

Removal of Cationic Dyes from Aqueous Solution using Organomodified Nanoclay

Sh. Mahmoudian

Department of Polymer Engineering, Kashan Branch, Islamic Azad University, Kashan, Iran

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ABSTRACT: In this work, organomodified nanoclay has been used as the adsorbent for the removal of basic blue 41, cationic dye from an aqueous solution. The performance of the organomodified nanoclay was tested in a batch system under varying pH (2–12), adsorbent dosage (0.1–2 g L⁻¹), initial dye concentration (10–60 mgL⁻¹), and contact time (5–100 min). The best conditions were achieved at pH of 7, 1 gL⁻¹ of adsorbent at contact time of 60 min. The results indicate that nanoclay adsorbs the cationic dye efficiently and could be employed in wastewater treatment for the removal of dyes that may be harmful to human health.

Keywords: *Adsorption, Cationic dye, Organomodified nanoclay, Wastewater treatment.*

INTRODUCTION

Water pollution caused by industrial wastewater has become a common problem for many countries. Today, dyes play a critical role in textile, paint and pigment manufacturing industries. To meet industrial demand, it is estimated that 1.6 million tons of dyes are produced annually, and 10–15% of this volume is discarded as wastewater [1, 2]. As a result, dyes are major water pollutants. Excessive exposure to dye causes skin irritation, respiratory problems and for some dyes increase cancer risk in humans. In addition, the presence of dyes in wastewater also contributes to high chemical oxidation demand and causes foul odor. Thus, it is of utmost importance to remove dyes from wastewater effectively to ensure safe discharge of treated liquid effluent into

watercourses [3, 4]. There are many technologies to remove organic dyes from industrial effluents including biological, adsorption, membrane, coagulation–flocculation, ozonation, and advanced oxidation processes. Because of the low biodegradability of organic dyes, conventional biological treatments are not efficient enough to degrade organic dyes and treat colored wastewaters; thus, organic dyes in aqueous solutions are degraded or removed through physicochemical processes [5, 6]. Among the physicochemical treatment methods, adsorption using solid adsorbent has been found to be efficient and economical. It is a mass transfer operation through which a solid material can selectively remove dissolved components from an aqueous solution by attracting the dissolved solute to its surface. This separation technique finds wide application in the

(*) Corresponding Author - e-mail: shmahmoudian2@gmail.com

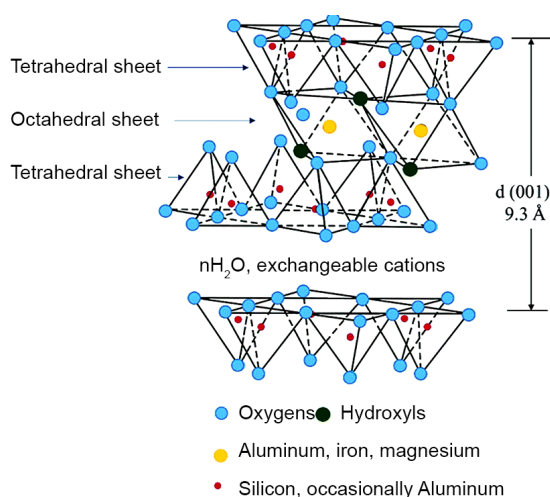


Fig. 1. Layered silicate structure [19]

removal of dye from aqueous media. To achieve and sustain efficient recovery of the desired water quality, a careful selection of adsorbent is of paramount importance [7-11]. Nanoclay is nanoparticles of layered mineral silicates, which is one of the cheapest nanomaterials that possesses properties such as being non-toxic to the environment, high specific surface area, high adsorption capacity, and high surface reactivity and stability. In recent years, nanoclay has been successfully applied for the removal organic substances of from water and wastewater [12-14]. Montmorillonite is one type of clay material, existing in most soils abundantly. Its structure is two tetrahedral sheets and one octahedral sheet (2:1). As shown in Fig. 1, the top and bottom are two silica tetrahedral sheets with an aluminum octahedral sheet in the middle. [15-18].

