EFFECT OF LAPONITE MODIFICATION ON THE ADSORPTION EFFICIENCY OF CATIONIC AND ANIONIC DYES

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Abstract. This study investigated the adsorption properties of various dye substances on both pristine and modified laponite samples. The aim was to determine how the organic modification of laponite affects its interlayer spacing, surface area, porosity, and overall adsorption behavior. The results demonstrated that by selecting a ratio of ODTMA to KPAA of approximately 100:2 during the organic modification process, the specific surface area increased significantly from 72 m^2/g to 359 m^2/g. These findings are of practical importance for the development of highly efficient laponite-based adsorbents and catalytic materials.

Keywords: laponite, intercalation, octadecyltrimethylammonium bromide (ODTMAB), cationic polyacrylamide (KPAA), adsorption.

Annotatsiya. Ushbu maqolada dastlabki va modifikatsiyalangan laponit namunalarining turli boyoq moddalarini adsorbsiyalash xossalari o‘rganildi. Laponitning organik modifikatsiyalash uning qatlamlararo maydoni, yuzasi va g’ovakligi adsorbsion xossasini qanday tasir qilishini aniqlash maqsad qilindi. Tadqiqot natijalari shuni ko‘rsatadiki organik modifikatsiya jarayonida ODTMA va KPAA nisbatini 100/2 atrofida tanlash orqali solishtirma sirt maydonini 72 m^2/g dan 359 m^2/g gacha oshganligini ko‘rsatdi. Olingan natijalar laponit asosidagi yuqori samarali adsorbent va katalitik materiallar yaratishda amaliy ahamiyatga ega.

Kalit so‘zlar: laponit, interkalatsiya, oktadetsiltrimetilammoniy bromid (ODTMAB), kationli poliakrilamid (KPAA), adsorbsiya.

ISSN 3030-3907

Аннотация. В данной статье изучены адсорбционные свойства исходных и модифицированных образцов лапонита по отношению к различным красителям. Целью исследования было определить, как органическая модификация лапонита влияет на межслойное пространство, поверхность и пористость, а, следовательно, и на адсорбционные свойства. Результаты показали, что при выборе соотношения ОДТМА и КПАА около 100/2 в процессе органической модификации удельная поверхность по сравнению с исходной увеличилась с 72 м²/г до 359 м²/г. Полученные данные имеют практическое значение для создания высокоэффективных адсорбентов и каталитических материалов на основе лапонита.

Ключевые слова: лапонит, Интеркаляция, октадецилтриметиламмоний бромид (ОДТМАБ), катионный полиакриламид (КПАА), адсорбция.

Introduction

In recent years, various chemical processes have been extensively carried out across multiple industrial sectors, including oil and gas, metallurgy, pharmaceuticals, food, and textile industries. A critical aspect of these processes is the effective removal of harmful components present in wastewater and gases through adsorption. Therefore, the development of new types of adsorbent materials, along with the optimization of their surface and porosity characteristics, has become a scientifically and practically relevant challenge.

Industrial wastewater is one of the main sources of water pollution, containing pollutants that pose serious risks to human health and the environment. In particular, the dyeing, textile, paper, and plastic industries are distinguished as sectors generating large volumes of colored wastewater. Dyes represent one of the most hazardous types of water pollutants and must be efficiently removed from wastewater before disposal. However, the high stability of dye molecules against light and oxidation complicates their removal using conventional physical or chemical methods. Therefore, the use of modified adsorbents with high adsorption activity has become increasingly important for the treatment of dye-containing wastewater [1].

LITERATURE REVIEW

Clay minerals are widely distributed in the natural environment, exhibiting low toxicity, cost-effectiveness, and ecological safety, along with good physicochemical stability [2,3]. This class of solid-phase compounds has been extensively used throughout human history in medicine and environmental applications due to their ability to effectively adsorb and immobilize pollutants, microcontaminants, and other harmful substances [4–10]. Clay minerals are recognized as efficient natural adsorbents because of their high cation exchange capacity, large surface area, swelling ability, good dispersibility in water, and non-

ISSN 3030-3907

toxicity, enabling the removal of bacteria as well as various organic and inorganic contaminants.

Synthetic layered silicates, particularly laponite, are widely employed as effective sorbent materials in environmental processes, especially for wastewater treatment, due to their unique physicochemical properties [11]. Laponite's high surface area, layer charge, and tunable chemical structure make it a promising component for adsorption and catalytic processes. In recent years, the development of nanotechnologies has enabled laponite-based materials to be transformed into low-dimensional structures, such as nanosheets and nanocomposite systems. This enhances their significance in creating multifunctional composite sorbents and allows for more efficient adsorption of organic and inorganic pollutants from aqueous media. Structurally, laponite is a 2:1 type layered silicate, with layers composed of octahedral and tetrahedral sheets. The ion exchange and intercalation zones between these layers can be expanded through modification or functionalized with new active sites. Therefore, altering the laponite structure with inorganic, organic, or hybrid components significantly improves its functional properties.

