

THE EFFECT OF STARCH MODIFICATION ON THE DYE ADSORPTION EFFICIENCY

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ABSTRACT

Researches in the field of nanotechnology indicate the possibility of the development and application of bionanocomposites based on clay minerals and biopolymers as promising materials for the removal of pollutants from contaminated water. Therefore, this study is based on an examination of the effect of intercalation of starch or cationic starch with kaolin clay or diatomaceous earth on the adsorption properties of the obtained materials for the removal of anionic and cationic dyes from aqueous solutions. Structural characterization of the obtained materials was performed by Fourier transform infrared spectroscopy while the morphology of the samples was determined by Scanning electron microscopy. The removal efficiency of methyl orange and crystal violet dyes was tested in a batch system, while the dye concentration after the adsorption process was determined by UV-Vis spectrophotometry. It was found that modification of cationic starch with clay and diatomaceous earth improved the efficiency for removing crystal violet dye from an aqueous solution.

INTRODUCTION

The discharge of wastewater with a high content of dyes used in various industries, such as textile, tanning, paper, food, pharmaceutical and cosmetic industries, can lead to contamination of surface and groundwater [1], [2]. Adverse effects can be reflected on flora and fauna, because the dyes in their structure may contain complex, carcinogenic, mutagenic, and toxic compounds, with chromophore groups of high molar mass, high water solubility, and low biodegradability. In addition to the negative impact on the environment, dyes can enter the human food chain, causing damage to human health. Dyes can cause many health problems such as allergies, dermatitis, skin irritation, cancer, and dysfunction of the reproductive system, as well as the central nervous system [3], [4].

Adsorption is considered one of the most applicable methods for dye removal from wastewater due to its high efficiency, simplicity, economy, and reusability [5]. An alternative to conventional adsorbents to remove dyes present in wastewater is the use of adsorbents based on the natural polymeric material, starch, due to the abundance of sources in nature, renewability, low cost, biodegradability, and non-toxicity. Among natural materials, clays also stand out as materials with good adsorption properties due to high surface area and cation exchange capacity, swelling, microporosity, layered structure, nano-size, as well as their lower cost compared to conventional adsorbents [6], [7].

The biocompatibility of clay and the biodegradability of starch make their combination a successful approach for the development of nanocomposites that can be used as effective adsorbents for dyes removal from aqueous solutions [7].

The aim of this study was to investigate the effect of starch modification with clay materials on dye adsorption efficiency. The prepared materials are based on starch/cationic starch and clay/diatomaceous earth. Structural characterization of the materials was performed by Fourier transform infrared spectroscopy (FTIR) technique while morphological properties were determined by Scanning electron microscopy (SEM). The possibility of their application for the removal of

anionic dye, methyl orange (MO) and cationic dye, crystal violet (CV) from an aqueous solution was investigated.

METHODS

Native wheat starch, cationic starch modified with glycidyltrimethyl ammonium chloride (with cationic degree 0.2), clay (kaolin), and diatomaceous earth were used for the preparation of adsorbent. The anionic dye – methyl orange and the cationic dye – crystal violet were used for the adsorption study. FTIR (Nicolet iS10, Fisher Scientific) and SEM (SEM JEOL JSM-6610LV) were used to characterize the tested adsorbents. A UV-Vis spectrophotometer for the visible range was used to determine the concentration of the tested dyes at 464 and 582 nm for MO and CV, respectively.

The preparation of the materials was performed in a two-stage procedure, according to the literature [8], [9] with some changes. 5 g of native starch (St) or cationic starch (CSt-G) was dispersed in 30 mL of deionized water and heated to 70 °C with constant stirring at 400 rpm for 1 h. Thereafter, 0.5 g of clay - kaolin or diatomaceous earth was dispersed in 30 mL of deionized water and added to a gelatinized native starch or cationic starch solution. The mixture was heated at 60 °C with stirring at 400 rpm for 3 h. The obtained materials were dried in an oven at 100 °C for 3 h and then ground into a powder.

Adsorption tests were performed in the batch system at room temperature. The adsorption efficiency of MO and CV was determined for constant adsorbent mass (0.05 g), solution volume (25 cm³), and initial concentration (10 mg/dm³) after 180 min of constant stirring of the dye solution. The amount of adsorbed dye was determined by measuring the concentration in the solution before and after the adsorption process, after time *t*. The adsorption efficiency (% E) of dyes from aqueous solutions, R, is calculated according to the equation (1) [10]:

$$\% E = \left(\frac{C_0 - C_t}{C_0} \right) \cdot 100 \quad (1)$$

where *C*₀ and *C*_{*t*} are the concentration of the dye at the initial time and after time *t* (mg dm⁻³), *V* is the volume of solution (cm³), and *m* is the amount of the adsorbent (g).