Montmorillonite has attracted more attention because of its potential to be intercalated by various types of cationic organic molecules between the aluminosilicate layers by ion exchange process which introduces different applications for these host-guest systems. The organoclays have superior compatibility with organic molecules, so they have found important applications such as pollutants removal, oil spill clean-up and polymer-clay nanocomposites. The selection of different groups for clay modification provides the required interaction between clay and other molecules. As shown in Fig. 2, nanoclay surface modification increase the interlayer distance that enhance the nanoclay efficiency in many applications such as adsorption process [20-22]. The aim of this study is

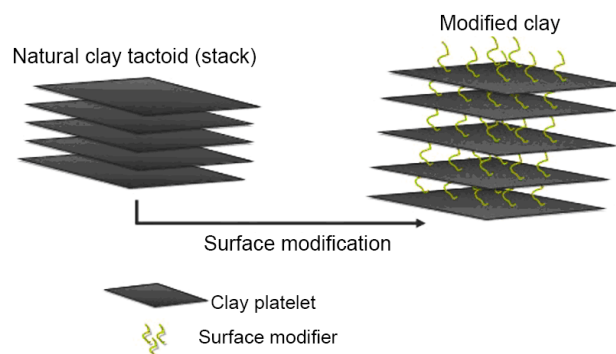


Fig. 2. Nanoclay structure modification scheme

to investigate the organomodified nanoclay efficiency for the removal of the cationic dye and to find out effects of adsorbent dosage, temperature, contact time and pH on the adsorption process.

EXPERIMENTAL

Materials

Organomodified Montmorillonite (MMT) nanoclay was obtained from Nanocore Inc. (Arlington Heights IL, USA.). The nanoclay was originally modified with 18- amino stearic acid. The commercial textile dye, basic blue 41, was obtained from a textile company and was used without additional purification. Fig. 3 shows the chemical structure of basic blue 41. All chemicals used in this study were of analytical-laboratory grade, being purchased from Merck.

Scanning electron microscopy analysis

A field-emission scanning electron microscope (FESEM) was conducted on FESEM (JEOL JSM-6701 F) to observe the morphology. Before observation by FESEM, the sample was coated by Pt using a sputtering instrument.

Adsorption studies

The batch equilibrium experiment was typically car-

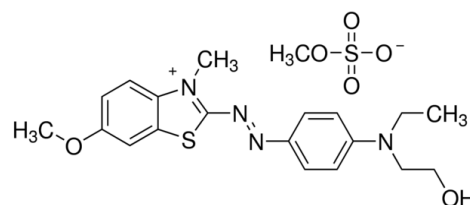


Fig. 3. Molecular structure of basic blue 41

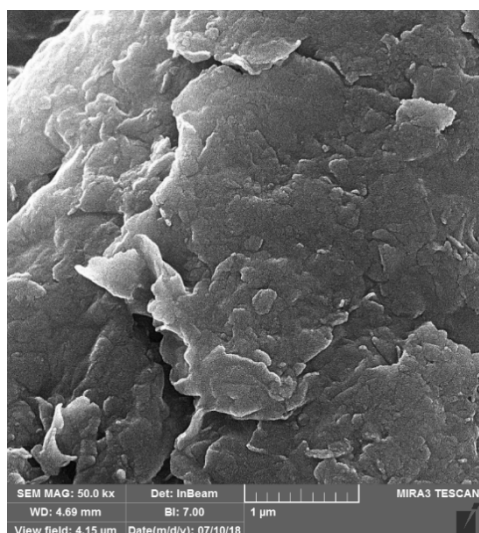


Fig. 4. SEM image of Organomodified nanoclay.

