Adsorption Behaviour of Hazardous Dye (Methyl Orange) on Cellulose-Acetate Polyurethane Sheets

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Abstract. Cellulose Acetate-Polyurethane (CA-PU) copolymer has been successfully prepared by a simple blending method and examined for its adsorption capacity against Methyl Orange (MO). Functional group characterization using Fourier Transform-Infrared (FTIR) confirms the urethane linkage formation as well as the presence of several essential functional groups (such as; O-H, C=O, and aromatic ring). Surface morphology changes are also observed using Scanning Electron Microscopy (SEM), where a smoother and porous structure is obtained in CA-PU. The adsorption isotherm is examined with Langmuir, Freundlich, Halsey, and Harkin-Jura models. MO adsorption on CA-PU sheets fits Freundlich isotherm ($R^2 = 0.9722$) with $K_F = 279.45$ mg/g. Kinetics studies of the adsorption with pseudo first-order and pseudo second-order plots exhibit that chemisorption is the adsorption limiting-rate.

1. Introduction
Increase of anthropogenic activities, most of the time, damage the environment, one of which through the release of toxic organic dyes to the environment. Hazardous dyes pollution can affect the environment by interfering the photosynthetic activities through sunlight blocking and increasing chemical oxygen demand (COD). Though it is not particularly harmful, the persistence of these dye compounds leads to long-term exposure, contributing to the mutagenic damage and carcinogenicity for aquatic biota [1]. Azo dyes are commonly used for wide purposes, such as in the textile, printing, and the pharmaceutical industries. Upon degradation, most of the azo dyes can produce aromatic amine and benzidine, which are responsible for carcinogenicity [2]. In this research, we take methyl orange as the model for the adsorptive removal of anionic azo dyes.

It is feasible to remove MO from aqueous solutions through adsorptive process. Several adsorbents have been investigated for its capability to remove MO, such as graphene oxide [3], aminated pumpkin seed powder [4], and cross-linked chitosan/β-cyclodextrin composite [5]. On the other hand, cellulose can be used as potential adsorbent material. Cellulose is a well-known abundant biopolymer, which can be obtained from various resources, including biomass. Nevertheless, cellulose performs a low adsorption capacity because of its limited functional groups that contribute to its active sites. To overcome the problem, cellulose is modified to become more functional groups-rich products [6-7].

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Cellulose acetate is the product derivative from cellulose that is used popularly in cigarette filters, textile fibers, pharmaceutical products, and composites. Its ability to adsorb dye pollutants has been investigated by many researchers [8-9]. It has high compatibility, non-toxic, relatively low-cost, and chemical-resistant properties [10]. The biopolymer also has a good interaction with water, while being insoluble. However, most of the time, it requires modifications. It is due to its weak thermal and mechanical properties as well as high swelling degree.

The addition of isocyanates into cellulose acetate mixture allows the formation of cellulose acetate-polyurethane (CA-PU) copolymer. Introduction of urethane linkage can affect its mechanical properties positively [11-12]. Moreover, the modification can balance the hydrophilicity of the cellulose-based material, in which the swelling degree problem has been reported to be solved [13]. Furthermore, the addition of polyurethane can increase the porosity of the material [14], thus can be expected to increase its surface area, resulting in higher adsorption capacity. Therefore, in this research, we prepare CA-PU copolymer by simple blending method with MDI percentage variation, to be applied later for MO adsorption from aqueous solution using a batch method.

2. Materials and Method

2.1 Materials

Materials used in this research included cellulose acetate (CA) with 39.3–40.3% acetylation degree, methylene diphenyl diisocyanate (MDI) purchased, 1,4-dioxane, silicon oil commercial as releasing agent purchased from, methyl orange (MO), distilled water, NaOH, acetone. All chemicals used are analytical grade and purchased from Merck, except for silicon oil and distilled water.

