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UKLANJANJE METIL ORANŽA KORIŠĆENJEM DVOSLOJNOG SLOJEVITOG HIDROKSIDA POREKLOM OD ISTROŠENE KISELINE

REMOVAL OF METHYL ORANGE USING LAYERED DOUBLE HYDROXIDE ORIGINATED FROM SPENT ACID LIQUOR

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Proizvodnja organskih boja je u stalnom porastu poslednjih decenija, pa njihova upotreba ostavlja negativan uticaj na životnu sredinu najčešće na živi svet u vodi. Otpadne vode koje nose rastvorene boje su toksične za sve organizme koji postoje u vodi, pa se takvi tokovi otpadnih voda moraju na odgovarajući način tretirati pre nego što se ispuste u životnu sredinu. Izrada efikasnih adsorbenata koji se mogu koristiti u prečišćavanju otpadnih voda postala je mandatorna. U toku pripreme adsorbenata često nastaju i sporedni proizvodi kao što su istrošene kiseline ili baze pošto se one obično koriste za aktivaciju površine adsorbenata. Istrošena kiselina nastala tokom aktivacije ekspandiranog vermikulita (EVer) korišćena je kao polazni materijal za pripremu dvoslojnog slojevitog hidroksida (DSH-EVer) metodom koprecipitacije pri niskoj prezasićenosti. Pripremljeni adsorbent je karakterisan metodom infracrvene spektroskopije sa Furijeovom transformacijom (FTIR) i skenirajuće elektronske mikroskopije sa energetski disperznom spektrometrijom (SEM-EDS). DSH-EVer korišćen je za uklanjanja metil oranža iz vodenog rastvora. Tokom eksperimenata, vreme kontakta je varirano i na taj način je određena brzina adsorpcije. Dobijeni rezultati pokazuju visok kapacitet adsorpcije od 63 mg g^{-1}.

Ključne reči: *DSH; metil oranž; boje; anjonska izmena*

Production of organic dyes has been constantly increasing in the last decades, hence their usage leaves a huge environmental impact usually on aquatic biota. Wastewaters carrying dissolved dyes are toxic to all organisms existing in water, therefore such wastewater streams have to be appropriately treated before they can be released into the environment. Development of effective adsorbents, which can be used in wastewater treatment, is mandatory. Another concern in the production of sorbing materials is the formation of spent acids or bases since they are commonly used for the activation of adsorbents. Spent acid liquor produced during the activation of expanded vermiculite (EVer) is utilized as the start material for the preparation of layered double hydroxide (LDH-EVer) by the method of co-precipitation process at low supersaturation. The prepared adsorbent was

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characterized by Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy with X-ray energy dispersive spectroscopy (SEM-EDS). Fabricated material is utilized as an adsorbent of methyl orange dye from aqueous solutions. During the experiments, contact time were varied and thus the rate of adsorption is determined. The obtained results show a high adsorption capacity of 63 mg g^{-1}.

Key words: *LDH; methyl orange; dyes; anion exchange*

1. Theoretical introduction

The discharge of wastewater effluents containing azo dyes from different sources has become a significant contributor to water pollution. Azo dyes are widely used as coloring agents in the industries such as textile, leather, paper, paint, food and cosmetics [1-4]. Additionally, they serve as pH indicators and spectrophotometric reagents in many research and experimental laboratories [5, 6]. The textile industry is the largest producer of dye wastewater [7]. During the dyeing process, about 20% of synthetic dyes used fail to adhere to fibers, leading to the release of unbonded dye into wastewater streams [8]. This accounts for the discharge of approximately 28,000 t of unfixed dyes into the environment each year [3]. Azo dyes are known for their stability, chemical versatility, high fixation, and resistance to light and moisture. However, these characteristics directly affect their degradability, making them a significant environmental concern [8].

Methyl orange (MO), a common anionic azo dye, soluble in water, was selected as a model compound for this study due of its broad use across industries and its potential adverse effects on the environment and living organisms. Azo-ionic dyes like MO have the ability to attach to suspended organic matter through electrostatic interactions, leading to their accumulation in sediments or wastewater sludge, thus prolonging their persistence in water bodies and impacting aquatic life and human health through the food chain [8]. Discharge of untreated azo dyes into water bodies results in the formation of aromatic amines – through the cleavage of their central azo bonds – known for their recalcitrance, bioaccumulative nature, and toxicity, mutagenicity, and carcinogenicity [8]. Additionally, even at low concentrations, these dyes in water reduce sunlight penetration, lower dissolved oxygen content, reduce gas solubility, inhibit plant growth, and increase organic pollution levels [3, 8].

