

# Cellulose-based membrane for adsorption of dye in batik industry wastewater

**Keywords:** fabrics, hydroxyl group, covalent bond, batik cloth, azo, diazo, or metal complex, anthraquinone dye, pollution

**Abbreviations:** PVA, polyvinyl alcohol; PEG, polyethylene glycol; CMC, carboxymethyl cellulose; MB, methylene blue

## Introduction

Batik is a traditional Indonesian cloth with a very diverse pattern of fabrics depending on the cultural background of the area where batik originates. Whatever the pattern of the batik cloth, all use almost the same dyeing technique, namely using synthetic and wax-resist dyes. The batik coloring process produces residual dye from the washing and rinsing process of the batik cloth.<sup>1</sup> Dyes commonly used in the batik industry are synthetic dyes because they are easy to obtain, cheap and produce bright colors and also because they are reactive due to reactive functional group and easily binds to the hydroxyl group of the fabric to form a covalent bond.<sup>2</sup> Types of batik dyes include anthraquinone-based, acidic, alkaline, containing azo, diazo, or metal complex.<sup>3</sup> In addition, synthetic batik dyes also contain heavy metals, namely Cd, Cr, Pb, Co, Cu, Hg, Ni, Mg, Fe and Mn.<sup>4</sup> One of the blue synthetic dyes that is often used in the coloring of the batik cloth is Reactive Blue 19, also known as Blue KN-R, it is a type of anthraquinone dye and is more difficult to decolorize than azo dyes because of its conjugated structure.<sup>5</sup> Indigosol dyes need to be activated using a solution of acid or nitrate and cause chromium residue in the waste water.<sup>6</sup> Unfortunately, most of the batik industry still discharges the waste from the batik dyeing process, directly into river bodies. This can cause pollution, because it causes changes in the quality, color and smell of river water. Efforts to overcome river water pollution can be carried out biologically, chemically and physically.

Filtering is a commonly applied physical method. Based on the size of the filtered particles, the types of filtering used are divided into four, namely microfiltration (100 nm-10  $\mu$ m), ultrafiltration (2-100 nm), nanofiltration (1-2 nm) and reverse osmosis-RO (0.1-1 nm).<sup>7</sup> Among the four types of membranes, the nanofiltration membrane is the most efficient, because its structure can filter wastewater into usable water.<sup>8</sup> The waste water for the batik industry in Malaysia contains a lot of Remazol and Vinyl Sulphone dyes. Filtering using a nanofiltration membrane made of aromatic polyamide with nonwoven and fibreglass wounded fibres support can filter water with Remazol Turquoise Blue dye more effectively than water with Remazol Yellow and Remazol Red dyes, which are characterized by the lowest color intensity after the filtering process.<sup>9</sup> The use of fiberglass in membrane technology requires quite high production costs, encouraging the search for alternative materials with more economical production costs, for example the use of cellulose. One of the materials used in the process of filtering wastewater is a cellulose-based membrane. This paper is a mini review of cellulose-based membranes for filtering waste water from the batik industry, especially waste caused by synthetic dyes.

## Cellulose acetate-based membrane

Putri et al.<sup>6</sup> made membranes from cellulose water hyacinth, polyvinyl alcohol (PVA) and polyethylene glycol (PEG) with a

Volume 4 Issue 6 - 2020

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**Received:** December 03, 2020 | **Published:** December 14, 2020

ratio of cellulose: PVA: PEG=6.5: 2.5: 1 (w/w), which can adsorb 38.75% chromium.<sup>6</sup> However, the filtering ability of cellulose-based membranes is still low, due to the compact and inactive structure of cellulose. An effort to improve this is by modifying cellulose into cellulose acetate, which is then used as a material for making membranes. Replacement of the hydrogen atom in the hydroxyl group of cellulose with an acetyl group ( $\text{CH}_3\text{CO}$ ), occurs through the esterification reaction of cellulose with acetic acid and acetic anhydride using a sulfuric acid catalyst (Figure 1). The esterification reaction which replaces 2 hydroxyl groups in cellulose produces cellulose triacetate which has properties, high melting temperature (300  $^{\circ}\text{C}$ ), high crystallinity and can only be dissolved in certain organic solvents, such as methylene chloride.