2.2. Preparation of CA-PU Sheet

CA-PU sheet was prepared following the procedure reported by G. Li et al. [12] with some modifications and simplifications. The first step was done by pouring 15 mL 1,4 dioxane into a beaker glass, heated on a hot plate at 70 °C for 1 minute. CA was weighed for 1 gram and slowly added to the beaker glass filled with 1,4 dioxane while stirred at 250 rpm. The temperature and stirring rate were maintained constant for 5 minutes. After that, MDI was added dropwise as many as the desired percentage (w/w CA) to the mixture. After the addition of MDI, the stirring rate was increased up to 750 rpm for 30 seconds and reduced back to 250 rpm for another 60 seconds to avoid the formation of air bubble. Next, the casting solution was poured onto the 3 x 12 cm$^2$ glass mold that had been coated with silicon oil as the releasing agent. It was left for 12 hours before released from the mold.

| No | CA (g) | 1,4 Dioxane (mL) | % MDI | Label |
|----|--------|------------------|-------|-------|
| 1  | 1      | 15               | 15    | MDI15 |
| 2  | 1      | 15               | 30    | MDI30 |
| 3  | 1      | 15               | 45    | MDI45 |
| 4  | 1      | 15               | 60    | MDI60 |

The obtained cellulose acetate-polyurethane (CA-PU) sheet is cut into small pieces (1 x 0.5 cm$^2$) and washed to remove the unreacted materials by leaving them in 100 mL acetone while stirred for 15 minutes at 500 rpm. After dried in a vacuum oven for 3 hours at 70 °C, CA-PU sheets are washed with NaOH 2% for 60 minutes. They are then neutralized with distilled water for multiple times and dried in a vacuum oven at 70 °C for around 12 h. CA-PU sheets obtained after this process are then stored in a plastic container for further use.

2.3. Characterization

Functional group analysis is carried out with Fourier Transform-Infrared (FTIR) (Shimadzu FTIR-Prestige 21 Series). Meanwhile, surface and cross-section morphology are analyzed with Scanning
Electron Microscopy (SEM) (Jeol. Jsm - 6510 LA). Samples used to compare before and after the copolymerization are CA, and CA-PU prepared with 45% MDI, respectively.

2.4. Adsorption

To determine which MDI percentage gives the best adsorption performance against methyl orange, MDI15, MDI30, MDI45, and MDI60 were used. The respective samples were weighed for 0.05 gram and added into Erlenmeyer 100 mL filled with 20 mL MO 20 ppm. The Erlenmeyer was mixed with a rotary shaker at 250 rpm for 3 h. MO solution before and after adsorption was determined for its concentration using UV-Vis spectrophotometer at 460 nm. Each concentration was determined three times to obtain the average value of the measured concentration. The removal percentage is then calculated using the following equation:

\[
\%\text{Removal} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%
\]

Where \( C_0 \) and \( C_t \) are initial and final MO concentrations, respectively.

Sample with the optimum MDI concentration, based on the previous procedure, was used for adsorption with concentration variation (30, 20, and 10 ppm). During each adsorption, 0.4 mL solution was taken periodically to determine the remaining concentration. The adsorption and the concentration determination were done continuously, until it reaches the equilibrium. The results are presented in the form of adsorption capacity, calculated from this following equation:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

Where \( q_t \) is adsorption capacity at \( t \) minute (mg/L), \( m \) is adsorbent weight (g) and \( V \) is MO volume (L).

3. Results and Discussion

3.1. Functional groups

As seen in Fig. 1, broad absorbance band at around 3700-3000 cm\(^{-1}\) is a response for hydrogen bond interaction due to the presence of O-H and N-H functional groups. The alcohol hydroxyl group can be observed at 3473 cm\(^{-1}\), where the change to narrow band after the copolymerization with PU indicates the formation of N-H groups. It confirms the formation of urethane linkage through hydroxyl and isocyanate reaction. Clearer absorbance peak at 1521 cm\(^{-1}\) is an evidence of the addition of aromatic ring from MDI. The absorbance peak at 3372 cm\(^{-1}\) and 1736 cm\(^{-1}\) correspond to O-H and C=O functional groups, respectively. The presence of functional groups such as C=O, O-H, and aromatic ring, contribute to the intensity of adsorption activities.