Intercalation is one of the modern and effective approaches for the targeted modification of layered minerals. It involves the insertion of ions, molecules, or nanoparticles into the interlayer spaces, allowing the regulation of basal spacing, surface charge, and the textural properties of the matrix while preserving the integrity of the crystal lattice. As a result, intercalated systems acquire a new set of adsorption and catalytic properties, proving highly relevant for applications in water and air purification technologies, the development of functional nanocomposites, and the design of advanced catalysts.

Furthermore, the incorporation of neutral molecules and polymers into the interlayer spaces, stabilized by hydrogen bonding and van der Waals interactions, is of significant importance. Intercalation of compounds such as polyethylene glycol (PEG) or polyacrylamide (PAA) enhances the adsorption capacity and thermal stability of the resulting composites, with the interlayer spacing potentially increasing up to 22–25 Å [12].

The intercalation process was carried out based on the cation exchange capacity of laponite. Synthetic laponite samples produced by Shandong Honrel Co. (China) were selected as the starting material. A 10 g portion of dried and sieved laponite was dispersed in 100 mL of distilled water at 60 °C and stirred until a homogeneous suspension was obtained. Simultaneously, at the same temperature, predetermined amounts of octadecyltrimethylammonium bromide (ODTMAB) and cationic polyacrylamide (KPAA) were dissolved in 100 mL of water, taking into account the cation exchange capacity of the clay and the required polyelectrolyte dosage. Intercalation was performed using ODTMAB solutions at

ISSN 3030-3907

50% and 100%, KPAA solutions at 2% and 6%, as well as combined ODTMAB/KPAA solutions in ratios of 50/2, 50/6, 100/2, and 100/6. The organic reagent solutions were added to the clay suspension under vigorous stirring, and the mixture was stirred and heated at 60 °C for 4 hours. The resulting mixture was then left to stand at the same temperature under gentle stirring for an additional 10 hours to complete the maturation process.

The adsorption properties of the pristine and intercalated samples were investigated using cationic (methylene blue) and anionic (Congo red) dyes. A UV–Vis spectrophotometer (UV-5100) was employed for the quantitative determination of dye adsorption. Standard solutions with concentrations ranging from 1 to 50 mg/L were prepared for each dye. The adsorption maxima were determined, with $\lambda_max \approx 664$ nm for methylene blue and $\lambda_max \approx 497$ nm for Congo red. Linear regression analysis was performed, ensuring a coefficient of determination of at least $R^2 \geq 0.999$.

For the adsorption experiments, 0.1 g of each sample was placed in 50 mL test tubes, and 25 mL of dye solutions (1–50 mg/L) were added. The mixtures were studied at 25 °C for 200 hours. Subsequently, the suspensions were centrifuged at 5000 rpm for 10 minutes, and 3–5 mL of the supernatant was collected for analysis. The residual dye concentration was measured using a UV–Vis spectrophotometer at the respective λ_max, and the amount adsorbed was calculated based on a calibration curve.

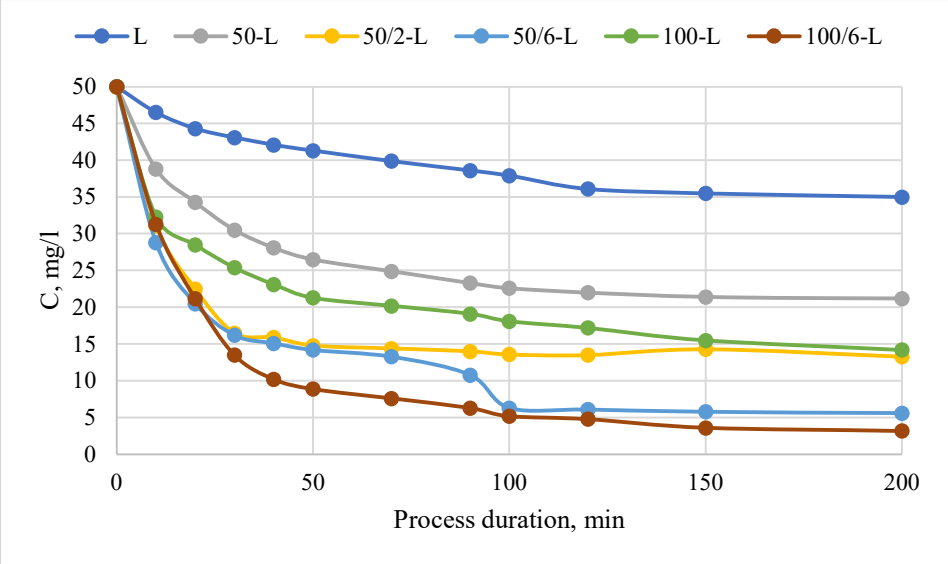


Figure 1. Kinetics of methylene blue concentration decrease in L solutions.

