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Fabrication and characterization of manganese ferrite/expanded vermiculite as a magnetic adsorbent of nickel ions

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Abstract

Adsorbents based on magnetic materials are the subject of numerous researches. Beside good magnetism and functional surface, manganese ferrite is unstable and prone to form low mechanical strength agglomerates, which necessitate its deposition on the substrate surface. Expanded vermiculite outer surfac, is a useful medium for the deposition of nanoparticles whereas intercation layer is suitable for holding cation species (distance of 2:1 layers may be greater than 10 Å). Due to its relatively high surface area, cation exchange capacity and natural abundance of vermiculite, this mica mineral and its composites could be valorized as potentially low-cost adsorbents. In this study, manganese ferrite/expanded vermiculite ($MnFe_2O_4$*/EV) composite was prepared by in-situ method. Deposited manganese ferrite particles on the surface of EV were formed in the solvothermal reaction using suitable reagents. Both composite and base material are characterized by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) specific surface area (SSA), cation exchange capacity (CEC) and pH point of zero charge (*pH_{PZC}*) determination. The adsorption properties of *$MnFe_2O_4$*/EV and EV have been investigated in a batch system at pH close to the *pH_{PZC}* for the removal of Ni (II) from water. Considering process parameters such as contact time, adsorbent dosage and temperature: adsorption type, isotherm parameters (Langmuir and Freundlich) and rate of adsorption parameters were determined. Results of the kinetic studies gave fine correlations with pseudo – second order and Weber – Morris model. Taking into consideration fact that EV had low CEC values and SSA, obtained composite have high adsorption capacity (more than 30 mg Ni *g^{-1}*). Also, X-ray diffractograms showed alteration of biotite vermiculite (formed during solvothermal action) into phlogopite (formed after adsorption process and aging). The methodology applied in this work may be utilized for the fabrication of other ferrite spinels, perovskites and other oxide systems.*

Keywords: *expanded vermiculite; heavy metals; magnetic adsorbent; manganese ferrite*

Izvod

Adsorbenti na bazi magnetičnih materijala su predmet brojnih istraživanja. Osim dobre magnetičnosti i funkcioncionalnoj površini, mangan ferit je nestabilan i teši formiranju aglomerata niske mehaničke čvrstine, čime se iziskuje njegova depozicija na površini supstrata. Spoljna površina ekspandovanog vermikulita je korisni medijum za depoziciju nanočestica dok interkalacioni sloj je podesan za zadržavanje katjonskih vrsta (rastojanje između slojeva može biti iznad 10 Å). Zahvaljujući relativno visokoj površini, kapacitetu katjonske izmene i prirodnoj zastupljenosti vermikulita, ovaj mineral liskuna i njegovi kompoziti mogu biti valorizovani kao *potencijalni povoljni adsorbenti. U ovoj studiji, kompozit mangan ferita/eksapndovanom vermikulitu (*$MnFe_2O_4$*/EV) pripremljen je in-situ metodom. Deponovane čestice mangan ferita na površini EV formirane su u solvotermalnoj reakciji korišćenjem podesnih reagenasa. Kompozit kao i bazni materijal karakterizovani su: infracrvenom spektroskopijom sa Furijeovom transformacijom (FTIR), difrakcijom X-zraka na prahu (XRPD), skenirajućom elektronskom mikroskopijom (SEM), specifičnom površinom (SSA) određenom metodologijom po BET-u, kapacitetom katjonske izmene (CEC) i pH tačke nultog naelektrisanja (*pH_{PZC}*). Adsorpciona svojstva *$MnFe_2O_4$*/EV i EV istražena su u šaržnom sistemu na pH vrednosti bliskoj pH tački nultog naelektrisanja za uklanjane Ni (II) iz vode. Uzimajući u obzir procesne parametre kao što su vreme kontakta, masa adsorbenta i temperatura određeni su: tip adsorpcije, izotermski parametri (Lengmir i Frojndlih) kao i parametri brzine adsorpcije. Rezultati kinetičkih studija dobro se korelišu pseudo – drugom redu reakcije i Veber – Morisovim modelom. Uzevši u obzir činjenicu da je uzorak EV imao malu vrednost CEC i nisku specifičnu površinu, dobijeni kompozit ima visok adsorpcioni kapacitet (preko 30 mg Ni *g^{-1}*). Osim toga, difraktogrami X-zraka pokazali su alteraciju biotitskog vermikulita (formiranog solvotermalnom akcijom) u flogopit (formiran nakon adsorpcionog procesa i starenjem). Metodologija primenjena u ovom radu može biti iskorištena za proizvodnju drugih feritnih spinela, perovskita i ostalih oksidnih sistema.*