Cellulose acetate-based membranes can be used for both ultrafiltration, nanofiltration and RO filtering techniques. The use of cellulose acetate as a membrane ultrafiltration has been carried out since 1975. Cellulose acetate is dissolved in acetone and magnesium perchlorate is added, then it is used to separate various compounds, ranging from low molecular weight (58), namely NaCl, to high molecular weight compounds (160,000) namely  $\gamma$ -globulin. The filtering results show that at 65  $^{\circ}\text{C}$ , 100% of the globulin can be filtered and only 6% NaCl can be filtered. When the filtering process temperature was increased to 85  $^{\circ}\text{C}$ , the ability to filter NaCl increased to 23%.<sup>10</sup> The reverse osmosis membrane made of cellulose acetate was able to filter 86.5% of Turquoise Blue and 87% of Yellow dyes, after 4 stages of filtering.<sup>3</sup> The weakness of cellulose acetate-based membranes is the absence of reactive functional groups, resulting in

low separation efficiency based on the affinity principle.<sup>11</sup> In addition, cellulose acetate-based membranes have low permeability and tend to be prone to fouling. Thus, various modifications are made, for example by surface modification or mixing.

Cellulose acetate-based membrane modification (produced by electrospinning technique) by deacetylation process (with 0.5 mol.L<sup>-1</sup> NaOH solution), followed by a coating process with polydopamine. The membrane composite manufacturing stage, begins with dissolving acetic acid powder in a solvent mixture of acetone and N, N-Dimethylacetamide (2:1), oscillated for 24 hours at 333 K to produce an electrospinning solution containing 17% cellulose acetate. The nanofiber membrane of cellulose acetate was then deacetylated using 0.5 mol.L<sup>-1</sup> NaOH solution. Furthermore, it was coated with polymerized dopamine after stirring at 30 °C for 40 hours. The resulting membrane was able to increase the adsorption capacity of methylene blue dye to 88.2 mg.g<sup>-1</sup> at a temperature of 25 °C and a pH of 6.5 after adsorption for 30 h.<sup>13</sup> The mixing of chitosan and cellulose acetate is intended to improve the hydrophilic properties of the membrane in the presence of reactive groups (amino and hydroxyl groups) of chitosan.<sup>14</sup> The challenge that must then be resolved is how to increase the resistance (durability) of chitosan-cellulose acetate membrane composites and avoid segregation that can arise due to the difference in surface pressure between chitosan and cellulose acetate. Gopi et al.<sup>15</sup> made a composite membrane from cellulose acetate and chitosan with a ratio of 14: 1; 12: 2; 8: 3 with glacial acetic acid solvent, then sonified for 45 minutes and dried at room temperature for 24 hours.<sup>15</sup> Modifications to the deacetylation process were carried out by immersing the composite membrane sheets in 6M KOH for 3 hours, followed by rinsing using distilled water 2 times, then drying at room temperature. The deacetylation process effectively removes

acetate groups, resulting in a positive charge on the membrane surface so that it efficiently adsorbs anionic dyes in wastewater.

### Carboxymethyl cellulose-based membrane

Modification of cellulose by carbon methylation will produce carboxymethyl cellulose (CMC), as illustrated in Figure 2. CMC is a long chain anionic polysaccharide, which is soluble in water. The use of CMC as a membrane to adsorb dyes in the batik industry wastewater has been carried out by many researchers. The adsorption of dye waste with CMC membranes was carried out using methylene blue (MB).<sup>17,18</sup> The adsorption capacity of methylene blue by CMC reached 300 mg.g<sup>-1</sup>, higher than membranes made of pure cellulose (50 mg.g<sup>-1</sup>).<sup>17</sup> Uptake of MB by the CMC membrane is rapid and reaches equilibrium after 30 minutes. CMC with a degree of substitution of 0.09 showed the adsorption capacity of MB (concentration 663 mg.L<sup>-1</sup>) of 652 mg.m<sup>-1</sup>, while the uptake capacity of MB by CMC with DS 0.06, was 369 mg.g<sup>-1</sup>, at pH 8 and temperature 30 °C.<sup>18</sup> The weakness of the CMC membrane is that its mechanical strength is still low, thus limiting its service life. The development of CMC-based composite membranes is carried out to increase mechanical strength, accelerate and increase the adsorption capacity of dyes. Other than in form of membrane, CMC was utilized to adsorb dye, in form of beads, microspheres, hydrogel or block of gel. Liu et al. (2017) made a CMC-k-carragenan-activated montmorillonite composite bead. MB removal (%) exceeded 92% after 120 min using CMC / kC / AMMT (1: 1: 0.4 ratio).<sup>19</sup> The reusability of composite beads was good for five adsorption-desorption cycles.<sup>19</sup> The microspheres of CMC crosslinked with epichlorohydrin were successfully adsorb 998.2 mg.m<sup>-1</sup> MB and could be regenerated and reused with acidic buffer solution at pH 4.003 at least 10 times.<sup>20</sup>

