



# Influence of the synthesis parameters on the properties of the sepiolite-based magnetic adsorbents



Aysha Ali Ahribesh<sup>a</sup>, Slavica Lazarević<sup>a</sup>, Ivona Janković-Častvan<sup>a</sup>, Bojan Jokić<sup>a</sup>, Vojislav Spasojević<sup>b</sup>, Tamara Radetić<sup>a</sup>, Đorđe Janačković<sup>a</sup>, Rada Petrović<sup>a,\*</sup>

<sup>a</sup> University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

<sup>b</sup> University of Belgrade, Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia

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## ABSTRACT

The magnetic nanocomposites (MNCs), used as adsorbents for Cd<sup>2+</sup> ions, were prepared by a co-precipitation method using both the untreated natural (SEP) and the partially acid-activated (ASEP) sepiolites as supports for magnetite. The synthesis conditions differed as follows: NaOH or NH<sub>3</sub> was added in the SEP or the ASEP suspension before or after the addition of Fe<sup>3+</sup> and Fe<sup>2+</sup>. The SEP-based MNCs prepared using NaOH had a lower magnetization, but higher adsorption capacities than the MNCs synthesized using NH<sub>3</sub>. The order of the mixing of the reagents had a small influence on the properties of SEP-based MNCs, especially when NaOH was used for the synthesis. Due to acidity of the surface functional groups of the ASEP, the magnetic composite could be synthesized only when NH<sub>3</sub> was added in the suspension of ASEP having Fe<sup>3+</sup> and Fe<sup>2+</sup> ions. Despite of the worse dispersibility of the magnetic particles, the adsorption capacity of the ASEP-based composite was higher than of the MNC with SEP prepared by the same procedure. All the MNCs showed a superparamagnetic behavior at room temperature and the adsorption capacities were higher than of pure compounds. The adsorption of Cd<sup>2+</sup> on the composites was best fitted with the Sips model, which suggested the chemisorption on the heterogeneous surface at energetically non-uniform sites until a monolayer was formed.

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## 1. Introduction

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles have a huge potential in the field of water treatment owing to their adsorption/reduction activities and the possibility to easily separate them from a treated water by applying an external magnetic field [1,2]. These advantages make magnetite appropriate for the removal of vast pollutants from contaminated waters, including different toxic cations and anions [3–6].

However, the strong tendency of the nanoparticles to aggregate and the chemical instability against oxidation reduce the surface area and the adsorption/reduction activities [7] that cause a decrease of the efficiency in the process of water pollutants removal. To prevent the aggregation of magnetite nanoparticles, different materials have been used as a support during magnetite synthesis, such as montmorillonite [7], zeolite [8,9], sepiolite [10,11], palygorskite [12], diatomite [2], pillared bentonite [13,14], activated carbon [15], microporous carbon [16], chitosan [17], cross-linked pectin [18] etc. In that way, the nanoparticles are dispersed in a solid matrix, precluding them from any local movement, as they are firmly embedded to the matrix. The magnetic properties of such composites depend on both the quantity of magnetite in the composite and the size of magnetite particles meaning that the

magnetization is higher if the quantity of magnetite is higher and the magnetite particles are larger. On the other hand, the adsorption capacity of the composite is higher if the magnetite particles are smaller. Therefore, in order to obtain the composite with good magnetic and adsorption properties, it is necessary to increase the quantity of magnetite in the composite and to optimize the size of magnetite particles, as well as to prevent the magnetite oxidation [2,7]. The quantity of magnetite in the composite can be increased by using support materials with a high specific surface area and an appropriate porosity.

Sepiolite, Si<sub>12</sub>Mg<sub>8</sub>O<sub>30</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>·8H<sub>2</sub>O, as a natural, fibrous clay mineral with a high specific surface area and nano-sized channels is a good candidate which insures the magnetite particle dispersion. In addition, the specific surface area and the porosity of sepiolite can be increased by an acid activation due to the removal of mineral impurities and structural Mg<sup>2+</sup> ions. If the treatment is very aggressive, the octahedral Mg<sup>2+</sup> cations are completely dissolved, while the tetrahedral sheets form a free amorphous silica gel, insoluble in the acid solution. However, by controlling the acid treatment, it is possible to increase the specific surface area and to preserve the sepiolite structure [19].