Ključne reči: *ekspandovani vermikulit; teški metali; magnetični adsorbent; mangan ferit*

Introduction

In the last decades, adsorbent materials scientific public have done numerous studies in aim to develop and improve materials utilized as adsorbents. Among plenty of various pollutants, nickel is one of the most toxic among heavy metals, substance priority list created by ATSDR placed nickel on the 58th position out of 275 chemicals [1]. Mineral materials are promising for utilization as adsorbents, since they are chemically and mechanically stable and for that reason their reusability is very high. Suitable mineral for heavy metal adsorption should possess high specific surface area, cation exchange capacity (if heavy metal exists as a cation species in aqueous solutions) and quicken separation.

Expanded vermiculite possess moderate CEC (25 – 250 $cmol_c$ kg^{-1}) [2] developed surface (flakes morphology) and it is quite abundant in nature. Natural vermiculite (as well as expanded vermiculite) possesses alkali and alkaline ground metals inside interlayer and those cations may be easily exchanged with positively charged reagent species. Since none mica possesses ferromagnetic properties, EV may be improved by deposition of ferromagnetic particles on its surface and thus obtaining ferromagnetic composite.

Manganese ferrite possesses ferromagnetic properties and may be prepared by solvothermal co-precipitation using well known methods [3,4]. This method may be very useful for EV treatment or modification since solvothermal conditions won’t shrink the 2:1 layers, but contrary the layers will further expand [5].

Aims of this work are: to describe pathway to prepare composite $MnFe_2O_4$/EV; to characterize obtained composite in the light of its most important physicochemical properties related to cation adsorption; to determine its adsorption properties towards Ni^{2+} ions from aqueous solution

Experimental

Materials needed for synthesis and overall characterization are listed below, all the reagents and solvents used are analytical grade:

- Iron (III) sulfate monohydrate (Superlab Belgrade)
- Manganese (II) sulfate monohydrate (Kemika Zagreb)
- Polyethylene glycol 3000 (Merck Darmstadt)
- Sodium acetate (Lach-Ner Kiffisia)

- Ethylene glycol (Centrohem Stara Pazova)
- Potassium hydroxide (Merck Darmstadt)
- Nitric acid (Zorka Šabac)
- Potassium nitrate (Alkaloid Skopje)
- Nickel (II) nitrate hexahydrate (Merck Darmstadt)
- Ethanol (Sani-Hem Novi Bečej, 96 vol %)
- Double distiled water (DDW)

Vermiculite samples were obtained from the western slopes of Kopaonik mountain, North East of Kremić village [6]. Those samples are thermally expended on 400 °C in preheated furnace (Elektron – Banja Koviljača/EPK) and after expanding and cooling, EV samples are grinded (KHD Humboldt Wedge AG, Germany) and micronized samples are sieved into particles ranging from 0.5 to 1.0 mm. The modification of the starting material is done by solvothermal co-precipitation processes with the goal to obtain amount of manganese ferrite equal to 10 mas% of the initial EV mass.

Synthesis of $MnFe_2O_4$ in partially follows the methodology met in work of Santhoshet al. [3] Further text describes the deposition of $MnFe_2O_4$ on EV surface. As first, 2.500 mmol of $MnSO_4 \cdot H_2O$ (0.4226 g) and 5.000 mmol of $Fe_2(SO_4)_3 \cdot H_2O$ (1.0447 g) and 40.0 ml of ethylene glycol are measured, all mixed together until clear sol is obtained, while dissolution process was enhanced by the use of US bath for 10 minutes. Then 3.0000 g of CH_3COONa together with 1.5000 g of PEG 3000 are added, and obtained mixture is stirred for half an hour. After stirring, mixture is inserted in PTFE autoclave together with 5.0000 g of EV, and treated for least 1 hour in ultra sound bath (US bath, Bandelin Sonorex RK 100) and 1 hour by vacuuming (water jet pump); after this period, the samples were stored at ambient conditions for 24 h.

for equalizing the reagents with intercalation layer of EV. After that autoclave is closed and put in furnace at 200 °C for 8 h. Solvothermal reactions that occur inside autoclave reactor could be presented by further chemical equations (1-4). After solvothermal reaction, sample is cooled to ambient temperature and rinsed with ethanol and DDW. Sample is dried on atmosphere pressure at 50 °C for 4 hours. Dried sample is stored in plastic container covered with plastic caps.

