

Removal of Methylene Blue in Water Through Different Membranes

[¹] Phyophyo San, [²] Suntorn Sangsong, [³] Nuttaporn Pimpha, [⁴] *Peerakarn Banjerdki

[¹] Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Rd, Chatuchak Bangkok, 10900, Thailand

[²] National Nanotechnology Center National Science and Technology Development Agency, Thailand Science Park, Pahonyolthin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand,

[³] National Nanotechnology Center, National Science and Technology Development Agency, Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand,

[⁴] *Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Rd, Chatuchak Bangkok, 10900, Thailand

[¹] phyophyo.s@ku.th, [²] suntorn.san@ncr.nstda.or.th, [³] nuttaporn@nanotec.or.th, [⁴] *pbanjerdki@gmail.com

Abstract:

Textile industries emit contaminated waste water (dyes) to the environment. Elimination of dye (methylene blue (MB)) in an aqueous solution over the uncoated, and coated membrane (media) with three layers, two layers of titanium dioxide (TiO₂), and one layer of natural clay was investigated. The solutions of TiO₂ and natural clay were coated on the media through the dip-coating method. In addition, the filtration performance of the clay media was assessed using cross flow filtration of Methylene blue solutions containing 50 ppm under 3 bar pressure. Total Dissolved solids (TDS) can't remove by using uncoated and TiO₂ coated media since the concentration of TDS after filtration was less than that of the initial but 28% of TDS can remove by one layer of clay coated media. 67% of MB color can eliminate by two layers of TiO₂ coated media, as well as 97% of MB, can eliminate by clay coated media at the maximum wavelength of 665 nm. The media permeability of uncoated media is 1843 L/m²h, two layers of TiO₂ coated media is 389 L/m²h, two layers of TiO₂ coated media is 223 L/m²h, and one layer of clay coated media is 1.6 L/m²h separately at TMP 3 Bar.

Keywords: Textile industry, Elimination of dye, Crossflow filtration, Methylene blue, Dip-coating, Natural clay

I. INTRODUCTION

Dye contamination in wastewater can cause a great issue for the environment. Water contaminated with different colors can alter plant life, and therefore a whole ecosystem can be destroyed. Methylene blue is a widely used dye. Although methylene blue is commonly used in huge quantities in medical settings, it is also frequently employed in industrial settings such as textile and printing. As long as the environmentally friendly business is increasingly emphasized, with the increased emphasis on environmentally friendly business, it is critical to figure out how to clean industrial wastewater cost effectively and efficiently [1]. The dyes are challenging to treat by biological treatment due to their complex molecular structures [2]. Color, pH, TDS, suspended solids (SS), chemical oxygen demand (COD), biological oxygen demand (BOD), metal, temperature, and salts are all high in dye effluents [3]. So, color and TDS will reduce in this experiment. Several applied treatment systems for textile effluent involve physical, chemical, biological and systems the combinations of these systems[2]. Although filtration processes have a high initial setup cost, salt reuse, and permeate compensation compensates for this. pre-treatment of feed water, hydrodynamic cleaning with high crossflow velocity, optimization of chemical and operational variables such as pH and recovery ratio, and modification of the media surface have all been investigated as ways to reduce media fouling and expenses. Before the nanofiltration process, there are numerous relevant pre-treatment techniques, including media processes such as microfiltration (MF) and ultrafiltration (UF). Many studies have been conducted on the decolorization of textile effluent using nanofiltration technologies [4].

Due to its high separation and mixing operation, fewer environmental costs, and smaller energy utilization, membrane technology has emerged as a possible industrial alternative to classic separation technologies such as energy-intensive distillation [5], [6]. Generally, microfiltration can make sure greater flux, while ultrafiltration provides better purification efficiency, but membrane fouling creates a key challenge in both cases, which constraints their utilization due to economic [7], [8]. The two most common materials utilized in membrane production are ceramics and polymers. Ceramic membranes are usually applied in MF and UF, with NF and RO thrown in for good measure. Ceramic membranes have numerous technical advantages over polymeric media, including a thin and distinct pore size distribution, advanced porosity, better separation, and advanced flux; thermal, mechanical, and chemical stability, and longer media lifetimes; and complex hydrophilicity, high fluxes at low pressures, and lower fouling [9], [10], [11]. Membrane deformation is an important technique to enhance the membrane's performance. According to the change of membrane, it is possible to further improve the performance of the membrane under manipulated optimized conditions. The top layer for the separation is typically made by dip coating of Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 and natural clay powder [12], [13].