Many physicochemical methods have been developed for treatment of wastewater containing dyes, including adsorption, osmosis, coagulation, flocculation, membrane separation, oxidation, photochemical degradation, ion exchange, and ozonation [9]. Currently, adsorption is the most widely adopted technique for dye removal due to its low cost, high efficiency, eco-friendliness, and ease of use, making it favored by researchers and widely applied [2]. Adsorbents, the core of this technology, come from various sources and types [2].

During the activation process of the vermiculite sample, a significant amount of waste solution is obtained, motivating this research to repurpose it into a new product—an adsorbent for removing MO from aqueous solutions. This study also aimed to assess the feasibility of utilizing layered double hydroxides (LDH), derived from waste solutions, for MO removal from aqueous solutions. It is important to note that while physicochemical methods like adsorption effectively decolorize pollutants, they do not facilitate pollutant degradation [3]. Furthermore, post-adsorption, the dye remains bounded to the adsorbent, which is difficult to remove and this problem remains unsolved [10].

2. Materials and methods

The synthesis of LDH, following the procedure outlined by Tomanec et al. [11], utilizing a waste solution derived from the activation of vermiculite (Ver) with hydrochloric acid (*Zorka Šabac*, 36 wt.%)

for 3 h at 72°C, while maintaining a solid/liquid ratio of 0.1 g mL^{-1}, was used. In Table 1 is given the composition of the resulting waste solution post-activation with HCl solution. Using a *Hanna HI 2210* pH meter, the pH of the solution was measured at 0.10 and then the solution was evaporated. The residue obtained post-evaporation was utilized in the preparation of the LDH-EVer sample.

Table 1. Quantitative analysis of the solution resulting from EVer sample activation with HCl

K [g L^{-1}]	*Na [g L^{-1}]*	*Mg [g L^{-1}]*	*Ca [g L^{-1}]*	*Fe [g L^{-1}]*	*Al [g L^{-1}]*
2.51	0.302	10.39	0.22	3.60	1.70

In 10 ml of deionized water (18 MΩ cm), 16 g of salts obtained by evaporating the acid solution were added, along with 2.97 g of $AlCl_3$ x $6H_2O$ (*NPK Engineering Belgrade*, 99.9 wt.%). Following dissolution, precipitation was carried out at low supersaturation by gradually adding 1.0 M NaOH (*Centrochem Belgrade*, 98 wt.%) with stirring. The pH of the solution after precipitation was 9.80 and remained unchanged for 2 h following the final addition of NaOH solution. Following filtration, the solid LDH-EVer sample underwent washing with deionized water, drying (at 50 °C for 4 h) and annealing (at 500°C for 3 h). The resulting sample was then ground using a mortar and pestle and stored in plastic containers designated for solid samples until further analysis. For an in-depth preparation procedure, refer to the study by Vuksanović et al. [12], while the methodology for the adsorption experiments can be found in the study by Bugarčić et al. [13].

The adsorption of MO dye was conducted in a batch system, a detailed study of the kinetics and the equilibrium of adsorption that were used to determine the rates and thermodynamics of the process. The initial dye concentration for both studies was set at 15 mg L^{-1}. Monitoring of the adsorption kinetics involved measuring the solution's absorbance during the MO adsorption process in a beaker, at a temperature of 25 °C. The adsorbate volume was 75 mL, and the LDH-EVer adsorbent mass was set at 10 mg.

Equilibrium adsorption experiments were carried out at temperatures of 25, 35, and 45 °C, wherein the adsorbent mass was varied from 1 to 10 mg, while maintaining a constant adsorbate volume of 7.5 mL. The concentration of MO dye was determined by measuring the light absorbance using a UV/VIS spectrophotometer *Shimadzu 1800* within a range from 200 to 800 nm. Subsequently, the MO concentration was recalculated using the Lambert-Beer law (Eq. 1), and the adsorption capacity was determined using Eq. 2.

$$C = \frac{A}{\varepsilon l} \tag{1}$$

$$q = \frac{(c_p - c)V}{m_{ads}} \tag{2}$$

The adsorption rate was determined utilizing two adsorption models, pseudo second order (PSO) model and Weber–Morris (WM) model, with their nonlinear forms presented in Eqs. (3) and (4) respectively.

$$Q_t = \frac{t}{\frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}} \tag{3}$$

$$Q_t = k_{id}\sqrt{t} + C \tag{4}$$

where t – time [min], k_2 – PSO rate constant [g (mg min)$^{-1}$], Q_e – sorption capacity at equilibrium [mg g^{-1}], k_{id} – interparticular rate constant [mg min^{-1} g/2], C – intercept [mg g^{-1}]

For structural and chemical characterization of the adsorbent, FTIR and SEM-EDS techniques were used.

3. Results and discussion

Figure 1 illustrates the progressive decrease in MO concentration over time. Within the same figure, UV spectra of MO containing adsorbates are presented throughout the adsorption duration. From the same Figure it can be seen that prepared adsorbent steadily removes MO dye from water.