![Figure 1. FT-IR spectrum of (a) CA powder and (b) CA-PU sheet](image-url)
3.2. Morphology Analysis
Surface morphology analysis with SEM exhibits the difference between CA and CA-PU sheets. Cellulose acetate aggregates can be seen in CA surface, while the smoother surface is observed in CA-PU. It suggests the introduction of urethane linkage between cellulose acetate monomers can disperse the molecule, thus the agglomeration can be avoided. However, heterogenous micro-sized pores are found in the CA-PU surface.

Cross-section morphology analysis exhibits the different pore structure of both materials. While in CA the pore structure is found to be more dense, indicating the formation of porous space after the addition of reactive MDI. This structure is favorable for liquid adsorption due to its capability to give spontaneous diffusion of the liquid-phase adsorbate to the solid surface. As an addition, both CA and CA-PU exhibit the presence of a typical dense layer which is responsible for the adsorption selectivity.

![Figure 2. SEM image of: (a) pure CA sheet; (b) CA-PU sheet surface; (c) pure CA sheet; and (d) CA-PU sheet cross-section.](image)

3.3. Adsorption behavior
3.3.1 Adsorption by CA-PU prepared with MDI percentage variation
The highest MO removal percentage (25.54%) is obtained by the CA-PU sheet with the smallest MDI composition (MDI15). By increasing MDI composition, the adsorbent ability to remove MO from the aqueous solution is declining. This can be ascribed to the presence of active sites which is attributed to the functional group of cellulose acetate as observed in the FT-IR spectrum. The aromatic ring and C=O or O-H functional groups, observed in the FT-IR spectrum, enable adsorption of MO on the prepared adsorbent via covalent and π-π stacking interactions. The addition of MDI consequently can reduce the amount of the active functional group per gram adsorbent, which leads to less adsorption capacity.
The addition of isocyanate more than 25% of the total weight is reported to reduce the mechanical properties as reported by J. L. Rivera-Arment et al. [15]. This is due to the increased possibility of uneven distribution of polyurethane in the copolymer blend. However, the copolymerization is necessary to improve pure CA’s mechanical, thermal, and chemical resistant properties. T. Riaz et al. [13] reported that the copolymerizing CA and PU increase the mentioned properties. Though it is not investigated in this research, such improvements are required for the application of this adsorbent material. Therefore, to investigate the adsorption behavior of the CA-PU sheet, MDI15 is taken for the adsorption isotherm and kinetics studies.

Figure 3. Effect of MDI addition on MO removal percentage

Figure 4. Effect of contact time on adsorption capacity with concentration variation of 30, 20 and 10 ppm

3.3.2 Effect of contact time

The sharp increase of the adsorption capacity within the initial 30 minutes contact time suggests the diffusion of adsorbates into the pore structure of CA-PU. The rapid diffusion may be ascribed to the hydrophilicity of the adsorbent, where it shows a good affinity with the adsorbate. The diffusion can take form of surface or pore diffusion, where both transport processes can occur at the same time. Given the fact that the adsorbent has a good hydrophilic affinity with the adsorbate, thus surface diffusion may play more important role during the adsorption [16-17]. This is due to the nature of CA that has been known for its high hydrophilicity, in which, however, leads to its high swelling degree. It may later adversely affect the adsorption by reducing the surface area, which determines the adsorption ability of the material. Co-polymerization with PU may balance the hydrophilicity of CA.

As can be observed from fig. 4 adsorption equilibrium is reached after 120 minutes of contact time. During this state, the rate of adsorbate-adsorbent interaction becomes constant, thus no longer affected by the increase of contact time. The adsorption capacity at the equilibrium of each initial concentration is different, where higher initial concentration leads to higher adsorption capacity. This is due to the fact that higher concentration can induce more force to transfer the mass aqueous MO into the CA-PU sheet solid medium.