Transmembrane pressure (TMP) microfiltration, also known as crossflow microfiltration, is a common method for eliminating the particulate matter from a liquid solution using a pressure differential through a membrane. Water and wastewater treatment, food processing, mining activities, and highly specialized biotechnology are just a few of the uses of TMP microfiltration. The capacity to handle membrane fouling adequately is critical to the efficiency and competitiveness of this approach in practically all applications. Fouling occurs when suspended and/or dissolved chemicals meet deposits on the membrane surface. Because permeate fluxes in microfiltration are frequently high, convective transport is a major contributor to fouling; nevertheless, varying on the usage and feed composition, other transport processes may also play a role. Fouling can be decreased membrane performance and occurs over time as more material is transferred to the membrane. Adsorption, biofilm growth, and the creation of gel layers, pore blocking, and particle deposition, the last mechanism typically being regarded as resulting in filter cake formation are the ways to obvious membrane fouling. Crossflow shear, relaxation, backwash, and bubbling are all attempts to handle fouling, and they can all be useful in decreasing (but not eliminating) fouling at the disadvantage of greater operating expenses [14].

Through uncoated and TiO_2 and clay coated media, this experiment used the crossflow filtering technology to eliminate dye from textile industry effluent. SEM technique was used to compare the uncoated and three various coated media. Using UV-Vis Spectrophotometer, the effect of the various media on color elimination can also be seen.

II. EXPERIMENTAL

A. Chemicals

Ceramic media with a filter size, of 10 inches (the porosity of 0.5 micros) was purchased from Mazuma. Aeroxide TiO_2 P25 with a 25 nm average diameter was bought from Chamorn Chawton. Natural clay was got from the Thai Nippon chemical Industry and Industrial GR Grade Denatured Ethyl Alcohol ($\text{C}_2\text{H}_5\text{OH}$) was achieved from DUKSAN and PVA was obtained from Sigma Aldrich. Ceramic protective seal material was purchased from Homeonetech, Thailand. Sigma Aldrich provided the MB hydrate ($\text{C}_{16}\text{H}_{20}\text{ClN}_3\text{OS}$), and MB solutions were made by mixing with deionized water with a starting concentration of 50 ppm. The water utilized in this study was deionized (DI) water.

B. Coating solution preparation and media coating procedures

Aeroxide TiO_2 P25 is used to prepare the TiO_2 coating solution. 1 wt% TiO_2 was mixed with Deionized water and stirred at room temperature for 30 minutes. Simultaneously, 0.5 g of PVA was dissolved in 25 ml of DI water for 30 minutes at 120°C . After that, dilute PVA was added to

the TiO₂ solution and continued stirring for 20 min at room temperature. The refined natural clay powders were diffused in DI water with the amount of 2 wt% clays after 2 hours of continuous stirring and placed in a sonication water bath for 30 minutes to prepare the clay coating solution. Since the clay suspension that resulted was extremely stable, solid sedimentation was not observed after a week.

In this experiment, a cement protective layer was applied as a top layer to increase the adhesion of the TiO₂ and clay layer on the media. The cement protective layer cannot be affected the media surface in short term by accurate effects and cannot be affected human health in long term by chronic effects because of its good physical and chemical properties. Similarly, preinstallation, during installation, and after installation of the cement protective layer, or while the operation of the water treatment system must not be harmful to the public or the natural environment because of any material released. From the layer. 1 wt% of cement was mixed with ethanol at 400 rpm at room temperature for 2 h to get the cement protective layer solution.

Three and Two layers of TiO₂ coated media were achieved by a simple dip coating process by immersing each layer in TiO₂ solution for 1 minute. The clay coated media was also created by immersing in clay solution with a simple dip coating process. The immersion time in clay solution is the same as the TiO₂ immersion time. After each layer, the coated media was dried at room temperature for 24 hr during the coating process. Afterward, the cement protective layer solution was coated as a top layer on the three different coated media by spray coating method with a spray gun at a pressure of 3 Bar from a distance of 15 cm for 250 ml. Later, the top layer of coated media was dried at room temperature overnight.

