MINERAL-BASED MAGNETIC NANOCOMPOSITE SORBENTS  

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The article is devoted to the synthesis of mineral-based magnetic nanocomposite sorbents and the study of the influence of modification by magnetite and molybdenum disulfide on the structural-sorption and surface properties of native saponite clay. Modification of native saponite clay with nanoscale magnetite increases the specific surface area and changes pore’s distribution of the original clay from monomodal to bimodal. Next modification of magnetic saponite by micro-sized and nano-sized molybdenum disulfide results in blocking of the secondary porous structure (bimodality disappears of magnetic saponite), but it is increasing the specific surface area. It was found that the sorption activity of modified and unmodified saponite in the region of low concentrations of cationic and anionic dyes (Methyl blue and Congo red) is almost the same. The study of Congo red dye adsorption from highly concentrated solutions showed significant differences in the sorption activities of modified and unmodified saponite samples: the largest sorption capacity characteristic of ternary composites (saponite modified by magnetite and by nano-sized molybdenum disulfide). These ternary composites had in 62 times more activity than native saponite clay and 10 times more than magnetic saponite. It is established that all the samples are characterized by basic properties, but the sample of native saponite modified by magnetite and nano-sized molybdenum disulfide has the largest number of active centers (both acidic and basic character). Thus, it is shown that the modification of the native saponite clay significantly affects not only the texture-sorption but also the surface properties of the native saponite clay. 

Keywords: saponite, magnetic mineral sorbents, nanocomposites, acid-base properties, sorption, dyes.

Introduction

Smectites are one of the largest and most important classes of the phyllosilicate clay-mineral group. The smectite group includes Montmorillonite Sodium, Montmorillonite Calcium, Bedellite and Vermiculite, and elongated smectites involve Neutronite, Saponite and Hectorite. The basic structural unit of smectite clay is a layer consisting of two mid-tetrahedral layers with a central octahedral layer of aluminum oxide. The general molecular formula of the smectite group is (Ca,Na,H)(Al,Mg,Fe,Zn)2(Si,Al)4O10(OH)2-xH2O. One characteristic of smectite clays is the replacement in the octagonal and tetrahedral layers. In the octahedral layers, Aluminum is changed by Magnesium and Ferrum; in the tetrahedral layers, Silicium is replaced by Aluminum. If the octahedral positions are mainly filled with Aluminum, then such smectite mineral is Bedelite; if this places are pledged with Magnesium, then such mineral is Saponite (Fig. 1); if spots are occupied by Ferrum it is Nontronite; and finally if the clay mineral is filled with Lithium, then it is Hectorite (Polyakov 2012 and Murray 2007).

Saponite is a natural sorbent that has high adsorption, ion exchange, catalytic and filtration properties. Saponite has a high cation exchange capacity and high selective activity for many inorganic (Mykhailenko 2015, Macblek 2000, Liansheng 2018 and Saeedeh 2014) and organic substances (Polyakov 2012, Liansheng 2018, Dontsova 2018 and Makarchuk 2017). For the first time in the world, industrial deposits of saponite clay were discovered in Ukraine, in the northern part of the Khmelnitskyi region (Tashkiv deposit). It is also the most well-known, studied and promising industrial saponite deposit in the world. Thus, the development of various commercial products
(Kumaresan 2019 and Chanturiya 2018) based on saponite, including sorption materials, is an actual problem.

Fig. 1. Spatial structural formula of saponite: – oxygen, – OH-groups, – Mg, – Si, *– Al.

Recently, the creation of magnetic composite sorbents based on clay minerals have become most popular (Mykhailenko 2015). The advantage of magnetic adsorbents is that their removal can be easily realized with a magnetic field. Adsorbents with magnetic properties have already been successfully used for the purification of various wastewaters, the collection of oil from the reservoirs surface and in medicine (Macblek 2000, Liansheng 2018, Saeedeh 2014 and Fatemeh 2018). Their advantages include fast recovery, low cost and high mechanical strength. The next improve the sorption properties of mineral-based magnetic sorbents, we propose further modification by the third phase, for example, by photocatalytic particles of transition metal chalcogenides (Dontsova 2018). In addition to varying the sorption properties, modification allows to change the structure of the clay mineral, which leads to an increase in the material porosity, specific surface area, the number of active centers, etc., and, as a result, to improve of its sorption properties.

