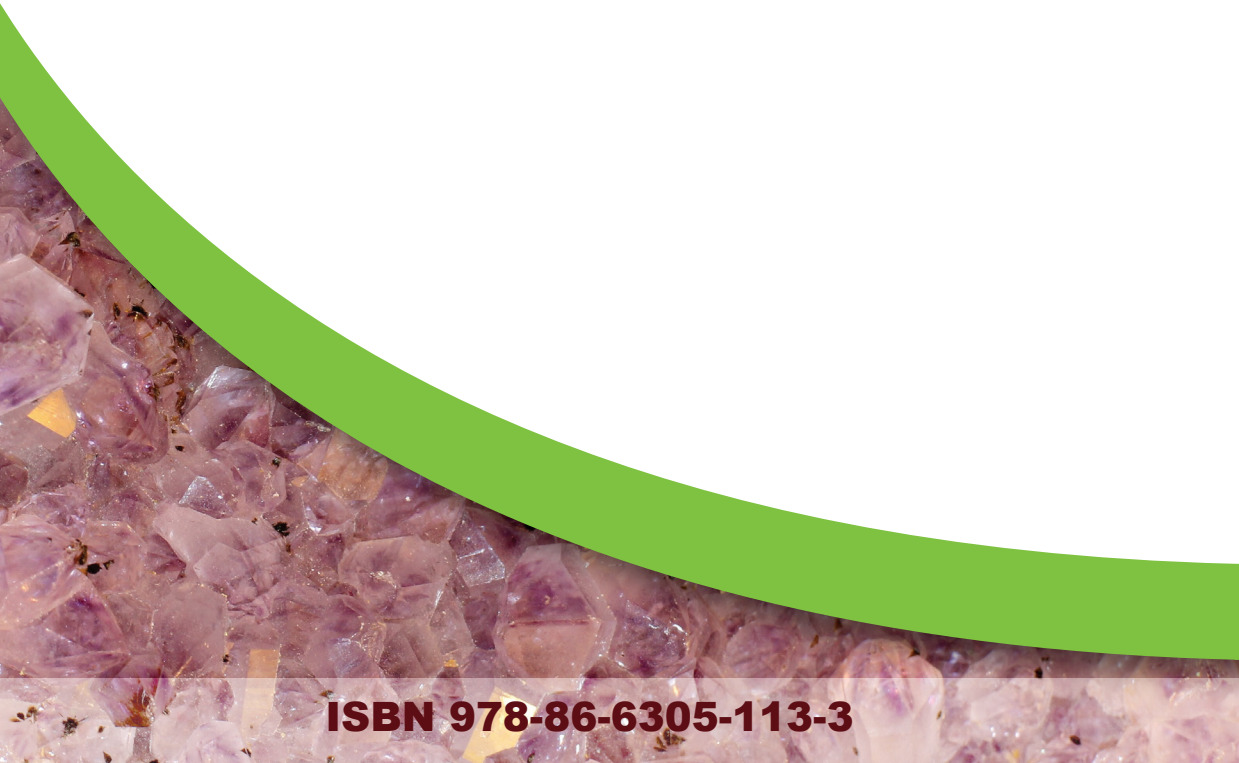
Deposition of cobalt ferrite on the surface of EV, via or hydrothermal co-precipitation method, had induced certain changes in EV which have reflected on its properties, CEC and SSA in the first place. These particles support the adsorption process as they provide extra surface for adsorption of Ni ions and impact the rates of diffusion through adsorbent particles. Composites based on these types of minerals should be considered as adsorbents of heavy metals present as cation species.

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REFERENCES

1. Suvorov, S.A., Skurikhin, V.V. (2003) Vermiculite - A promising material for high-temperature heat insulators. *Refractories and Industrial Ceramics*, 44, 186-193.
2. Kaur, S., Singh, S., Singh, L. (2019) Opto-electric and physio-chemical changes in oxygen ion irradiated natural Vermiculite mineral. *Applied Radiation and Isotopes*, 148, 7-12.
3. Martins, C.C., MacHado, C.G., De Santana, D.G., Zucareli, C. (2012) Vermiculita como substrato para o teste de germinação de sementes de ipê-amarelo. *Semina: Ciências Agrárias*, 33, 533-540.
4. Zhou, W., Zhang, H., Li, K., Liu, F., Zhu, J. (2018) Synthesis and thermal properties of a capric acid-modified expanded vermiculite phase change material. *Journal of Materials Science*, 54, 2231-2240.
5. Deng, Y., He, M., Li, J. (2019) Non-isothermal crystallization behavior of polyethylene glycol/expanded vermiculite form-stable composite phase change material. *Materials Letters*, 234, 17-20.
6. Malandrino, M., Abollino, O., Giacomino, A., Aceto, M., Mentasti, E. (2006) Adsorption of heavy metals on vermiculite: Influence of pH and organic ligands. *Journal of Colloid and Interface Science*, 299, 537-546.
7. Rente, A.F.S., Moraes, D.S., Lamarão, C.N., Rodrigues, E.M.S., Marques, G.T. (2018) New sodium activated vermiculite process. Testing on Cu²⁺ removal from tailing dam waters. *Journal of Hazardous Materials*, 366, 34-38.
8. Weiss, A., Koch, G., Hofmann, U. (1955) Zur Kenntnis von Saponite. *Berichte der Deutsche Keramische Gesellschaft*, 22, 12-17.
9. Belhouideg, S., Lagache, M. (2014) The Effect of Moisture on the Mechanical Properties of Compacted Exfoliated Vermiculite. *Engineering Structures and Technologies*, 6, 124-130.
10. Daković, A., Tomašević-Čanović, M., Dondur, V., Rottinghaus, G.E., Medaković, V., Zarić S. (2005) Adsorption of mycotoxins by organozeolites. *Colloids Surfaces B: Biointerfaces*, 46, 20-25.
11. Milonjić, S.K., Ruvarac, A.L., Šušić, M. V. (1975) The heat of immersion of natural magnetite in aqueous solutions. *Thermochimica Acta*, 11, 261-266.
12. Mori, T., Tsai, S.-C. (2011) *Taguchi Methods Benefits, Impacts, Mathematics, Statistics, and Applications*, ASME Press, New York, 800.



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