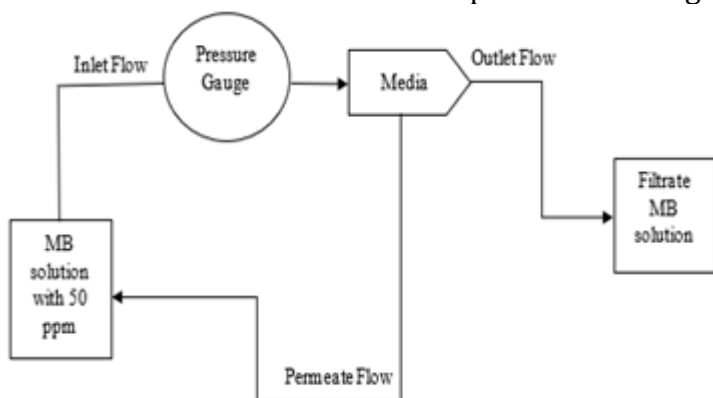


Fig.1. The schematic diagram for the elimination of MB from aqueous water by crossflow filtration
C. Elimination of MB from aqueous water by crossflow filtration

Crossflow filtration of MB, a typical textile dye, was utilized to assess the efficiency of the uncoated and three coated media. As in Fig.1, the MB solution with 50 ppm was pumped laterally into the media, while the pressure gauge and associated control valve keep the TMP constant. By collecting permeate in a balance over time, the filtration rate was determined. To calculate flux and permeability, the following formulas were used.

$$J_w = V / A \times t \quad (1)$$

where V (L) represents volume of permeate, t (h) represents time of filtration, and A (m²) represents the area of effective media.

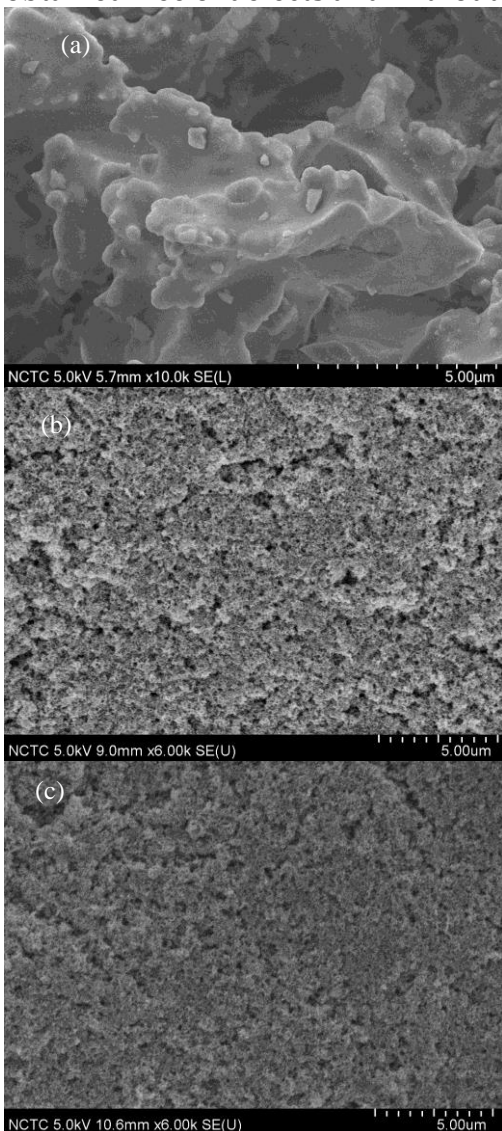
A UV-Vis Spectrometer (Perkin Elmer, model Lambda 650) was used to define the color eliminate percent of MB solution over the wavelength within the range of 500 to 800 nm. Since the observable light absorbance of the sample is at the wavelength of 665 nm, all the samples were measured at this wavelength to track the progression of color elimination. The color elimination rate was calculated using the following formula:

$$E_{\text{color}} (\%) = \frac{\text{Abs}_{\lambda_{\text{max}0}} - \text{Abs}_{\lambda_{\text{max}}}}{\text{Abs}_{\lambda_{\text{max}0}}} \times 100\% \quad (2)$$

where, $\text{Abs}_{\lambda_{\text{max}}}$ was the highest absorbency value of MB solution at 665 nm after filtration and $\text{Abs}_{\lambda_{\text{max}0}}$ was original absorbency value of MB solution before filtration.