The purpose of this work is the synthesis of ternary magnetic nanocomposite sorbents based on saponite clay by modification of micro-sized and nano-sized molybdenum sulfide; their characterization and study of sorption properties.

**Experimental**

The saponite of the Tashkiv field, Khmelnitsky region was used as a clay mineral. FeCl₃·6H₂O and FeSO₄·7H₂O reagents were used for nanoscale magnetite synthesis. Synthesis of the magnetic fluid and magnetic saponite sorbent was performed according to (Makarchuk 2017). Additional modification was performed by micro-size and nano-saze molybdenum (IV) sulfide (MoS₂). For this purpose, freshly prepared non-dried SapFe₃O₄ and the corresponding molybdenum sulfide were introduced into the distilled water and stirred vigorously for 30 minute. Then the suspension was filtered and the obtained precipitate was dried for 24 hours at 80 °C. Thus, the four sorption materials were obtained: native saponite (Sap), magnetic saponite sorbent (SapFe₃O₄), modified magnetic saponite sorbent by micro-sized MoS₂ (SapFe₃O₄m) and modified magnetic saponite sorbent by nano-sized MoS₂ (SapFe₃O₄n) (Table 1).
Table 1. Composition of composite sorbents based on saponite clay

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase composition</th>
<th>Mass content, % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sap</td>
<td>Saponite clay</td>
<td>100</td>
</tr>
<tr>
<td>SapFe₃O₄</td>
<td>Saponite clay Fe₃O₄</td>
<td>93</td>
</tr>
<tr>
<td>SapFe₃O₄m</td>
<td>Saponite clay Fe₃O₄ MoS₂ (micro-size)</td>
<td>92</td>
</tr>
<tr>
<td>SapFe₃O₄n</td>
<td>Saponite clay Fe₃O₄ MoS₂ (nano-size)</td>
<td>92</td>
</tr>
</tbody>
</table>

Nanocomposite mineral-magnetic sorbents were characterised by scanning electron microscopy (SEM-1061, Ukraine) and by the method of low-temperature adsorption-desorption of nitrogen (Quantachrome Autosorb Nova 2200e, USA).

Studies of sorption properties were carried out on model dye solutions: Methyl blue (MB) and Congo red (CR). The concentration of the dyes was determined by spectrophotometric method (721 UV/VIS Spectrophotometer, China) (Hashem 2012).

The adsorption of organic dyes from aqueous systems were calculated according to equation:

\[
a = \frac{x}{m}, \text{mg/g,}
\]

where \(a\) – adsorption \(x\) mg of dye per \(1\) g of sorbent, mg/g;
\(x\) – the amount of adsorbed dye from \(100\) cm\(^3\) solution, mg:

\[
x = \frac{(C_0 - C_r) \cdot 100}{1000}, \text{mg,}
\]

where \(C_0\) – initial dye concentration in the model solution;
\(C_r\) – residual dye concentration, mg/dm\(^3\).

To compare the adsorption properties of the composite sorbents, the degree of removal (\(Re, \%\)) of the pollutant was calculated:

\[
Re = \left(\frac{C_0 - C_r}{C_0}\right) \cdot 100.
\]

**SEM characterization of obtained sorbents**

SEM images of Sap, SapFe₃O₄, SapFe₃O₄m, SapFe₃O₄n are presented in Figure 2. As can be seen from Figure 2, on the surface of the SapFe₃O₄, SapFe₃O₄m, SapFe₃O₄n samples, there are additional white dots compared to SEM image of saponite. This is due to the presence of surface modifiers. The chemical analysis of the surface by scanning microscopy showed a relative increase in ferrum content in SapFe₃O₄ sample compared to saponite, and in the samples SapFe₃O₄m and SapFe₃O₄n the molybdenum and sulfur are appear (Table 2). Therefore, the point chemical analysis confirms the deposition of magnetic fluid and MoS₂ modifiers on the surface of saponite clay.
Fig. 2. SEM images of the surface Sap (a), SapFe₃O₄ (b), SapFe₃O₄m (c) SapFe₃O₄n (d).