$$\mathrm{CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-} \tag{1}$$

$$\mathrm{Fe^{3+} + 3OH^- \rightleftarrows Fe(OH)_3} \tag{2}$$

$$\mathrm{Mn^{2+} + 2OH^- \rightleftarrows Mn(OH)_2} \tag{3}$$

$$\mathrm{Mn(OH)_2 + 2Fe(OH)_3 \rightarrow MnFe_2O_4 + 4H_2O} \tag{4}$$

In order to determine cation exchange capacity (CEC) mass concentrations of sodium, potassium, magnesium, calcium, iron, manganese were done for both samples[7]. Spectrophotometer used for cations determination was Perkin Elmer AAnalyst 300. Point of zero charge (pH_{PZC}) was determined by method described by Milonjić et al [8]. Structure and morphology of the EV and its modifications were done using the Scanning Electron Microscopy (MIRA3 TESCAN), while determination of samples specific surface area (SSA) was done by Brunauer–Emmett–Teller (BET) methodology on Micrometrics ASAP 2020 in linear part of nitrogen BET adsorption isotherm on the temperature of nitrogen boiling ($p = p_{atm}$). Before nitrogen adsorption all the samples were degassed on vacuum for a 10 h at 150 ^{o}C. Adsorption was done using nitrogen 99.9 vol. % purity.

Diffractometer Philips PW-1710 was used for XRD analysis – automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The diffraction data were assembled in the 2θ Bragg angle range from 4 to 65°, counting for 1 s (qualitative identification) at every 0.02° step. The divergence and receiving slits were fixed at 1 and 0.1 mm, respectively.

The Fourier Transformed Infra-Red spectroscopy (FTIR) was used to determine the surface functional groups in samples. The FTIR spectra of all samples were measured before and after adsorption. Thermo Fisher Scientific Nicolet IS-50 spectroscope was used for FTIR analysis. The analysis was done in ATR mode in the wavenumber range from 4000 to 400 cm^{-1} with the resolution of 4cm^{-1} in 32 scans.

Adsorption experiments were done in a batch system by mixing the precise amount of samples in 7500 µl of adsorbate containing nickel (initial concentration 9.85 mg dm^{-3}). Constant temperature needed for each set of isothermal experiments was provided by water bath. All experiments were done in triplicate for attenuating the measurement uncertainty according to template given by Table 1. According to solubility product of $Ni(OH)_2$ [9], pH value at which the precipitation will occur at 0.135 mmol Ni dm^{-3} is 9.03 so pH value of the adsorbate solutions prior to adsorption was set to 7.50. The pH values of the adsorbates were set by using diluted aqueous solutions of KOH. Standardization of the initial heavy metal solutions (1000 mg dm^{-3}) was done following the method Accu Standard 1000 ppm. Nickel concentrations were measured by AAS method using Perkin Elmer AAnalyst 300 spectrophotometer.

Table 1: Adsorption experiments template.

Experiment number	Temperature / ^{o}C	Time / min	Adsorbent mass/ mg
1	45	90	10
2	45	90	7.5
3	45	90	5.0
4	45	90	2.5
5	45	5	1
6	45	15	1
7	45	30	1
8	45	90	1

Adsorption experiment results obtained after 90 minutes of contact time are counted as equilibrium adsorption resuts and fitted using Lagmuir isotherm model, equation (5) and Freundlich isotherm model, equation (6).

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag*{5)}$$

$$q_e = K_F C_e^{1/n} \tag*{6)}$$

All other resuts are related to lower contact time, and they represent adsorption rate results and they are fitted with pseudo second order (PSO) model, equation (7) and Weber – Morris model, equation (8).

$$q_t = \frac{t}{\left(1/_{k_2 q_{max}^2}\right) + \left(1/_{q_{max}}\right)} \qquad 7)$$

$$q_t = K_{id} t^{0.5} + C \qquad 8)$$

Results and discussion

Summary results of CEC, pH_{PZC} and S_{BET} for both EV and $MnFe_2O_4$/EV are given in Table 2.

Table 2: CEC, pH_{PZC} and S_{BET} of EV and $MnFe_2O_4$/EV.

	Cation Exchange Capacity/$cmol_c kg^{-1}$							pH_{PZC}	S_{BET}/ m^2g^{-1}
	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe^{3+}	Mn^{2+}	Σ		
EV	6.5	32.4	1.0	0.9	0.1		40.9	6.42	3.28
$MnFe_2O_4$/EV	1.6	5.0	58.1	0.6	0.3	0.8	66.4	7.56	6.87

Data presented in Table 2 indicated that the total CEC value of $MnFe_2O_4$/EV adsorbent is significantly higher than EV's whereas 85% of all exchangeable ions are Na^+. Sodium ions originate from sodium acetate which was used in hydrothermal reaction during the precipitation of Mn(II)/Fe(III) hydroxides inside PEG micelles (Na^+ ions are encapsulated into those micelles). It may be also concluded that start material represent typical Mg rich vermiculite with very low CEC. Specific surface area of the modified sample is higher than base material SSA, it is expected since deposed $MnFe_2O_4$ particles provide extra surface on the EV 2:1 layers. Values of pH_{PZC} may be explained by surface chemistry of start material and fabrication methodology [10]. Briefly, weakly acidic nature of EV interlayer cations reflects on its pH_{PZC} value, while presence of weak base (acetate ions) during the solvothermal synthesis shifted pH_{PZC} to higher value.