D. Media characterization

The surface morphology and the quality of uncoated and three coated media surfaces were determined by Scanning electron microscopy (SEM) (Hitachi SU 5000) at $5\mu\text{m}$. Fig. 2 (a), (b), (c), and (d) displays the surface view of uncoated, three and two layers of TiO_2 coated, and one layer of clay coated media. In this figure, the difference between the top surface with uncoated and three different coated media can be found. The media with a clay coated layer exhibited a typical unequal structure, indicating that the surface layer adhered well to the media. By analyzing the surface morphology of the four different media, it can be noticed that clay coated media was obtained free of defects and without cracks.



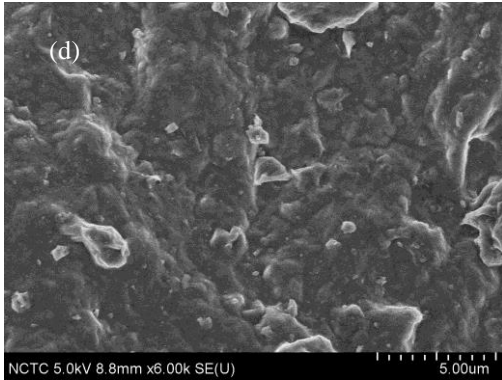
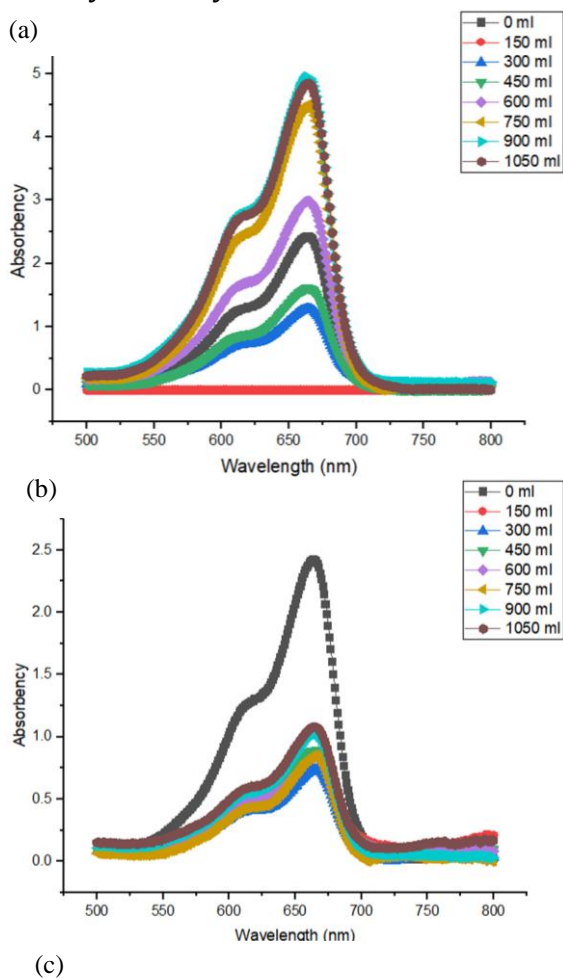


Fig.2 (a) (b) (c) (d). SEM images of uncoated, 3 TiO₂ coated, 2 TiO₂ coated, and clay coated media

III. RESULTS AND DISCUSSIONS

A. Effect of different media on decolorization

As shown in Fig. 3, the spectra of MB solution with four different media were evaluated to examine the elimination of MB color components. All the samples were collected every 150 ml. The initial MB solution with a concentration of 50 ppm is designated as 0 ml. Fig. 3 reveals that the spectrum changes of MB between initial and different media after filtration with a major absorption peak between 650 to 670nm. By comparing the four different media, clay coated media reduced the strength of absorption of the MB component in the solution, as shown in Fig.3 (c). Fig. 4 indicated the results of dye removal by filtering with four different media in the experiment. In these experiments, it can see two layers of TiO₂ coated media can remove 67% and one layer of clay coated media can remove 97% of the original MB individually.