Table 2. Point chemical analysis of the surface of the samples by scanning microscopy

<table>
<thead>
<tr>
<th>Element</th>
<th>Sap</th>
<th>SapFe₃O₄</th>
<th>SapFe₃O₄m</th>
<th>SapFe₃O₄n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>5.4</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>4.9</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>24.6</td>
<td>2.5</td>
<td>1.55</td>
<td>1.31</td>
</tr>
<tr>
<td>Ca</td>
<td>20.8</td>
<td>2.1</td>
<td>0.9</td>
<td>0.78</td>
</tr>
<tr>
<td>Fe</td>
<td>41.3</td>
<td>91.2</td>
<td>3.4</td>
<td>4.1</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>-</td>
<td>54.8</td>
<td>53.1</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>39.1</td>
<td>38.9</td>
</tr>
</tbody>
</table>

Structural adsorption characteristics of the sorbents

The specific surface area of all samples was determined by the Brunauer-Emmett-Teller equation, and the porosity was investigated by the Barrett-Joyner-Holland method (Thommes 2015). Figure 3 shows nitrogen isothermal adsorption-desorption for saponite clay and modified composite sorbents. As can be seen from Figure 3, all the presented isotherms according to the IUPAC classification are of type IV, which is characteristic of mesoporous materials. All samples under study are characterized by an average pore size in the range of 4 nm. It can also be argued that modification of saponite by magnetite and molybdenum disulfide has a significant effect on the adsorption and textural characteristics of the composites. Thus, the transition from the native saponite to modified nanocomposite sorbents changes the loop of capillary-condensation hysteresis from H3 through the hybrid type H1+H3 to H1. The transition to a hybrid type of hysteresis loop for magnetic composite sorbent is due to the deposition and partial blocking of cylindrical pores by Fe₃O₄ particles.

Table 3 summarizes the porous structure characteristics of all the samples. As can be seen from the data, the increase of the specific surface area by BET from 35 m²/g to 53 m²/g during the transition from the native saponite (4.3 nm) to the magnetic composite SapFe₃O₄ is caused by the formation of a secondary structure, what is confirmed by the bimodality (4.3 nm and 12.5 nm). Further growth with the growth of the specific surface area for SapFe₃O₄m and SapFe₃O₄n associated with the
formation of a secondary structure of molybdenum sulfide on the SapFe₃O₄ surface. As expected, the surface area of the ternary composite modified with nano-sized MoS₂ is the largest.

Fig. 3. Isotherms of adsorption-desorption of nitrogen on Sap (a), SapFe₃O₄ (b), SapFe₃O₄m (c) and SapFe₃O₄n (d).

Table 3. Characterization of the porous structure of saponite-based samples

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Sap</th>
<th>SapFe₃O₄</th>
<th>SapFe₃O₄m</th>
<th>SapFe₃O₄n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface S, m²/g</td>
<td>35</td>
<td>53</td>
<td>57</td>
<td>61</td>
</tr>
<tr>
<td>Mesopore volume V_total, sm³/g</td>
<td>0,12</td>
<td>0,12</td>
<td>0,11</td>
<td>0,08</td>
</tr>
<tr>
<td>The prevailing pore diameter d, nm</td>
<td>4.3</td>
<td>4.3; 12.5</td>
<td>3.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Sorption properties of magnetic nanocomposites and saponite clay**

Sorption properties of sorbents were studied with CR and MB model solutions (initial concentration of dyes is 100 mg/dm³). The pH of all model dye solutions was in the range of 7. The kinetic of CR removal from model solutions by all sorbents are shown in Figure 4. The obtained dependences evidence that the removal of dyes from water solutions by composite sorbents is better than native saponite clay, the degree of CR removal is for Sap – 47 %, SapFe₃O₄ – 95 %, SapFe₃O₄m – 96 %, SapFe₃O₄n – 98 %.

The sorption properties of the composite sorbents (SapFe₃O₄, SapFe₃O₄m, SapFe₃O₄n) and the native saponite clay (Sap) were analyzed by form the adsorption isotherms of Congo red and Methyl blue from model solutions. The adsorption isotherms were plot at low and high dyes concentrations. At low dye concentrations SapFe₃O₄n and Sap had shown the best sorption capacity (Fig. 5). SapFe₃O₄m and SapFe₃O₄ had slightly lower rates. The obtained sorption capacities of all sorbents do not differ much, that is, these sorbents are equally effective at removing dyes at low concentrations. Thus, the dye sorption capacity in low range of concentrations was in according to the following order: SapFe₃O₄n > Sap > SapFe₃O₄m > SapFe₃O₄.
Fig. 4. The dependence of CR residual concentration on the adsorption process duration.