ried out to investigate the adsorption behavior. In each adsorption experiment, an amount of the adsorbent was added into the MB solution (50 mL) at the different concentrations (5–100 mg L⁻¹). The solution was stirred at room temperature to obtain a uniform adsorbent dispersion with the different dosages (0.5–3 g L⁻¹) and times (5-100 min). The desired dye solutions pH (2-12) was achieved through adjustment with 0.1 M of HCl and 0.1 M of NaOH. The solutions and solid phase were separated by centrifugation at 7000 rpm for 5 min in a Sigma 3-30k centrifuge. The dye concentration was determined on a double beam UV-Vis spectrophotometer by measuring absorbance at a maximum absorbance wavelength (λ_{max}). Each set of experiments was performed three times.

RESULTS AND DISCUSSION

Scanning electron microscopy analysis

The morphology of nanoclay was characterized using FESEM. Fig. 4 shows that nanoclay has a layered structure and smooth surface with the layer thickness in rang of nanometer.

Effect of time and initial dye concentration on adsorption

The effect of contact time on the adsorption of the dyes on nanoclay for different dye concentrations is illustrated in Fig. 5. Adsorption equilibrium time is de-

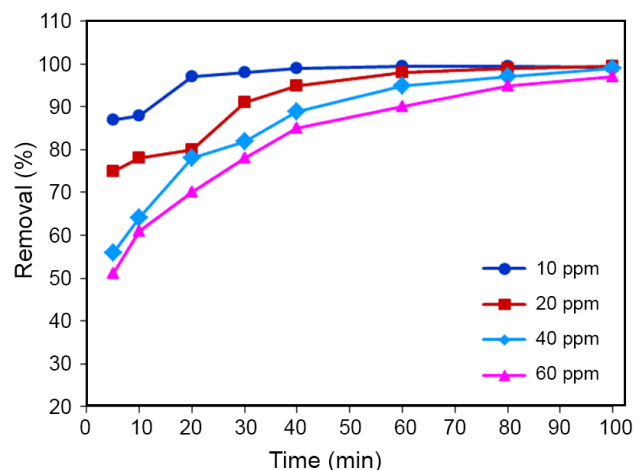


Fig. 5. Effect of initial dye concentration on dye adsorption as a function of time.

termined as the time after which the concentrations of the dyes solution remain unchanged during the course of adsorption process. The adsorption of cationic dye was fast initially, after that proceeds at a slower rate, and finally reaches equilibrium at about 60 min. This trend may be found due to the fact that initially the adsorption sites were vacant so that the dye interacts easily with the adsorbents. The results also show that, removal percentage decreased by increasing initial dye concentration. The decrease in dye adsorption could be due to the lack of available binding sites required for the high initial concentration of dye whereas the higher uptake of dye at low concentration may be due to the availability of more binding site on surface of the adsorbent for lesser number of adsorbate species. However by increasing the contact time up to 100 min,

