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FACULTY OF TECHNOLOGY



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Original scientific article

DEPOSITION OF GOETHITE AND FERRIHYDRITE ONTO EXPANDED VERMICULITE SURFACE: CHEMICAL PROPERTIES AND POTENTIAL APPLICATION

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Abstract

Current demand on adsorbent materials is in constant growth, hence scientific society is in ceaseless research subjecting cheap and optimal adsorbent. Abundant raw materials which may be utilized as adsorbent of cation species are mica minerals, and vermiculite as one of them is widely examined. Since wastewater may contain anion or/ and non-ionic pollutants it is needed to functionalize adsorbent so it may attract those species as well. Goethite and ferrihydrite are potential candidates for such modification since they: have large specific surface area (SSA), possess hydroxide group and they are not toxic to the environment. Goethite/ expanded vermiculite (Goe/EV) and ferrihydrite/ expanded vermiculite (Fer/EV) are successfully prepared and those composites have showed better adsorption related chemical properties than expanded vermiculite (EV) itself. Utilizing BET methodology, it is determined that Fer/EV possess five-time larger SSA than EV, while Goe/EV is two times larger. Measuring cation exchange capacity (CEC) it is determined that modified samples have only ~10% smaller values of CEC. Summary, both composites have shown higher affinity toward cationic dye, malachite green and also showed their adsorbent potential toward anionic dye, tartrazine. Thanks to facile preparation of such materials and its cost, it may be concluded that they are prospective choice as adsorbents, in first order of heavy metals and dyes.

Keywords: expanded vermiculite, adsorbent functionalization, goethite, ferrihydrite, wastewater treatment.

Introduction

Mica minerals are among the most abundant group of minerals that readily exist in Earth's crust (Ralph, 2017), and also they possess quite interesting properties. Vermiculite, as well as other smectites is expandable mica mineral. Vermiculite expanded form, expanded vermiculite (EV) can be facile produced via thermal process during intensive heating of vermiculite particles from ambient conditions up to 300 °C (Suvorov & Skurikhin, 2003). Thus obtained, EV is already used as heat insulator (Suvorov & Skurikhin, 2003), radiation shield (Kaur et al., 2014) as germination medium (Wisdom et al., 2017) as a matrix for phase change materials (Gencel et al., 2021; Yang et al., 2020). Beside all mentioned usability, this material may be used as adsorbent as well (Brião et al., 2021; Bugarčić et al., 2021). Thanks to its simplicity, applicability and low cost, adsorption is one of the most promising methods that can be used in wastewater management. Adsorption properties of EV towards cation species come from its moderate cation exchange capacity (CEC) from 25 to 250 cmol_{eq}/kg (Weiss et al., 1955). However, negative surface of T-O-T layers repels anions, therefore

EV couldn't be utilized as an adsorbent of anions. Such defect of material could be exceeded enriching the surface T-O-T sheets of EV with minerals with hydroxide functionality. Thanks to possibility to form hydrogen bonds hydroxide group could bind both cations and anions, that way those composites would be even superior adsorbent than EV itself. Goethite (Goe) and ferrihydrite (Fer) quite fit the requirements of the mineral with hydroxide functional group, they also possess huge surface area and they are quite stable and harmless to the environment (Baragaño et al., 2020; Malakar et al., 2022). In this study, deposition of Goe and Fer on EV surface was done by coprecipitation in thin layer of nonsolvent. Thus, prepared composite was characterized in the manner of its adsorption (towards malachite green (MG) and tartrazine (TAR)) and physicochemical properties (Cation Exchange Capacity (CEC) and BET specific surface area).

Materials and Methods

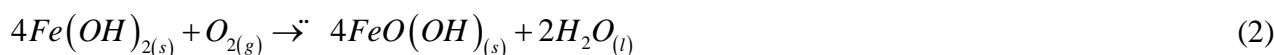
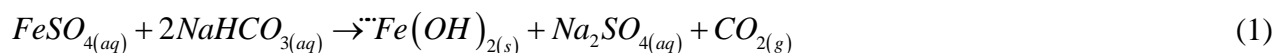
Samples of EV used for preparation of composites are provided from Vatra ltd, Beograd. All the chemicals mentioned in subsection below were of analytical grade, while dialysis bags used are obtained from Spectra/Por® Biotech made from Regenerated Cellulose (RC), MWCO 3500.