In present study, both untreated natural and the partially acid-activated sepiolites were used to prepare the magnetic nano-composites (MNCs) for the removal of Cd<sup>2+</sup> from water. For this purpose, a chemical co-precipitation method was used and the synthesis parameters were varied in order to obtain MNC with a high adsorption capacity

\* Corresponding author.

E-mail address: [radaab@tmf.bg.ac.rs](mailto:radaab@tmf.bg.ac.rs) (R. Petrović).

and good magnetic properties. The influence of the different synthesis conditions, such as: iron salts concentration; the ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ; nature of the base used for the co-precipitation; the rate of the addition of the base solution; ratio of  $\text{OH}^-/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ; temperature; and drying modality on the properties of the pure magnetite synthesized by a co-precipitation method has been investigated [20,21], but the MNCs with sepiolite were synthesized only under constant conditions. So far, only one MNC sample with natural sepiolite was synthesized [10] as an adsorbent for atrazine, as well as MNC with acid-activated sepiolite, used for  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  ions removal from water [22]. Therefore, the goal of this study was to investigate the influence of the synthesis parameters, such as the type of the base used for the co-precipitation, the type of support (natural or acid-activated sepiolite) and the order of the mixing of the reagents, on the properties and the adsorption capacities for  $\text{Cd}^{2+}$  of the magnetite/sepiolite composites.

## 2. Materials and methods

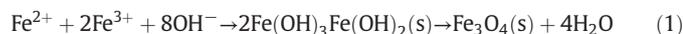
### 2.1. Materials

The natural sepiolite (SEP) from Andrići (Serbia) and the acid-activated sepiolite (ASEP), prepared according to a previous study [19], were used as the starting materials. Briefly, the ASEP was prepared by 10 h stirring of the dispersion of 10 g of the SEP in  $100 \text{ cm}^3$  of 4 M HCl solution, at room temperature, followed by centrifugation, washing and drying at  $110 \text{ }^\circ\text{C}$  for 2 h.

The reagent grade chemicals, such as NaOH,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , were used without any further purification.

### 2.2. Preparation of sepiolite-magnetite nanocomposites and pure magnetite

The sepiolite-magnetite nanocomposites were prepared by the co-precipitation of magnetite in the presence of the SEP and ASEP. The reaction of magnetite synthesis could be expressed as [20]:



Two different procedures were applied for the MNCs synthesis, where the molar ratio of  $\text{Fe}^{2+}:\text{Fe}^{3+}$  was 1:2, as in the synthesis of pure magnetite.

#### 2.2.1. First procedure

5 g of SEP or ASEP powder was first added into  $500 \text{ cm}^3$  of 1 M NaOH or  $\text{NH}_3$  solution under stirring to make a suspension which was further kept under a  $\text{N}_2$  atmosphere for 30 min. After dissolving 4.51 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.306 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $100 \text{ cm}^3$  of distilled water that was deoxygenated by bubbling  $\text{N}_2$  gas for 30 min, the solution was kept under a  $\text{N}_2$  atmosphere in a water bath at  $\sim 60 \text{ }^\circ\text{C}$ . Then, the suspension of SEP or ASEP in NaOH solution was dropped into the solution, followed by the stirring of the mixture for 2 h at the same temperature.

#### 2.2.2. Second procedure

First, 4.51 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in  $500 \text{ cm}^3$  deionized water and then 5 g of SEP or ASEP was added, followed by treatment in an ultrasonic bath for 15 min. The dispersion was bubbled by a  $\text{N}_2$  gas for 30 min before the solution of 2.306 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $100 \text{ cm}^3$  deoxygenated water was added. The mixture was stirred for 30 min under a  $\text{N}_2$  atmosphere and then placed in a water bath, at  $\sim 60 \text{ }^\circ\text{C}$ , followed by the drop wise addition of the NaOH or  $\text{NH}_3$  solution (25%) until a black precipitate was formed. The suspension was aged for 2 h at the same temperature.

#### 2.2.3. Pure magnetite synthesis

The solution of 4.51 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.306 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in  $100 \text{ cm}^3$  deionized deoxygenated water was kept under a  $\text{N}_2$  protection in a water bath at  $\sim 60 \text{ }^\circ\text{C}$  and the NaOH solution (25%) was added drop

wise until a black mixture was formed ( $\sim 15 \text{ cm}^3$ ). The mixture was stirred and aged for 2 h at  $60 \text{ }^\circ\text{C}$ .