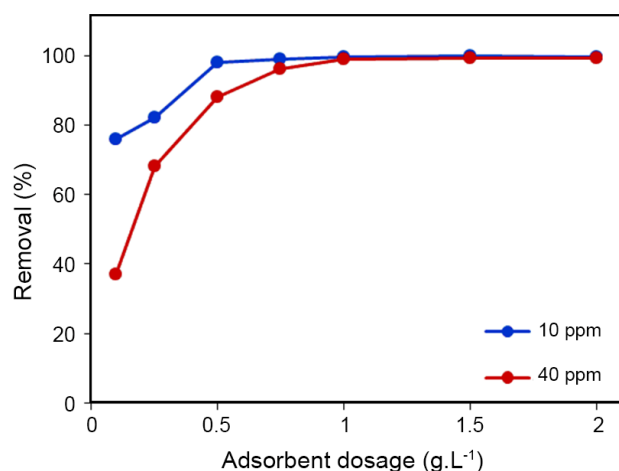


Fig. 6. Effect of organomodified nanoclay dosage on dye adsorption

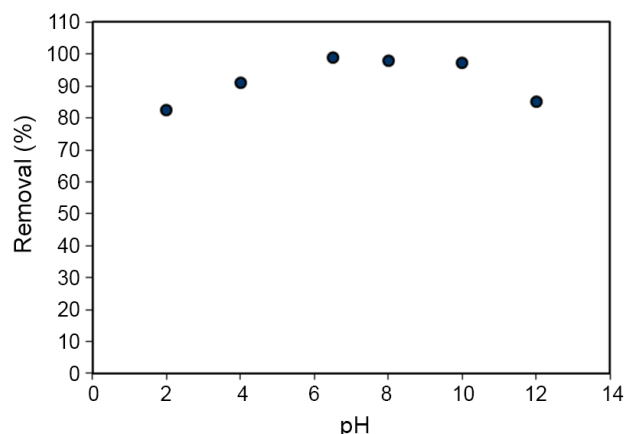


Fig. 7. Effect of pH on dye adsorption by organomodified nanoclay.

the dye removal percentage for all dye concentrations reaches to more than 97%.

Effect of adsorbent dose

The amount of surface available for adsorption certainly depends on the mass of the adsorbent. For this reason, the effect of nanoclay dosage on dye adsorption was studied in the range of 0.1–2 g L⁻¹. From Fig. 6, it was clearly observed that the removal percentage increased with increasing adsorbent dosage. The highest removal percentage for the solutions with 10 and 40 ppm of dye concentration was attained when the dosage of nanoclay was 0.5 and 1 g L⁻¹ alternatively. Increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface and availability of more adsorption sites. The good adsorption capacity of the modified nanoclay can be attributed to the electrostatic interaction between the nanoclay modifier and dye molecules.

Effect of pH

Fig. 7 shows the effect of pH in the range of 2–12 on the adsorption of dye onto organomodified nanoclay. It could be observed that a maximum adsorption uptake of 99 percent was achieved at pH 7. At lower pH, the competition between cationic dye and excess H⁺ ions obstructed the adsorption process, but a decrease in the proton concentration with increasing pH favored the reaction. The adsorption uptake at equilibrium slightly decreased at higher pH.

CONCLUSIONS

In the present study, the removal of a cationic dye from synthetic wastewater was investigated by using organomodified nanoclay. Factors affecting the adsorption process such as adsorbent dose, contact time, pH, and initial dye concentration were thoroughly studied. The maximum removal of dye was found to be 99% at pH 7 by organomodified nanoclay. The adsorption process equilibrium achieved within 60 min. From this study, it can be concluded that organomodified nanoclay could be used as an adsorbent for cationic dye removal from wastewater.

REFERENCES

- [1] Rai, H. S., Bhattacharyya, M. S., Singh, J., Bansal, T., Vats, P., and Banerjee, U. (2005). Removal of dyes from the effluent of textile and dyestuff manufacturing industry: a review of emerging techniques with reference to biological treatment, *Critical reviews in environmental science and technology*, 35, 219-238.
- [2] Mani, S., Chowdhary, P., and Bharagava, R. N. (2019). Textile wastewater dyes: toxicity profile and treatment approaches, In *Emerging and Eco-Friendly Approaches for Waste Management*, 219-244, Springer.
- [3] Dajic, A., Mihajlovic, M., Mandic-Rajcevic, S., Mijin, D., Jovanovic, M., and Jovanovic, J. (2019). Improvement of the Textile Industry Wastewater Decolorization Process Using Capillary Microreactor Technology, *International Journal of Environmental Research*, 13, 213-222.
- [4] Kant, R. (2012). Textile dyeing industry an environmental hazard, *Natural science* 4, 22-26.
- [5] Iddique, K., Rizwan, M., Shahid, M. J., Ali, S., Ahmad, R., and Rizvi, H. (2017). Textile Wastewater Treatment Options: A Critical Review, In *Enhancing Cleanup of Environmental Pollutants*, 183-207, Springer.
- [6] Forgacs, E., Cserháti, T., and Oros, G. (2004). Removal of synthetic dyes from wastewaters: a review, *Environment International*, 30, 953-971.
- [7] Seow, T. W., and Lim, C. K. (2016). Removal of