RESULTS AND DISCUSSION

The results of the FTIR analysis are shown in Figure 1.

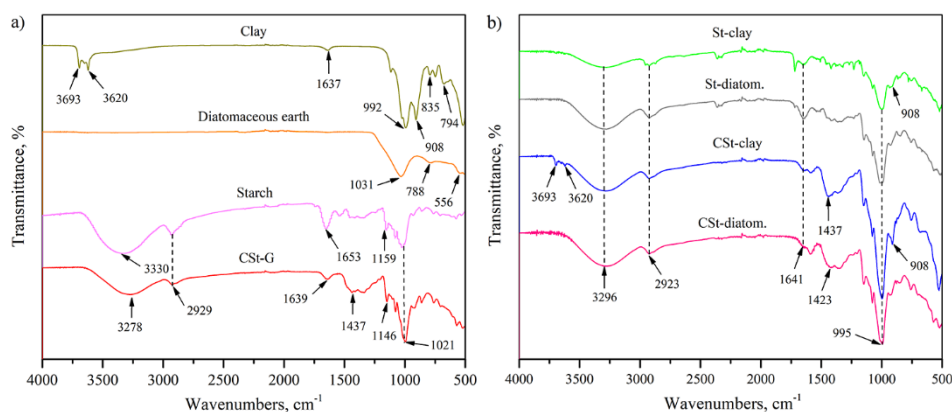


Figure 1. FTIR spectra of a) raw clay - kaolin, diatomaceous earth, native starch, and cationic starch and b) St-clay, St-diatomaceous earth, CSt-clay, and CSt-diatomaceous earth.

The spectra with characteristic peaks for the materials structures before the modification are shown in Figure 1a. For kaolin clay, bands at 3620 and 3693 cm⁻¹ correspond to the vibration of OH stretching which is bonded with Al on the surface. A peak corresponding to the O-H bending of water molecules appeared at 1637 cm⁻¹. For Si-O stretching, a broad intense peak was detected at 992 cm⁻¹

while the band at 908 cm^{-1} represents Al-O stretching of the kaolin structure. The bands at 835 and 794 cm^{-1} represented Fe-OH and Si-O stretching vibration [11]. On the FTIR spectrum of diatomaceous earth, a wide absorption band appears at 1031 cm^{-1} , which corresponds to Si-O-Si vibrations. The peak at about 788 cm^{-1} also corresponds to the structure of the silicate. The absorption peak of lower intensity at about 556 cm^{-1} corresponds to Si-O deformation and Al-O stretching [12]. For native starch and cationic starch, bands at 3330 and 3278 cm^{-1} corresponds to O-H stretching, 2929 cm^{-1} for C-H stretching, 1653 and 1639 cm^{-1} for H-O-H bending, while the signals at about 1000 - 1200 cm^{-1} were due to C-O stretching vibration. An additional peak at CSt-G spectrum at 1437 cm^{-1} originates from C-N stretching the quaternary ammonium cationic group (R_4N^+) [1]. All major peaks in the FTIR spectra of the synthesized samples (Figure 1b) coincide with the FTIR spectra of the starting materials (Figure 1a) with a slight shift of the peaks.

SEM micrographs of the prepared materials are shown in Figure 2. The main difference between the modification with native starch and cationic starch is in the appearance of the surface of the material. The surface of the materials in Figures 2a and 2b is smoother due to the smooth surface of the native starch, compared to the materials with cationic starch (Figures 2c and 2d), which has a rough surface with protrusions and holes. Also, in Figures 2a and 2c layered structures originating from clay can be seen, while in Figures 2b and 2d parts of the rod shape structure originating from diatomaceous earth are visible. The loss of clear boundaries between the materials, i.e. the connection of the starch structure with the structure of clay and diatomaceous earth, indicates a successful modification.