In the pristine laponite, the concentration of methylene blue decreases most slowly: during the first 20 minutes, it drops from 50 mg/L to only 44.3 mg/L, and after 200 minutes, 35 mg/L of the dye remains in the solution. Partial modification of laponite without polyacrylamide (50-L) improves adsorption compared to the initial sample, but its efficiency is lower than that of systems containing the polymer. The addition of 2% KPAA (50/2-L) nearly doubles the initial adsorption

ISSN 3030-3907

rate: within 20 minutes, the solution concentration decreases to 22.5 mg/L, reaching a steady-state value of approximately 13–14 mg/L. The best result is observed when 6% KPAA is combined with 50% ODTMAB: after 30 minutes, the concentration is 16.2 mg/L, and after 200 minutes, only 5.6 mg/L remains. The high efficiency is attributed to the polymer's effect, which maintains a sufficiently negative surface charge and significantly increases the specific surface area.

Table 1.

Parameters of the Langmuir equation for methylene blue adsorption

Sample	A_0, mmol/g	K	S, m^2/g	ΣV, sm^3/g
100/2-L	0,045	38,947	29,16	0,072
100/6-L	0,083	32,417	53,784	0,098
50/2-L	0,182	31,848	117,94	0,123
50/6-L	0,165	40,393	106,92	0,12

The adsorption capacity (A_0) for methylene blue consistently increases with the introduction of organic modifiers; however, the maximum values are observed at moderate polymer concentrations. The highest adsorption capacity, A_0 = 0.182 mmol/g, and a specific surface area of 118 m^2/g were recorded for the 50/2–L sample. When 6% KPAA was added, the surface area slightly increased (up to 107 m^2/g), while the adsorption capacity decreased to 0.165 mmol/g, indicating that excess polymer chains partially blocked the pores and began to restrict diffusion. The Langmuir constant (K) for pristine laponite was 38 L/mmol, whereas for the modified samples it ranged from 31 to 40 L/mmol. These values indicate that a high affinity toward the sorbate molecules was retained, although the energy of the active sites began to distribute more uniformly.

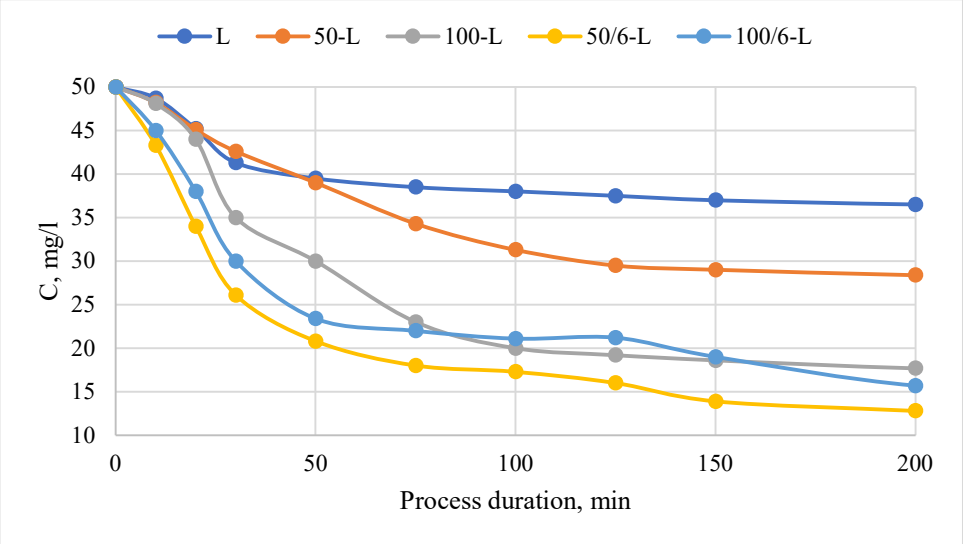


Figure 2. Kinetics of Congo red concentration decrease in L solutions

ISSN 3030-3907

Compared to pristine laponite, the modified samples exhibit slightly higher interaction with Congo red: after 200 minutes, 36.4 mg/L of the dye remains in the solution. The lower layer charge of laponite promotes faster formation of positively charged organolayers: in the 50-L sample, the residual concentration decreases to 28.4 mg/L, and in the 100-L sample, to 17.7 mg/L. The greatest reduction is observed in the sample containing 50% ODTMAB and 6% KPAA, where the dye concentration drops to 11.8 mg/L after 200 minutes. At the same time, when ODTMAB is fully intercalated with the same amount of polyacrylamide, the final concentration is higher (15.1 mg/L), indicating that excess organic material in laponite begins to block the pores.