Fig. 5. The adsorption isotherms of dyes: Congo red (a) and Methyl blue (b) (dyes concentrations 1-10 mg/dm$^3$).

Figure 6 shows that significantly higher sorption activity at removing dyes from model highly concentrated aqueous solutions is exhibited by composite sorbents compared to using the native saponite clay.

Fig. 6. The adsorption isotherm of Congo red (dye concentrations of 10-4000 mg/dm$^3$).
Modification of saponite clay with magnetite increases its sorption capacity from 30 mg/g to 180 mg/g, i.e., there is a 6-fold improvement in characteristics. Next modification of SapFe₃O₄ by microsize molybdenum disulfide increases the sorption capacity up to 540 mg/g, what is 3 times higher than for SapFe₃O₄, and modification of magnetic saponite by nano-size molybdenum disulfide increases the sorption capacity (1870 mg/g) in 10 times comparing to it. The increase in the sorption capacity of SapFe₃O₄n towards dyes cannot be explained only by changes in texture characteristics. In our view, such a significant increase in sorption capacity may be due either to the appearance of additional surface active centers on the surface of the magnetic composite material or to the emergence of the photocatalytic activity of molybdenum disulfide in the magnetic nanocomposite SapFe₃O₄n. In this regard, additional studies were conducted on the acid-base properties of the sorption nanocomposite samples under study.

**Acid-basic properties of sorbents**

The acid-base properties of all sorbents were investigated according to (Dontsova 2018). Figure 7 illustrates changes in the pH of the sorbent suspension in bidistilled water for Sap, SapFe₃O₄, SapFe₃O₄m and SapFe₃O₄n over time. The value of isoionic point (pHᵢᵢᵥ) for Sap, SapFe₃O₄, SapFe₃O₄m and SapFe₃O₄n is 9.3, 8.4, 7.7 and 9.1, respectively. These values indicate the base properties of the surface for all samples. The saponite is characterized by the highest basicity and the SapFe₃O₄m has the smallest basic properties. A more detailed study of the acid-base properties of the sorbent samples was carried out by adsorption of the Hammett indicators in the aqueous medium. For this purpose the Hammett indicators used: o-Nitroaniline (pK = −0.29), Fuchsine (pK = 2.1), Bromophenol Blue (pK = 3.9), Methyl Red (pK = 5.25), Bromothymol Blue (pK = 6.8), Phenol Red (pK = 7.6), Thymol Blue (pK = 8.8), Indigo Carmine (pK = 12.8). Figure 8 presents the distribution curves of the adsorption centers of the Hammett indicators on the surface Sap, SapFe₃O₄, SapFe₃O₄m and SapFe₃O₄n. Analysis of the obtained data on the distribution of adsorption centers on the saponite surface indicates the predominance of Brønsted base sites (pK = 8.8, pK = 12.8) and Lewis acid sites (pK = −0.29), as well as a small number of Brønsted acid sites (pK = 2.1, pK = 5.25). Surface modification saponite by magnetite leads to reduction of Brønsted base sites (pK = 8.8) and increase Brønsted acid sites (pK = 5.25), which explains the decrease pHᵢᵢᵥ, and a higher adsorption affinity for anionic dyes compared to saponite. Number of Lewis basic sites (pK = −0.29) compared to the saponite in SapFe₃O₄ increases.

![Fig. 7. Changing the pH of aqueous suspensions for Sap, SapFe₃O₄, SapFe₃O₄m and SapFe₃O₄n over time.](image)
Next modification of the magnetic sorbent SapFe₃O₄ by micro-sized molybdenum disulfide increases the number of Brønsted base sites on its surface (pK=8.8, pK=12.8), but comparing its with SapFe₃O₄ₙ number of centers is decreases. Number of Lewis basic sites (pK=–0.29) compared to saponite in SapFe₃O₄ is increasing, but less than SapFe₃O₄ₙ. Next modification of the SapFe₃O₄ samples by nano-sized MoS₂ increases the number of Brønsted basic sites on its surface (pK=8.8, pK=12.8) compared with SapFe₃O₄, but it is still smaller than the saponite. In addition, re-modification by graphene-like particles MoS₂ leads to an even greater increase in Lewis acid sites (pK=–0.29).