- dye by adsorption: a review, *International Journal of Applied Engineering Research*, 11, 2675-2679.
- [8] Cai, Z., Sun, Y., Liu, W., Pan, F., Sun, P., and Fu, J. (2017). An overview of nanomaterials applied for removing dyes from wastewater, *Environmental Science and Pollution Research*, 24, 15882-15904.
- [9] Tan, K. B., Vakili, M., Horri, B. A., Poh, P. E., Abdullah, A. Z., and Salamatinia, B. (2015). Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms, *Separation and Purification Technology*, 150, 229-242.
- [10] Suba, V., and Rathika, G. (2016). Novel adsorbents for the removal of dyes and metals from aqueous solution—a review, *Journal of Advanced Physics*, 5, 277-294.
- [11] Zhou, Y., Lu, J., Zhou, Y., and Liu, Y. (2019). Recent advances for dyes removal using novel adsorbents: a review, *Environmental Pollution*, 252, 352-365.
- [12] Salam, M. A., Kosa, S. A., and Al-Beladi, A. A. (2017). Application of nanoclay for the adsorptive removal of Orange G dye from aqueous solution, *Journal of Molecular Liquids*, 241, 469-477.
- [13] Cavallaro, G., Lazzara, G., Rozhina, E., Konnova, S., Kryuchkova, M., Khaertdinov, N., and Fakh-rullin, R. (2019). Organic-nanoclay composite materials as removal agents for environmental decontamination, *RSC Advances*, 9, 40553-40564.
- [14] Adeyemo, A. A., Adeoye, I. O., and Bello, O. S. (2017). Adsorption of dyes using different types of clay: a review, *Applied Water Science*, 7, 543-568.
- [15] Gupta, V. (2009) Application of low-cost adsorbents for dye removal—A review, *Journal of environmental management*, 90, 2313-2342.
- [16] Ho, Y., Ng, J., and McKay, G. (2000). Kinetics of pollutant sorption by biosorbents: review, *Separation and purification methods*, 29, 189-232.
- [17] Mahvi, A. H., and Dalvand, A. (2019). Kinetic and equilibrium studies on the adsorption of Direct Red 23 dye from aqueous solution using montmorillonite nanoclay, *Water Quality Research Journal*.
- [18] Lagaly, G. (1993). From clay mineral crystals to colloidal clay mineral dispersions, *Surfactant Science Series*, 427-427.
- [19] Kievani, M. B., and Edraki, M. (2015). RETRACTED ARTICLE: Synthesis, characterization and assessment thermal properties of clay based nanopigments, *Frontiers of Chemical Science and Engineering*, 9, 40-45.
- [20] Do Nascimento, G. M. (2016). Structure of Clays and Polymer–Clay Composites Studied by X-ray Absorption Spectroscopies, *Clays, Clay Minerals and Ceramic Materials Based on Clay Minerals*, 1.
- [21] Uddin, F. (2008). Clays, nanoclays, and montmorillonite minerals, *Metallurgical and Materials Transactions A*, 39, 2804-2814.
- [22] Gahlot, R., Taki, K., and Kumar, M. (2020). Efficacy of nanoclays as the potential adsorbent for dyes and metal removal from the wastewater: a review, *Environmental Nanotechnology, Monitoring & Management*, 100339.

AUTHOR (S) BIOSKETCHES

Shaya Mahmoudian, Department of Polymer Engineering, Kashan Branch, Islamic Azad University, Kashan, Iran, *Email: shmahmoudian2@gmail.com*