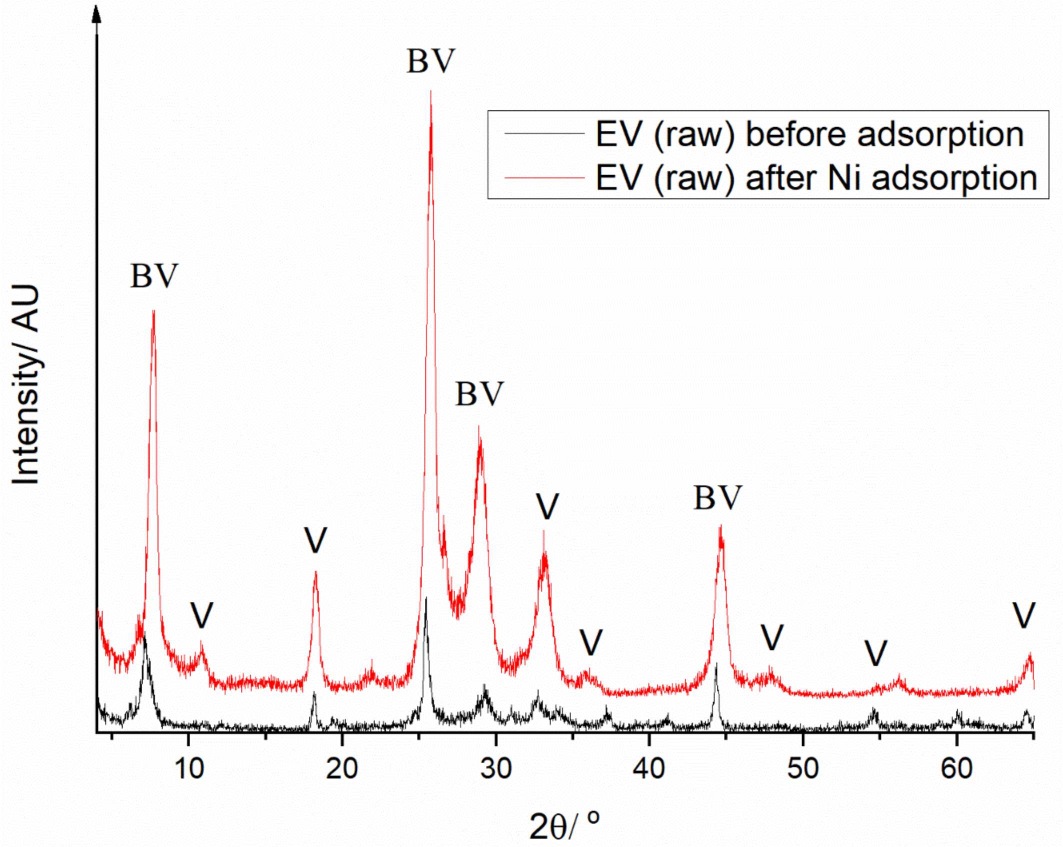

***Figure 1**. XRD patern of EV before and after adsorption, BV mark represent biotite vermiculite and V, vermiculite reflection.*