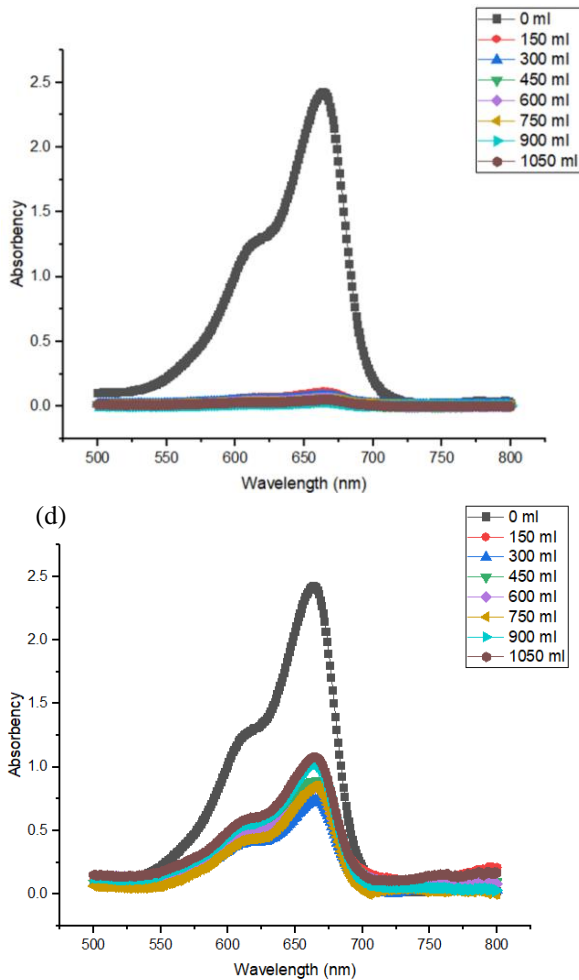
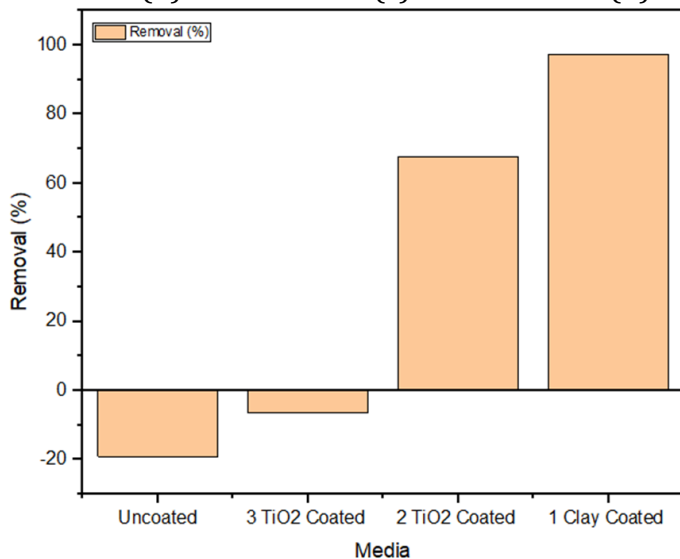


Fig.3. The spectra changes of MB solution (50 ppm) after filtration by different media (a) uncoated (b) 3TiO₂ coated (c) 2 TiO₂ coated (d) 1 clay coated



(c)

Fig.4. Color removal percent of different media

B. Effect of Different Media on TDS and pH Removal

The four media were tested one by one in a cross (d) ing cell with a media module. All the tests were performed at TMP 3 Bar and room temperature. Fig. 5 shows the effectiveness of TDS and pH removal by media. The samples were evaluated every 150 ml. TDS concentration of MB

solution after filtering was greater than the initial concentration in Fig. 5 (a) and (b), and TDS concentration of MB solution after filtration was the same as the initial concentration in Fig. 5. (c). Consequently, uncoated, three and two layers of TiO₂ coated media fail to extract TDS from MB solution adequately. However, after filtering by one layer of clay coated media, the TDS content of the MB solution was lower than that of the original can be seen in Fig.5 (c).