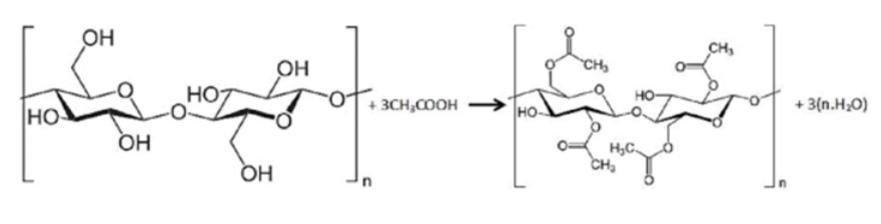


Figure 1 The reaction of cellulose with acetic acid produces cellulose acetate.

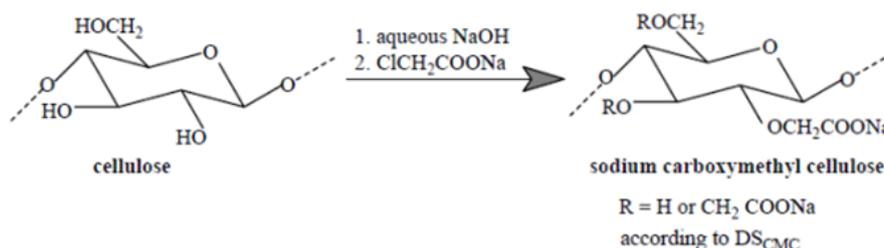


Figure 2 Reaction scheme of the carboxymethylation of cellulose.<sup>16</sup>

The hydrogels of CMC-acrylamide-graphene oxide were utilized for adsorption of Acid Blue-133 with maximum adsorption capacity of 185.45 mg.g<sup>-1</sup>.<sup>21</sup> CMC and tannin were combined and crosslinked with epichlorohydrin, shows maximum adsorption capacity of 1300 mg.g<sup>-1</sup>, when concentration of MB was lower than 2000 mg.L<sup>-1</sup>.<sup>22</sup> Zhang et al. (2014) developed a CMC composite membrane by grafting acrylic acid (CA) and was able to adsorb Methyl Orange, Disperse Blue 2BLN and malachite green chloride reached to 84.2%

(at pH <4, 50°C), 79.6% (at pH 7, 50°C) and 99.9% (at pH >9, 50°C), respectively. The surface area of CMC-CA adsorbent was 594.45 m<sup>2</sup>/g, with micropore volume and average pore diameter of 0.093 cm<sup>3</sup>/g and 6.5 nm, respectively.<sup>23</sup> Gorgieva et al (2020) developed a composite membrane from CMC as an adsorbent for anionic dyes and cellulose nanofibers as a reinforcing filler with citric acid as a cross linking agent. To obtain a highly porous (>90%) membrane structure with a pore size between a few nm to 200 μm, the freeze-cast technique

is used. The resulting membranes showed high and stable flux rates (150–190 kL/m<sup>2</sup> h MPa) with ~100% cationic dye adsorption, fast dynamic (8,536–5,446 kg/g min) and capacity (1828–1398 g/kg), high dye removal capacity (≥90%) even after 50th reusing cycle.<sup>24</sup> In addition to the presence of reactive functional groups, the adsorbent structure also greatly affects the effectiveness of filtering dye particles in batik industrial wastewater. Nano-adsorbent composite of CMC / graphitic-carbon nitride / zinc-oxide prepared by sol-gel technique, showed the adsorption ability of methylene violet of 96.43 mg / g at pH 8, because it has a large surface area, namely 9,214 m<sup>2</sup>/g.<sup>25</sup>

## Concluding remarks

Dyes from the batik industry can contaminate river waters if not treated first. A simple method that is effective in reducing river water pollution due to dye waste is filtering using a membrane. Membranes made from cellulose, especially those that have been modified into cellulose acetate or carboxy methyl cellulose, are able to function to filter out particulate dyes. Even the performance increases when combined with acrylamide-graphene oxide or graphitic carbon nitride - zinc oxide.

## Acknowledgments

None.

## Conflicts of interest

The authors declare that there is no conflict of interest.

## Funding

None.

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