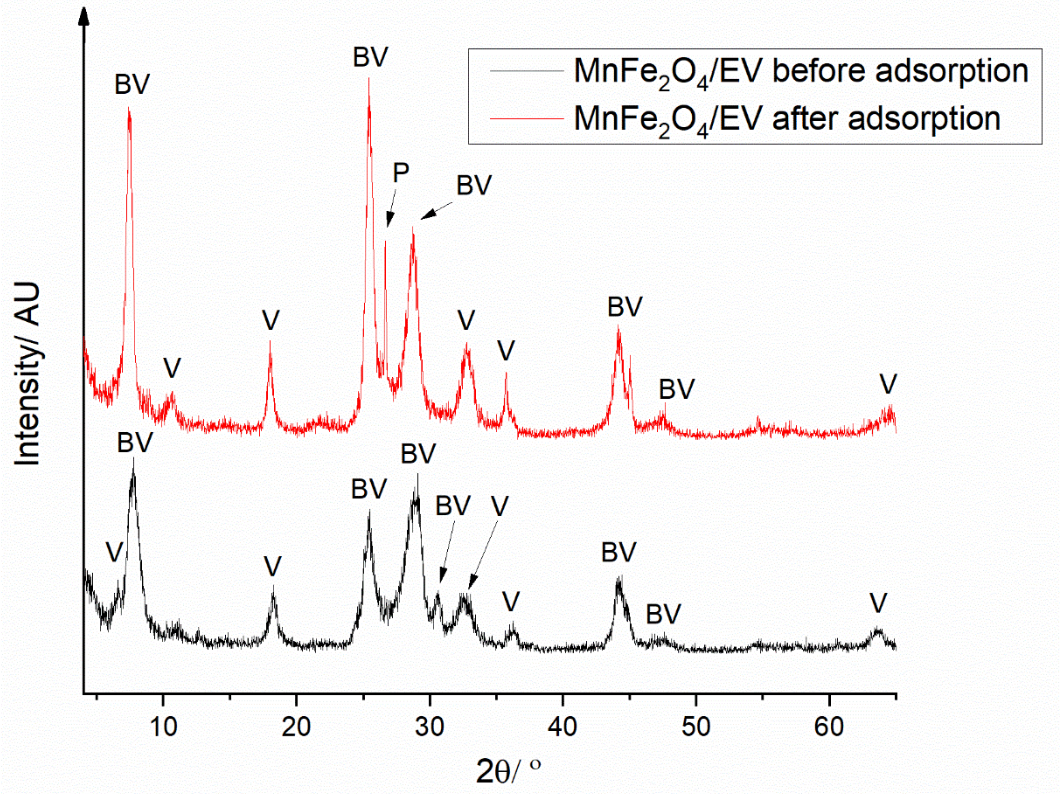

***Figure 2**. XRD patern of $MnFe_2O_4$/EV before and after adsorption, BV mark represent biotite vermiculite, P- phlogopite and V – vermiculite reflection.*

Diffractograms of all samples are presented in Figures 1 and 2. The absence of the peaks corresponding to the ferrite spinels (usually at 35.74, 43.44, 57.47, 63.12^o 2θ) is due to the low presence of the spinel ferrite. The partial transformation of EV into biotite-vermiculite (BV) was observed after thermal modification. Distance between the 2:1 layers increased after ferrite deposition (from 12.34 - native sample to 13.47 Å - the modified one).

Figure 2 shows that after Ni^{2+} adsorption, the BV partially altered into the phlogopite (P). It is possible that iron cations in BV octahedral sheets started to migrate towards the interlayers which caused the alteration to phlogopite.

The FTIR spectra of EV and its modification are shown on Figures 3 and 4. As it may be seen on fore mentioned figure there are some significant changes on spectra after nickel adsorption, which may be seen as a shoulder around 1200 cm^{-1}, also there are some other minor changes in spectra related to vibrations of Al-O/Si-O vibrations and also $MnFe_2O_4$ vibrations. More detailed analysis may be checked within our previous work [10].