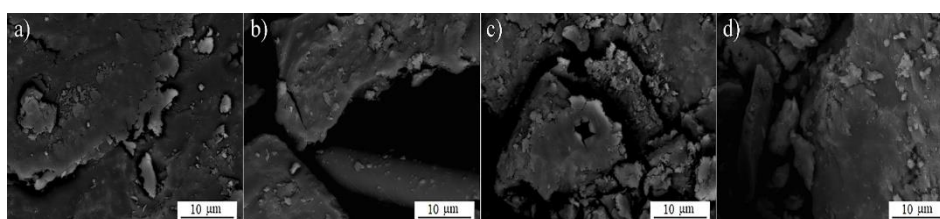


Figure 2. SEM micrographs of a) St-clay, b) St-diatomaceous earth, c) CSt-clay, and d) CSt-diatomaceous earth.

The results of the adsorption study are shown in Figure 3.

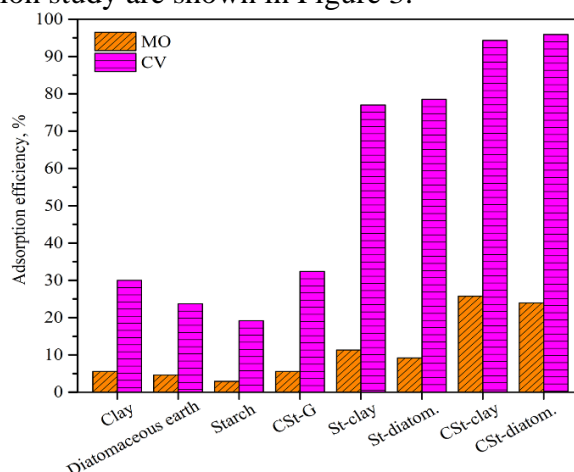


Figure 3. Adsorption efficiency of MO and CV dyes on the different materials.

Modification of starch and cationic starch contributed to the increase of adsorption efficiency in relation to the starting materials for both dyes. The results show that the prepared materials are more efficient in removing the CV dye from an aqueous solution compared to the MO dye. The differences

in the efficiency of CV and MO dye removal can be due to different dye structures, as well as differences in molar mass. Adsorption efficiency of over 90% was achieved for CV dye on cationic starch modified with clay and diatomaceous earth.

CONCLUSION

In this paper, the influence of starch modification with kaolin clay and diatomaceous earth on the adsorption properties of final materials was investigated. Adsorption was tested for the removal of methyl orange and crystal violet dyes from aqueous solutions. The results of the FTIR analysis indicated the presence of characteristic groups for the structure of starch, cationic groups for the structure of cationic starch, as well as silicate groups in the structure of kaolin clay and diatomaceous earth. SEM analysis also confirmed that the material modification was successful. Cationic starch modified with clay and diatomaceous earth proved to be a very effective material for removing crystal violet dye from an aqueous solution.

Acknowledgment

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REFERENCES

- [1] Lawchoochaisakul, S., Monvisade, P., and Siriphannon, P., *Carbohydr. Polym.*, 253 (2020) 117230.
- [2] Aly, A. A., and Hebeish, A. A., *Int. J. Sci. Res.*, 4 (2015) 4-12.
- [3] Lellis, B., Fávoro-Polonio, C. Z., Pamphile, J. A., and Polonio, J. C., *Bio. Res. Innov.*, 50 (2019) 1-16.
- [4] Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., and El Harfi, A., *Heliyon*, 5 (2019) e02711.
- [5] Pirbazari, A. E., Hashemian, S. F., and Yousefi, A., *J. Chem. Eng. Process Technol.* 6 (2015) 1000231.
- [6] Awad, A. M., Shaikh, S. M. R., Jalab, R., Gulied, M. H., Nasser, M. S., Benamor, A., and Adham, S., *Sep. Purif. Technol.*, 228 (2019) 115719.
- [7] Orta, M. M., Martin, J., Santos, J. L., Aparicio, I., Medina-Carrasco, S., and Alonso, E., *Appl. Clay Sci.*, 198 (2020) 105838.
- [8] Jain, S. K., Duttu, A., Kumar, J., and Shakil, N. A., *Arab. J. Chem.*, 13 (2020) 7990-8002.
- [9] Koriche, Y., Darder, M., Aranda, P., Semsari, S., and Ruiz-Hitzky, E., *Dalton Trans.*, 43 (2014) 10512.
- [10] Ilgin, P., Ozay, H., and Ozay, O., *Cellulose*, (2020) 1-16.
- [11] Kourim, A., Malouki, M. A., Ziouche, A., Boulahbal, M., and Mokhtari, M., *Defect and Diffus. Forum*, 406 (2021) 457-472.
- [12] Hanna, A. A., Sherief, M. A., and Aboelenin, R. M. M., *Res. J. Pharm., Biol. Chem.*, 5 (2014) 198-205.