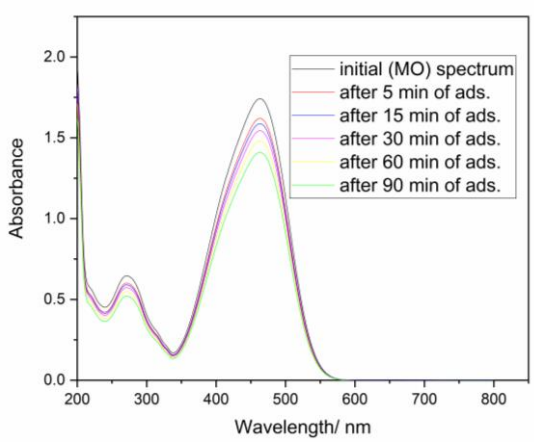

Figure 1. UV/Vis spectra of MO depending as a function of the contact time of adsorbate solution with LDH-EVer

After 90 min of observation, MO concentration was reduced for 23%, which is a good sign of efficiency of prepared materials. Table 2 shows the values of parameters obtained by the correlation of the PSO and WM models. The results of the adsorption kinetics experiment indicate a notable alignment with the PSO reaction model, while the WM model emerged as the most fitting among the diffusion models, showcasing the highest level of alignment.

Table 2. Correlation parameters values influencing the kinetics of MO adsorption experiment on the LDH-EVer sample (T=298 K; C_0=15 mg L^{-1}; m:V=8:60 g L^{-1})

Model	*PSO*		*WM*	
Parameter	k_2 [g (mg min)$^{-1}$]	Q_e [mg g^{-1}]	k_{id1} [mg/(min$^{1/2}$g]	k_{id2} [mg/(min$^{1/2}$g)]
Value	0.000698	69.4	5.89	2.96

In the provided Table 2, the expected equilibrium capacity, Q_e, is 69.4 mg g^{-1}, showcasing a very good adsorption outcome comparable to the results of other studies performed on similar samples. Also in this table it can be seen that the diffusion of MO dye takes place in two phases. The initial phase exhibits rapid diffusion and represents the diffusion of the dye to the adsorbent particle, while the subsequent phase represents the intraparticle diffusion, as the dye permeates through the pores of the adsorbent. The values of Gibbs energy change, along with the changes in standard enthalpy and entropy of the process, were determined through data correlation. In Table 3 is provided the thermodynamic parameters associated with the MO adsorption process on the LDH-EVer sample.

Table 3. Gibbs energy change and standard enthalpy and entropy changes for MO adsorption process on LDH-EVer sample

ΔG^{θ} [kJ mol^{-1}]	ΔH^{θ} [kJ mol^{-1}]	ΔS^{θ} [J (mol K)$^{-1}$]
-38.6	28.6	9.84

Table 3 shows that the adsorption process is spontaneous and moderately endothermic. The primary factor driving spontaneity of the process is the increase in entropy during adsorption. This observation aligns with expectations, considering MO dye's classification among anionic dyes, and the LDH-EVer adsorbent's characteristic of harboring exchangeable anions within its interlayer structure.

4. Conclusion

The dye constituents found in industrial wastewater must be efficiently removed prior to their discharge into water bodies to protect public health, the environment, and aquatic ecosystems. To reduce the environmental impact of human activities, it is necessary to establish and execute effective wastewater treatment systems and processes. Among various techniques, the adsorption process stands out as a widely employed method for dye removal due to its advantages, making it an optimal and sustainable solution. Numerous diverse adsorbents are available for this purpose.

In this study, we utilized the waste solution obtained from the chemical activation of the Ver sample with HCl for synthesizing LDH via the precipitation method at low supersaturation using NaOH solution. The obtained LDH-EVer sample was utilized for the adsorption of MO from the aqueous solution. The resulting LDH-EVer sample exhibited promising adsorption capabilities, removing up to 69.4 mg g^{-1} of MO from the aqueous solution.

The research findings indicate that the adsorption process occurs in two phases, with intraparticle diffusion being the limiting phase. Equilibrium adsorption experiments indicated an endothermic adsorption process with a significant increase in entropy, which can be attributed to the ion exchange of hydroxyl anions with the MO anion. These insights contribute to our understanding of the mechanisms involved in dye removal processes and underscore the potential of LDH-EVer as an effective adsorbent in wastewater treatment applications.

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6. Nomenclature

Ver – vermiculite
EVer – expanded vermiculite
DSH – dvoslojno slojeviti hidroksid
LDH – layered double hydroxide
SEM – scanning electron microscope
EDS – X-ray energy dispersive spectroscopy
FTIR – Fourier-transform infrared spectroscopy
MO – methyl orange
PSO – pseudo second order
WM – Weber – Morris model

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