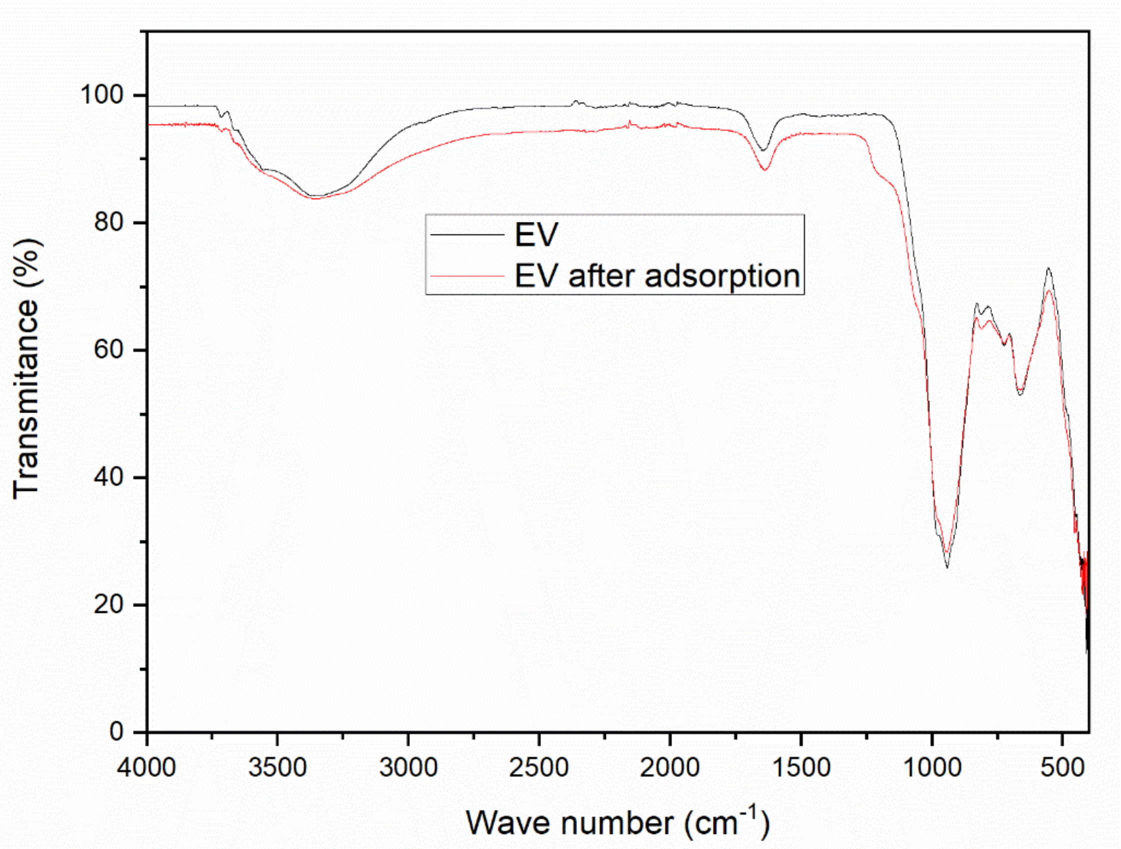

***Figure 3**. FTIR spectra done in ATR mode of EV.*

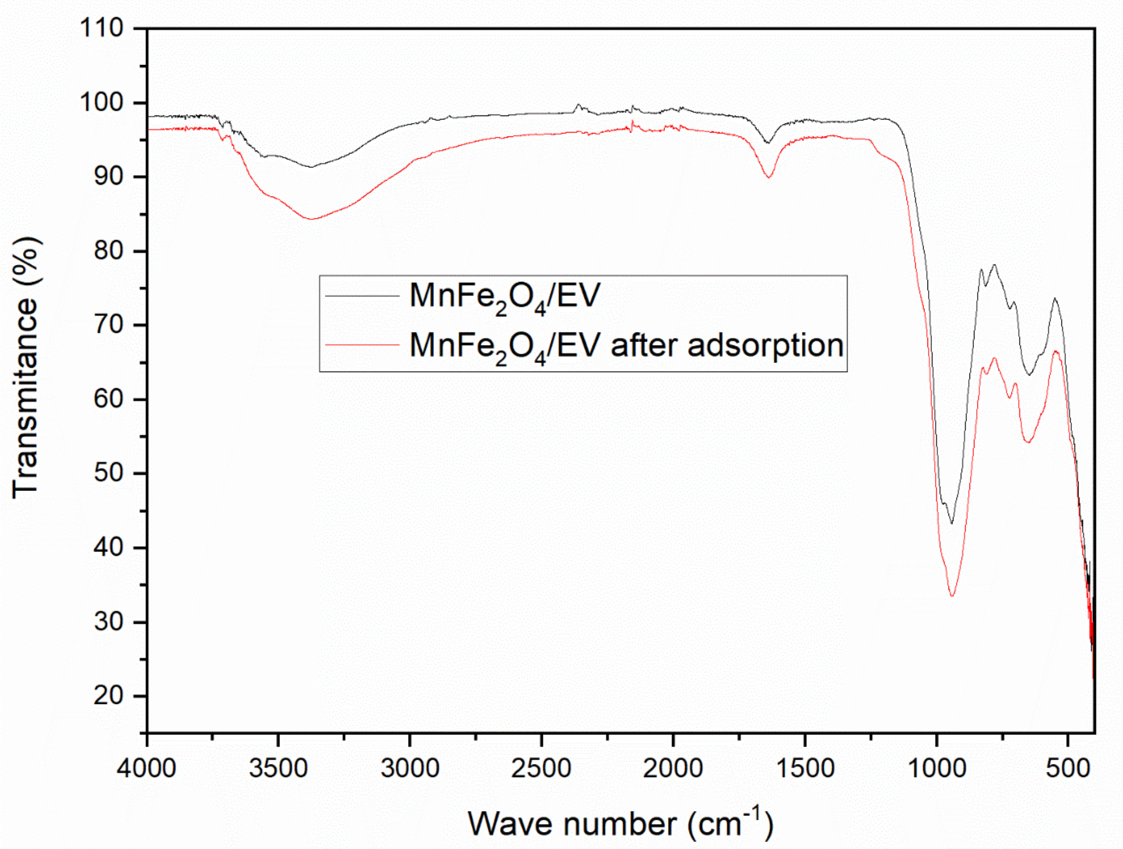

Figure 4. *FTIR spectra done in ATR mode of $MnFe_2O_4$/EV.*

The SEM images of the samples are given in Figure 5. Flat and homogeneous surface of the initial EV sample could be observed at Figure 5 (left). The SEM micrographs confirmed the presence of the ferrite spinels crystals on the surface of the EV formed during the consecutive nucleation and crystal growth. Diameters of deposited $MnFe_2O_4$ particles vary from approximately 100 to 300 nm.

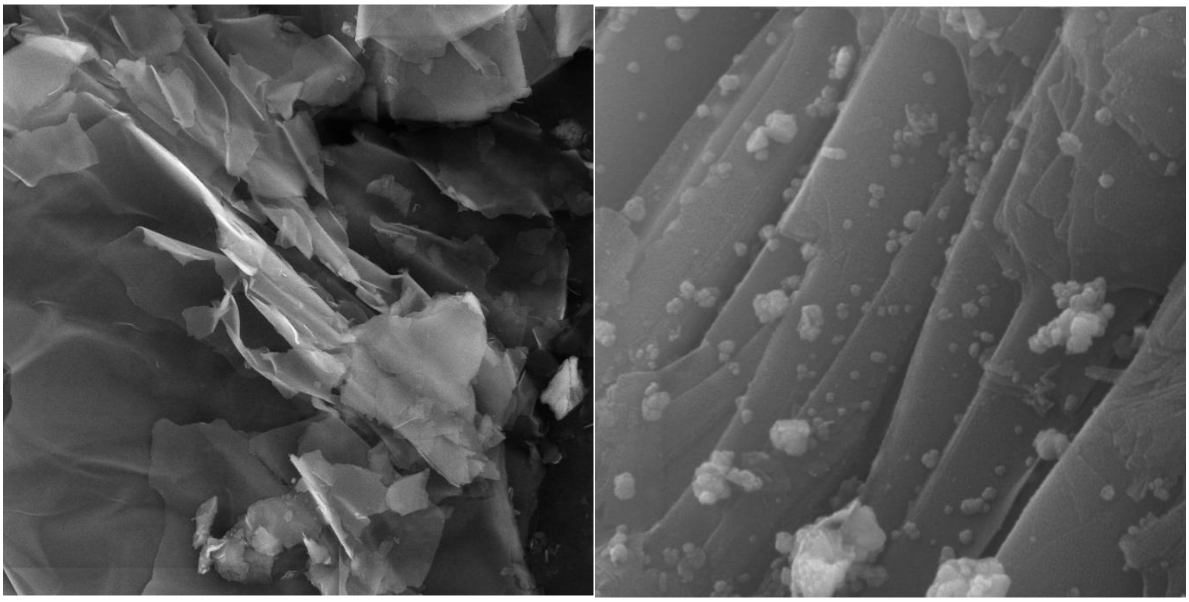

Figure 5. *SEM images of EV (left) and $MnFe_2O_4$/EV (right).*

Summary fitted equilibrium adsorption results are given by Table 3, results of those experiments are fitted with Langmuir and Freundlich adsorption isotherm.

Table 3. Equilibrium adsorption of nickel on EV and its composite on 318 K, initial concentration of nickel 9.85 ppm

Sample	K_L/ dm^3 mg^{-1}	q_{max}/ mg g^{-1}	K_F/ $mgg^{-1}(dm^3mg^{-1})^{1/n}$	1/n
EV	0.762	24.82	10.457	0.385
$MnFe_2O_4$/EV	1.083	30.51	15.241	0.351

From the Table 3 it is clear that modified composite possess improved adsorption performance (measured by q_{max} values from Langmuir adsorption isotherm). Such increase in adsorption capacity is explainable by increase of the CEC value for composite when compared with base material. Langmuir constant has also increased (K_L) which means that overall adsorption process is more spontaneous. Also, 1/n values from Freundlich adsorption isotherm confirmed that modified sample ($MnFe_2O_4$/EV) is even more heterogenous than base material (this value is lower for modified sample) which is expected.

Rate of the nickel adsorption is determined measuring adsorption capacity as a function of contact time, the best correlation among reaction rate models were provided using pseudo second order (PSO) model, while the best diffusion model was Weber – Morris. Experimental results fitted using nonlinearized PSO model are provided on Figure 6, while Weber – Morris and PSO parameters are shown in Table 4.