Deposition of the Goe has been performed in three identical consecutive steps. Total mass of the reagents used for goethite synthesis was calculated in the way that total mass of produced goethite in those 3 steps is 10 mas% of the EV mass. Prior to deposition EV sample is etched in two steps:

- I step using solution of peroxydisulfuric acid ($\omega=1.5$ mas%) $m:m=50$ g kg^{-1} for 15 minutes of gentle stirring (up to 50 rpm) the dispersion in a glass
- II step using solution of hydrofluoric acid ($\omega=3.0$ mas%) $m:V=50$ g dm^{-3} for 30 minutes of gentle stirring (up to 50 rpm) the dispersion in a polyethylene glass

After etching, the sample was thoroughly rinsed with deionized water (DW) until negative reaction on fluoride ions, and dried on 80°C for 2.5 hours.

Concept for preparation of goethite can be found in work of Schwertman and Cornell (Schwertman & Cornell, 2000) procedure that may be found in cited book is modified in a few details. In order to obtain Goe/EV sample 5.0000 g of EV is placed into three-necked balloon ($V=100$ cm^3) together with 10.0 cm^3 of xylene, 2.00 cm^3 of nitrogen aerated water and 0.3300 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and vacuumed (using water jet pump) for 15 minutes and sonicated (ultrasound (US) bath, Bandelin Sonorex RK 100) another 15 minutes. After this 0.2000 g of NaHCO_3 ($n(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}):n(\text{NaHCO}_3)=1:2$) is dissolved into 2.00 cm^3 of nitrogen aerated water and this solution is droplet added in balloon in nitrogen atmosphere. When evolution of CO_2 is finished, gas inlet is switched on synthetic air. This reaction is left for 24 h, after it obtained composite is filtered and rinsed with ethanol and DW until negative reaction on sulfate ions. Wet sample Goe/EV is dried on 40°C for 6 hours. This deposition of goethite is repeated three times and thus obtained composite is stored in plastic containers. Reactions that occur during synthesis of goethite can be presented with chemisms (1,2).



Procedure for preparation of 6-line ferrihydrite can be found in the book Iron Oxides in the Laboratory by Schwertman and Cornell (Schwertman & Cornell, 2000) however found procedure is changed in a few details so preparation of composite Fer/EV is done in procedure described below:

At first, it is measured 5.0000 g of EV and placed into a tube together with 1.00 cm^3 of DW in order to wet the base material. Wetting of the sample is done the same as in previous case, in assistance of

US bath (US bath, Bandelin Sonorex RK 100) and applying the vacuum (water jet pump). In another glass it as added 10.0 cm³ of xylene and 4.00 cm³ of water and put into a furnace and preheated on 75 °C when the reaction mixture reached this temperature it is added 2.0000 g of unhydrolyzed Fe(NO₃)₃·9H₂O together with already wet EV sample and rapid stirred for 1 minute. Glass together with reagents is moved in oven again for 10 minutes and after the polymerization of iron (III) hydroxides is done, the glass is cooled rapidly plunging it into ice water, and after cooling the sample is centrifuged (3000 rpm for 3 minutes), the liquid phase is decanted and solid raw sample is placed into dialysis bag where the sample is dialyzed for 5 days (water is changed 3 times a day). When the dialysis is done, solid sample is rinsed with DW and ethanol and dried on 60 °C for 6 hours.

In order to determine cation exchange capacity (CEC) mass concentrations of sodium, potassium, magnesium, calcium and iron were done for all samples, methodology used for CEC determination was done according to work of Daković et al (Daković et al., 2005).

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 ($p = p_{\text{atm}}$). Before nitrogen adsorption all the samples were degassed on vacuum for a 10 h at 150 °C. Adsorption was done using nitrogen 99.9 vol.% purity.

Adsorption of malachite green and tartrazine ($c_i=10 \text{ mg dm}^{-3}$) were done on 298 K in a batch system ($m:V=8:60 \text{ g dm}^{-3}$) Concentration of the dyes during adsorption was measured using UV/Vis spectrophotometer Shimadzu 1800 measuring absorption of the light in the wavelength range from 200 to 800 nm on the pre-filtered aliquot sample. Concentration is calculated via Beer-Lambert law equation (3).

$$c = \frac{A}{\varepsilon \cdot l} \quad (3)$$

In the expression (3) A is the absorbance on the wavelength of strongest peak, while $\varepsilon \cdot l$ value was obtained via calibration (determined as a slope of linear part of the function A vs c for standardized solutions of used dyes).