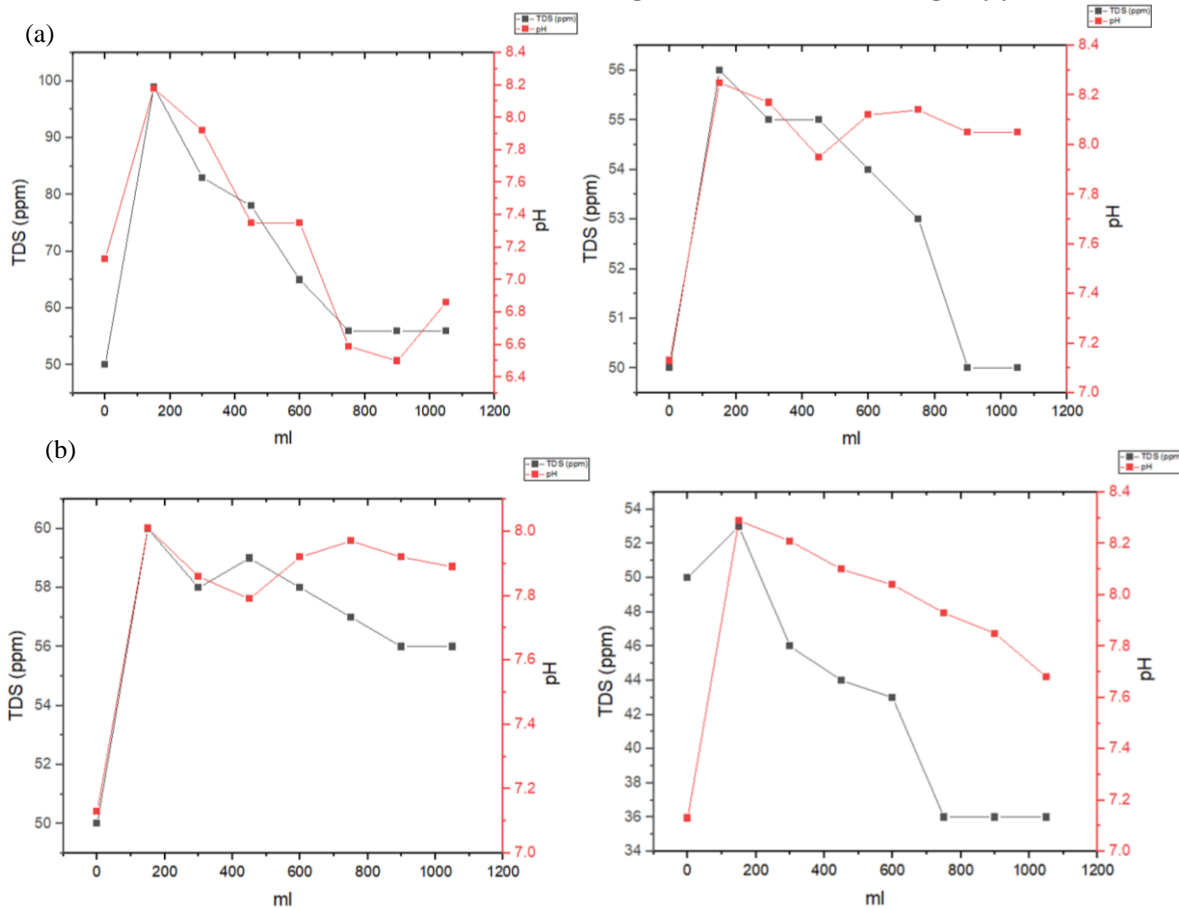


Fig.5. Effect on TDS and pH removal of (a) uncoated (b) 3 TiO₂ coated (c) 2 TiO₂ coated, (d) 1 clay coated media

C. Media flux and TDS removal percent comparison

Fig. 6 shows the water fluxes and permeability of uncoated, three and two layers of TiO₂ coated, and one layer of clay coated media. The uncoated media exhibited the maximum water permeability and the lowest TDS removal percent because its pore size was larger than the three coated media. Within the four different media, the water flux of clay coated media had the least permeability and maximum TDS removal percent (28%) with the smallest pore size. At 3 Bar TMP, the water permeabilities of uncoated, three and two layers of TiO₂ coated, and one layer of clay coated media were 1843, 389, 223, and 1.6 L/m² h, respectively.