![Fig. 8. Distribution of active adsorption sites on the surface of the studied sorbent samples](image)

Fig. 8. Distribution of active adsorption sites on the surface of the studied sorbent samples

Thus, in our opinion, it is precisely with the increase of the content of the Lewis basic sites from Sap to SapFe₃O₄, SapFe₃O₄ₙ and SapFe₃O₄ₙ that we can associate the increase of the adsorption capacity towards the cationic dye. The increase in sorption activity in relation to the Congo red is due both to the increase in the Brønsted acid sites and, in the case of the ternary nanocomposites SapFe₃O₄ₙ and SapFe₃O₄ₙ presence the photocatalytic activity of molybdenum disulfide in it.

**Conclusions**
Modification of the native saponite sorbent by magnetite allows not only to give it magnetic properties, but also to significantly improve the structural-adsorption characteristics (increase of the specific surface area from 35 to 53 m²/g). Next modification of the micro-sized and nano-sized of MoS₂ contributes to a further increase of the specific surface area up to 57 and 61 m²/g, respectively. The porosity of the native clay changes from monomodal to bimodal pore distribution, which indicates the development of additional porous structure on macropores of saponite as a result of adsorption of nanoscale magnetite.

Studies of sorption properties in the range of low dyes concentrations have shown that all sorbents have approximately the same sorption capacity. Further increase in the concentrations revealed a significant increase in the sorption capacity for the modified sorbents, namely: for SapFe₃O₄ the sorption capacity was 180 mg/g; for modified of micro-sized molybdenum disulfide was 540 mg/g. The sorption capacity of nano-sized molybdenum disulfide modified was 1870 mg/g, which exceeds the values of native clay 3.4 times, SapFe₃O₄ 10 times and SapFe₃O₄ₙ 62 times. Defined acid-base properties indicate the basic character of all sorbents. The modification significantly affects not only the textual but also the surface properties of the native saponite clay: the modification significantly increases the number of active sites compared to the unmodified saponite.
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References


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МАГНІТНІ НАНОКОМПОЗИТНІ СОРБЕНТИ НА МІНЕРАЛЬНІЙ ОСНОВІ

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Стаття присвячена синтезу магнетит-вмісних нанокомпозитних сорбентів на основі сапоніту та вивченню впливу модифікації магнетитом та дисульфідом молібдену на структурно-сорбційні та поверхневі властивості нативної сапонітової глини. Модифікація нативної сапонітової глини нанорозмірним магнетитом збільшує питому площу поверхні та змінює розподіл пор вихідної глини від одномодального до бімодального. Наступне модифікування магнетит-вмісного сапоніту за допомогою дисульфіду молібдену змінює мікро-розмір глини і модифікує деякі його властивості, в результаті чого виникає бімодальність магнетит-вмісного сапоніту, але збільшується питома площа поверхні композиту. Було встановлено, що сорбційна активність модифікованого та немодифікованого сапоніту в області низьких концентрацій катіонних та аніонних барвників (метиловий синій та конго-червоний) майже однаакова. Вивчення адсорбції конго червоного від його високо-концентрованих розчинів показало значні відмінності в сорбційній активності модифікованих та немодифікованих розчинів: найбільша сорбційна емність характерна для потрійних композитів (сапоніт, модифікований магнетитом та нанорозмірним дисульфідом молібдену). Цей потрійний композит мав активність у 62 рази більше, ніж нативний сапоніт і 10 разів більше, ніж магнетит-вмісний сапоніт. Встановлено, що ефективність адсорбції визначається основними властивостями сорбентів, але зразок нативної сапонітової глини суттєво впливає на властивості сорбції за рахунок структурно-сорбційних характеристик. Таким чином, показано, що модифікування нативної сапонітової глини впливає на властивості сорбції, що впливає на її структурно-сорбційні властивості.

Ключові слова: сапоніт, магнетит-вмісні мінеральні сорбенти, нанокомпозити, кислотно-основні властивості, сорбція, барвники.

МАГНИТНЫЕ НАНОКОМПОЗИТНЫЕ СОРБЕНТЫ НА МИНЕРАЛЬНОЙ ОСНОВЕ

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Статья посвящена синтезу нанокомпозитных сорбентов на основе сапонита и изучению влияния модификации магнетитом и дисульфидом молибдена на свойства природной сапонитовой глины. Показано, что модификация сапонита увеличивает ее удельную поверхность и изменяет пористую структуру.

Ключевые слова: сапонит, магнетитсодержащие минеральные сорбенты, нанокомпозиты, кислотно-основные свойства, сорбция, красители.