Results and discussion

Determined values of CEC together with contribution of each cation in summary CEC value are given within Table 1. As it can be seen from Table 1 the largest contribution of CEC value in raw sample is provided by presence of magnesium ions in interlayer. On the other hand, composite Goe/EV was obtained via co-precipitation method using sodium salt as a reagent, for that reason sodium ions gave larger contribution to CEC than others present. In the case of Fer/EV composite there were no other reagents used than iron (III) salt and water, so the CEC value is similar as for the start material (EV) with slightly higher contribution of iron (III) ions when compared with EV sample (see Table 1).

Table 1. Cation exchange capacity of EV and its composite and their SSA measured utilizing BET methodology

| | Cation Exchange Capacity/cmole _c kg ⁻¹ | | | | | | S _{BET} / m ² g ⁻¹ |
|--------|--|------------------|-----------------|----------------|------------------|------|--|
| | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | Fe ³⁺ | Σ | |
| EV | 6.1 | 32.1 | 0.8 | 0.9 | 0.1 | 40.0 | 3.28 |
| Goe/EV | 3.2 | 4.8 | 27.8 | 0.5 | 0.2 | 36.5 | 6.61 |
| Fer/EV | 3.0 | 30.6 | 0.7 | 0.8 | 1.1 | 36.2 | 15.1 |

Results of SSA determined via BET methodology are placed in Table 1, and as it can be seen both modifications (Goe/EV and Fer/EV) possess higher SSA than bas material EV. And this is expected since Goe and Fer prepared utilizing routes described by Schwertman and Cornell have SSA of 80 and 200 m² g⁻¹ respectively (Schwertman & Cornell, 2000). However, since the yield of the oxides are

not the same (6-line ferrihydrite is much less yielded than goethite) SSA of Fer/EV is only about 150 % higher than Goe/EV.

Measuring absorbance of standardized solutions of MG and TAR were utilized to determine values of $\varepsilon \cdot l$ slope and their respectively values are xx and zz $\text{dm}^3 \text{g}^{-1}$.

With determined values of $\varepsilon \cdot l$ absorbance results (A) from adsorption experiments are simple recalculated into c using equation (3) and adsorption capacity is calculated using expression (4).

$$q_t = \frac{c_i - c_t}{m_{ads}} * V \tag{4}$$

Where q_t (mg g^{-1}) is adsorption capacity after amount of time, c_t and c_i (mg dm^{-3}) are measured and initial concentration of the dyes in a solutions, m_{ads} (g) is of used adsorbent and V (dm^3) is volume of the solution in the batch. The results of adsorption experiments are presented at Figures 1 and 2 as function of achieved adsorption capacity versus contact time of adsorbent with adsorbate solution.