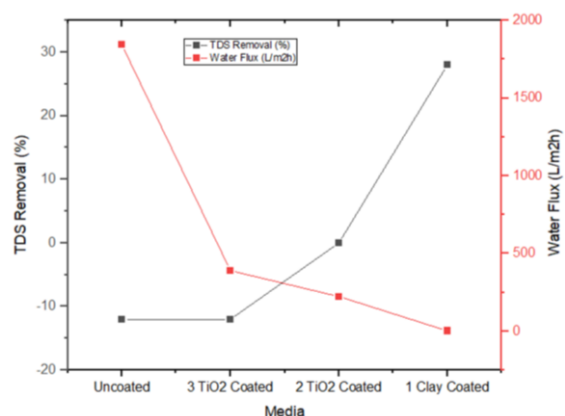


Fig. 6. Flux and TDS removal rates of different media

IV. CONCLUSIONS

The dye elimination (MB) from the solution was examined in this work by utilizing four different media: uncoated, three and two layers of TiO₂ coated, and one layer of clay coated media. Under identical testing conditions, uncoated, three, and two layers of TiO₂ coated media showed -19.3 %, -6.4 %, and 67 % in MB solution, respectively. One Layer of clay coated media can remove 28 percent of TDS with a flux of 1.6 L/m² h at that time the TDS concentration of the remaining three media was lower than the initial concentration after filtration. Moreover, clay powder is also less expensive than TiO₂ powder. According to this paper [15], the flux of clay media for Direct Red 80 and Rhodamine B dyes are 71 and 80 L/m²h while the flux of clay coated media for MB solution in this work is 1.6 L/m² h. Additionally, drying at ambient temperature between coating phases might conserve electricity more than the reference one. As a result, clay coated media is a low-cost environmentally friendly nanofiltration media with a defect free surface, the highest water flux, and good color removal percent.

REFERENCES

1. Wang, S., et al., The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, 2005. **284**(2): p. 440-446.
2. Zhang, J., et al., Degradation of methylene blue in aqueous solution by ozone-based processes. *Journal of Industrial and Engineering Chemistry*, 2009. **15**(2): p. 185-189.
3. Yaseen, D. and M. Scholz, Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *International Journal of Environmental Science and Technology*, 2018. **16**.
4. Tang, C. and V. Chen, Nanofiltration of textile wastewater for water reuse. *Desalination*, 2002. **143**(1): p. 11-20.
5. Younssi, S., M. Breida, and B. Achiou, Alumina Membranes for Desalination and Water Treatment. 2018. p. 221-254.
6. Shuit, S.H., et al., Membrane technology as a promising alternative in biodiesel production: A review. *Biotechnology advances*, 2012. **30**: p. 1364-80.
7. Kumar, R. and A. Ismail, Fouling control on microfiltration/ultrafiltration membranes: Effects of morphology, hydrophilicity, and charge. *Journal of Applied Polymer Science*, 2015. **132**.
8. Hakami, M., et al., Ceramic Microfiltration Membranes in Wastewater Treatment: Filtration Behavior, Fouling and Prevention. *Membranes*, 2020. **10**.
9. He, Z., et al., Ceramic-based membranes for water and wastewater treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2019. **578**: p. 123513.

10. Li, C., et al., Ceramic nanocomposite membranes and membrane fouling: A review. *Water Research*, 2020. **175**: p. 115674.
11. Burggraaf, A.J. and K. Keizer, Ceramic Membranes, in *Concise Encyclopedia of Advanced Ceramic Materials*, R.J. Brook, Editor. 1991, Pergamon: Oxford. p. 62-67.
12. Jung, J., et al., Sol-Gel Deposited Double Layer TiO₂ and Al₂O₃ Anti-Reflection Coating for Silicon Solar Cell. *Journal of Nanoscience and Nanotechnology*, 2018. **18**: p. 1274-1278.
13. Choi, H., E. Stathatos, and D.D. Dionysiou, Sol-gel preparation of mesoporous photocatalytic TiO₂ films and TiO₂/Al₂O₃ composite membranes for environmental applications. *Applied Catalysis B: Environmental*, 2006. **63**(1): p. 60-67.
14. Lorenzen, S., et al., Direct observation of fouling phenomena during cross-flow filtration: Influence of particle surface charge. *Journal of Membrane Science*, 2016. **510**: p. 546-558.
15. Souad, S., et al., Fabrication of low-cost ceramic ultrafiltration membrane made from bentonite clay and its application for soluble dyes removal. *Journal of the European Ceramic Society*, 2020. **40**: p. 2453-2462.