In all cases, the separated solid phase was washed three times with deoxygenated deionized water ( $100 \text{ cm}^3$ ) and finally with ethanol ( $50 \text{ cm}^3$ ). The drying was performed under vacuum at  $60 \text{ }^\circ\text{C}$  until constant mass. A qualitative assessment of the magnetization of the composites was demonstrated by a hand-held magnet.

The experimental conditions of the composites preparation are systematized in Table 1, together with the assessment of the magnetization.

### 2.3. Characterization

The X-ray diffraction (XDR) analysis of the samples was carried out with an ITAL STRUCTURES APD 2000 diffractometer using  $\text{CuK}\alpha$  radiation, in the  $2\theta$  angle range from  $3^\circ$  to  $50^\circ$ , with a  $0.02^\circ$  step. The average crystallite sizes of the sepiolite and the magnetite were calculated by applying the Scherrer equation [23].

The FTIR analysis was performed on a MB BOMAN HARTMANN 100 instrument in the wave number range from  $4000$  to  $400 \text{ cm}^{-1}$ . The samples were prepared by the KBr method, with a sample to KBr ratio of 1:150.

The particles morphology of the samples was observed by a Tescan MIRA3 field emission gun scanning electron microscope (FESEM), with electron energies of 20 kV in a high vacuum. The samples were sputter-coated with an Au–Pd alloy to ensure the surface conductivity.

The TEM analysis of samples was performed on a JEOL T-100 instrument. The samples were ultrasonically dispersed in ethanol to form a dilute suspension. A drop of the suspension was applied onto a holey carbon film supported by a copper-mesh TEM grid and air-dried at room temperature.

The specific surface area ( $S_{\text{BET}}$ ) and the pore size distribution of the samples were determined using the nitrogen adsorption–desorption isotherms obtained by a Micrometrics ASAP 2020 instrument. Before the sorption measurements, the samples were degassed at  $150 \text{ }^\circ\text{C}$  for 10 h under reduced pressure. The  $S_{\text{BET}}$  of the samples were calculated according to the BET method [24], taking into account the linear part of the nitrogen adsorption isotherm. The volume of the mesopores and the pore size distribution were analyzed according to the Barrett, Joyner and Halenda (BJH) method [25], from the desorption isotherm. The volume of the micropores was calculated according to the  $\alpha$ -plot analysis [26].

The differential thermal and thermo-gravimetric analyses were conducted on an SDT Q600 TGA/DSC instrument (TA Instruments), at a heating rate of  $20 \text{ }^\circ\text{C}/\text{min}$ , with  $<10 \text{ mg}$  of the sample. The analyses were done in air, with a flow rate of  $100 \text{ cm}^3/\text{min}$ .

The magnetic measurements were performed using a Quantum Design MPMS XL-5 SQUID magnetometer. The DC magnetization measurements were carried out as a function of temperature ( $T = 5\text{--}300 \text{ K}$ ) in the magnetic field of 100 Oe. The magnetization vs. magnetic field

**Table 1**

The experimental conditions of the composites preparation and the assessment of the magnetization.

Sample	Support	Base	Procedure <sup>a</sup>	Magnetization
SEP-M,NaOH(1)	SEP	NaOH	1	Yes
SEP-M,NaOH(2)	SEP	NaOH	2	Yes
SEP-M,NH <sub>3</sub> (1)	SEP	NH <sub>3</sub>	1	Yes
SEP-M,NH <sub>3</sub> (2)	SEP	NH <sub>3</sub>	2	Yes
ASEP-M,NaOH(1)	ASEP	NaOH	1	No
ASEP-M,NaOH(2)	ASEP	NaOH	2	No
ASEP-M,NH <sub>3</sub> (1)	ASEP	NH <sub>3</sub>	1	No
ASEP-M,NH <sub>3</sub> (2)	ASEP	NH <sub>3</sub>	2	Yes

<sup>a</sup> 1 – The base was added in the water suspension of the support and then the suspension was mixed with the solution of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. 2 – The base was added in the water suspension of the support with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.

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