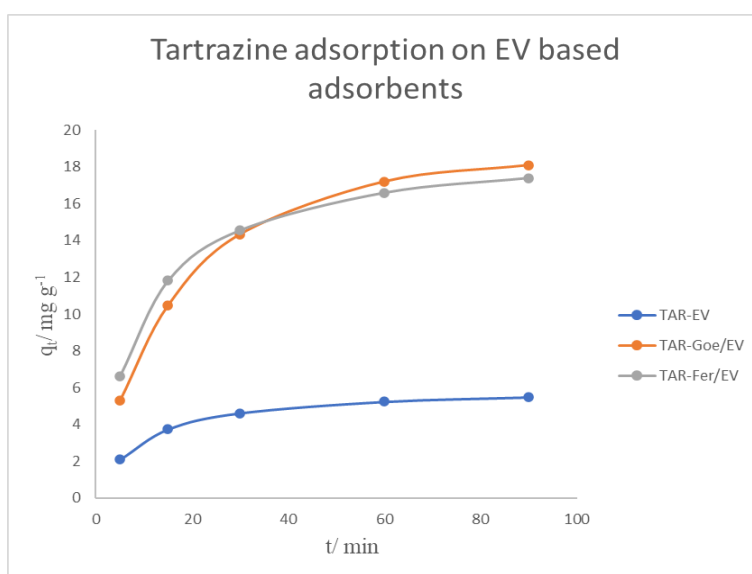


Figure 1. Tartrazine adsorption trend on EV and its modifications

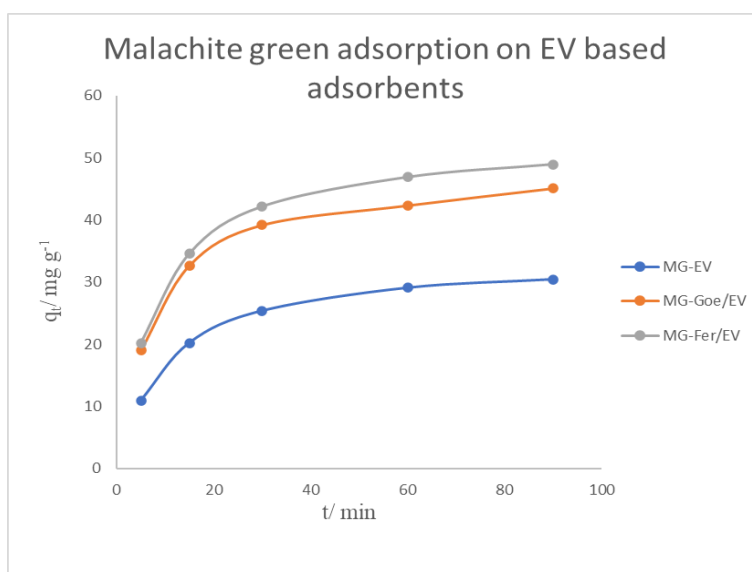


Figure 2. Malachite green adsorption trend on EV and its modifications

As it can be seen from Figure 1, prepared composites possess much higher adsorption capacities towards tartrazine than EV itself. This is expected as a result since EV itself possesses negative surface (T-O-T layer) and thanks to this property EV can't attract negatively charged molecules such as tartrazine and adsorption capacity towards anion species is limited. In the presence of Goe and Fer negatively charged molecules of tartrazine anion could be attracted on support surface and adsorption capacity is better. From the same figure it can be seen that adsorption trend of this dye on Goe/EV is slower however at certain point Goe/EV overcomes Fer/EV composite. Most likely this is due to limiting mass transfer through inner pores of Fer which possess significantly larger SSA than Goe, however inner pores during the adsorption become more and more unavailable and adsorption reaches equilibrium state.

Adsorption capacity of cationic dye, MG on both composites surpassed the base material (EV) adsorption capacity towards same dye as it can be seen from Figure 2. Composite Fer/EV possesses better adsorption properties towards MG than Goe/EV composite, thanks to bigger SSA, as it can be seen from Table 1. Molecular structures of TAR and MG can also help in understanding such results, at Figures 3 are given structures of TAR and MG.

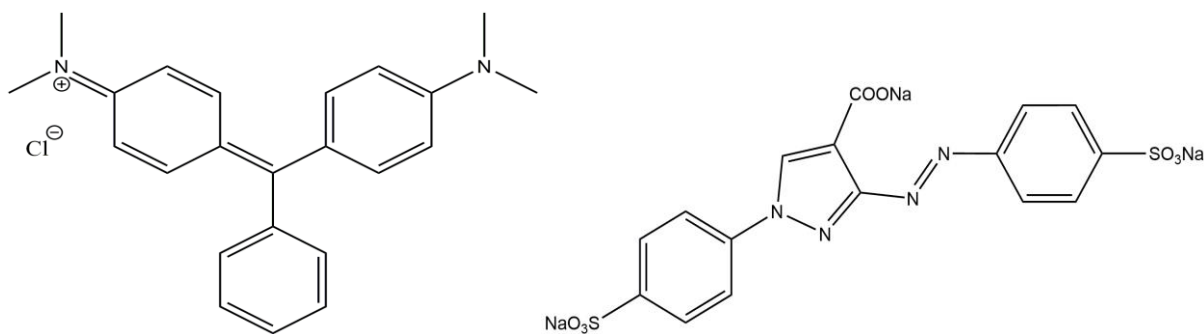


Figure 3. Molecular structures of MG (left) and TAR (right)

As it can be seen from structures MG compound is a salt where positive charge is carried by nitrogen atom and this charge is dispersed through all the benzene rings thanks to complete aromatic behavior of this cation. This cation easily bonds on T-O-T structure of EV matrix all followed by ion exchange with cations in interlayer and adsorption on particles of oxides present on the surface of EV in the case of composites. Structure of TAR shows another salt where negative charge is carried by two sulfonate anion and carboxylate anion so total charge of the anion is -3. This anion is repulsed by the EV surface of T-O-T layer, however presence of Goe and Fer supports the bonding of anion thanks to ion-dipole interaction in the smaller intensity and hydrogen bond in higher intensity.

Conclusion

Deposition of both Goe and Fer on the surface of EV alters the adsorption properties of EV towards the dyes. Presence of these two iron oxides enable the adsorption of anionic dyes and in the same time improve the adsorption capacity of cationic dyes. Thanks to higher CEC and improved SSA obtained composites are prospective choice for adsorption of cationic species in the first place and anionic species in decent amount for such materials in a second place.

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