Table 2.

Parameters of the Langmuir equation for Congo red adsorption

Simple	A_0, mmol/g	K	S, m^2/g	ΣV, sm^3/g
L	0,0570	56,2	72,10	0,053
100-L	0,1544	59,7	195,36	0,171
100/2-L	0,2839	44,6	359,15	0,181
100/6-L	0,2574	55,3	325,61	0,172
50/2-L	0,2215	59,9	280,22	0,161
50/6-L	0,2543	71,2	321,66	0,176

The pristine laponite sample exhibited relatively low adsorption capacity for Congo red, amounting to 0.057 mmol/g. Complete replacement of the surface cations with octadecyltrimethylammonium bromide (ODTMAB) led to a sharp increase in the maximum adsorption capacity (A_0), reaching 0.154 mmol/g. These data indicate that positively charged organophilic layers play a key activating role in the adsorption mechanism of anionic dyes, significantly enhancing the electrostatic interactions between the sorbent and the sorbate. The addition of 2% cationic polyacrylamide (KPAA) during modification further increased the adsorption capacity: for the laponite sample with an ODTMAB/KPAA ratio of 100/2, this value reached 0.284 mmol/g. At the same time, the Langmuir constant ($K \approx 60$ L/mmol) remained nearly unchanged, indicating that strong electrostatic interactions are maintained during the adsorption process.

The introduction of 6% cationic polyacrylamide (KPAA) slightly reduces the maximum adsorption capacity (A_0) of laponite, decreasing it to 0.257 mmol/g. This effect is attributed to the partial blockage of pores by excess polymer chains, which reduces the number of active sites accessible for adsorption. Meanwhile, for laponite samples modified with 50% ODTMAB, the addition of 2% KPAA

ISSN 3030-3907

provides the most optimal result, with A_0 = 0.222 mmol/g. Increasing the polymer content to 6% results in only a moderate increase in adsorption capacity and a slightly lower affinity (K = 49–71 L/mmol). This indicates that excessive incorporation of polymer chains can block a portion of the active sites on the sorbent surface and limit the ion exchange process.

CONCLUSION

The organic modification process fundamentally alters the surface charge, hydrophobicity, and porous structure of laponite. As a result, the material's ability to selectively adsorb and retain target pollutants is significantly enhanced. The study results indicate that laponite composites modified with octadecyltrimethylammonium bromide (ODTMA) and cationic polyacrylamide (KPAA) are capable of efficiently adsorbing model cationic and anionic dyes.

The structural changes are clearly reflected in the textural parameters of the laponite samples. The specific surface area of pristine laponite is 59.5 m^2/g. Modification with 50% ODTMAB nearly doubles this value, promoting pore development and activation of surface active sites. However, when 100% ODTMAB is applied, partial pore blockage occurs, resulting in a slight decrease in surface area.

The introduction of 2% KPAA into the 50% ODTMAB system increases the specific surface area up to 280 m^2/g, which is attributed to the predominance of polymer chains in the interlayer space and their stabilizing effect on the surface structure. The addition of 6% KPAA to 100% ODTMAB further increases the surface area, reaching up to 325 m^2/g.

The highest value is observed in the system containing 100% ODTMAB and 2% KPAA, with the specific surface area reaching 359 m^2/g. This significant increase is attributed to the synergistic interaction between the organic cations and the polymer, resulting in the expansion of interlayer spaces, formation of diffusion channels, and an increase in the number of adsorption sites.

Cationic methylene blue is primarily adsorbed on the free negative sites of the laponite surface. For pristine laponite, the adsorption capacity is A_0 = 0.051 mmol/g. In the sample modified with a 50% ODTMAB + 2% KPAA composition, this value increases to 0.182 mmol/g. This enhancement is attributed to the high specific surface area and the preservation of exchangeable charges.

In the adsorption of anionic Congo red, the adsorption capacity of laponite increases to 0.154 mmol/g after full modification with ODTMAB, and further rises to 0.284 mmol/g with the addition of 2% KPAA. When 6% KPAA is introduced, the capacity slightly decreases to 0.257 mmol/g. This behavior is attributed to partial blockage of the pores by excess polymer chains, which reduces the activity of the active sites. The optimal result is observed at an ODTMAB/KPAA ratio of

ISSN 3030-3907

100/2, confirming complete intercalation of the organic cation and polymer into the interlayer space.

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ISSN 3030-3907