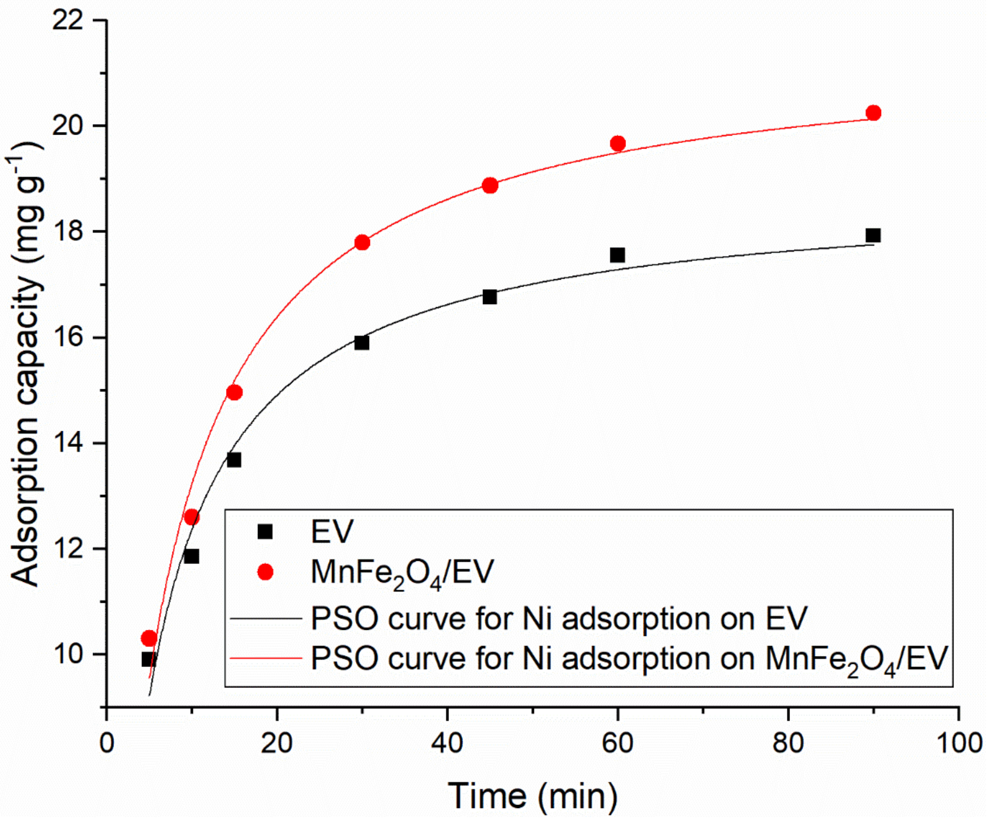

Figure 6. *PSO fitting curves for adsorption of Ni on EV and* $MnFe_2O_4$*/EV on 318 K.*

At the Figure 6 may be seen that adsorption capacity for Ni adsorption on modified sample is increased but constants obtained from nonlinearized fitting show that rate of adsorption is impeded (Table 4).

Table 4. Parameters for adsorption rate experiments of nickel on EV and its composite on 318 K, initial concentration of nickel 9.85 ppm

Sample	PSO parameters		Weber – Morris parameters	
	q_{max}/ mg g^{-1}	k_2/ g (min mg)$^{-1}$	K_{id} / mg g^{-1} min$^{-0.5}$	C / mg g^{-1}
EV	19.280	0.008162	1.72	6.03
$MnFe_2O_4$/EV	22.045	0.006412	2.00	6.14

Such decrease in rate of adsorption come from the presence of magnetic $MnFe_2O_4$ particles. Their role is to provide surface for adsorption and to give the material ferromagnetic properties but, on the other side they slow down the transfer of adsorbate species on EV surface, which is measurable by values of k_2 PSO constants.

Conslusions

Deposition of $MnFe_2O_4$ on EV surface altered this mineral and changed its physicochemical properties esspecialy CEC and S_{BET}. Solvothermal action increased the distance between 2:1 layers but presence of manganese ferrite particles impeded the rate of adsorption also base medium of synthesis mixture shifted pH_{PZC} to higher value. However, modified sample possess significant amounts of sodium ions in interlayer which provided this material higher adsorption capacity, while presence of manganese ferrite provided substrate (EV) with ferromagentis properties. Since the best fitting of adsortpion rate results were obtained using PSO it may be concluded that adsorption follows the ion exchange mechanism. Future studies will be pointed towards alternative fabrication pathways with aim of obtaining materials with even higher SSA and presence of function groups (such as OH group) which will improve adsorption process further.

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