3.3.3 Isotherm studies

To understand the mechanism of MO adsorption onto the CA-PU sheet surface, Langmuir and Freundlich isotherm models are used. Langmuir isotherm models are based on the assumption that adsorption occurs in a single layer, where all the active sites have uniform adsorption energy [18]. For the Langmuir isotherm model, the linear equation is as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} + \frac{C_e}{q_{max}}$$  (3)
Where, \( q_e \) and \( C_e \) respectively are adsorption capacity and MO concentration at the equilibrium; \( Q_{\text{max}} \) and \( K_L \) respectively are Langmuir constants for adsorption capacity maximum and adsorption energy, respectively. On contrary, the Freundlich isotherm model, derived from Langmuir isotherm, is based on the assumption that the adsorption occurs in multilayers, where the active sites have heterogeneous energy [19]. The linearized form of the Freundlich isotherm model equation can be stated as follow:

\[
\log q_e = \log K_f + \frac{1}{n_f} \log C_e
\]  

(4)

Where, \( K_f \) (L g\(^{-1}\)) is Freundlich isotherm constant and \( n \) is adsorption intensity-related constant.

The isotherm in this research is initially judged by the correlation coefficient (\( R^2 \)), given by respective Freundlich and Langmuir plots. Both give high correlation coefficients (> 0.75), where they are 0.992 and 0.9722 for Langmuir and Freundlich plots, respectively. Though Freundlich plots give a lower correlation coefficient, \( \frac{1}{n} \) value obtained from the slope is not negligible (0.713). \( \frac{1}{n} \) explains adsorption linearity, where its value starts from 1 and downward [20].

Due to the stated fact, the adsorption is tested with other isotherm model plots that are based on the assumption of multilayer adsorption; Halsey and Harkin-Jura isotherms [21-22]. Halsey isotherm follows the assumption that adsorbates are distant from the adsorbent’s surface. While in Harkin-Jura isotherm, the multilayer adsorption occurs on the adsorbent surface with heterogeneous pore size distribution. The linear equations of both isotherms, respectively are as follows:

\[
q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_e
\]

(5)

\[
\frac{1}{q_e} = b - \left( \frac{1}{A} \right) \log C_e
\]

(6)

Where: \( K_H \) and \( n_H \) are Halsey isotherm constants; while \( A \) and \( B \) are Harkin Jura isotherm constants.

Correlation coefficients obtained from respective Halsey and Harkin-Jura isotherms are high, indicating their applicability for MO adsorption on CA-PU sheets. These results suggest the adsorption might follow the Freundlich isotherm better than Langmuir isotherm.

**Table 2.** Isotherm constants of Langmuir, Freundlich, Halsey, and Harkin-Jura models for MO adsorption on CA-PU sheets.

| Isotherm model | \( R^2 \) | Isotherm Constant |
|---------------|---------|------------------|
| Langmuir      | 0.991   | \( q_m \) (mg/g) 0.185 \( K_L \) (mg/g) 0.786 |
|               |         | \( R_L \) 10 ppm 0.113 20 ppm 0.060 30 ppm 0.041 |
|               |         | \( K_L \) (mg/g) 78.6 |
| Freundlich    | 0.972   | \( n \) 1.402 \( K_F \) (L/g) 279.45 |
| Halsey        | 0.972   | \( n \) 1.402 \( K_H \) 0.167 |
| Harkin-Jura   | 0.916   | \( A \) (mg/g) 0.739 \( B \) 1.430 |

Adsorption fitting both isotherms are common in a liquid phase, especially in low concentration. Low concentration gives less driving adsorption force. Thus, the adsorption is likely to be monolayer. To assess this possibility, dimensionless Langmuir constant (\( R_L \)) is calculated for each concentration. The formula is as follow:
The value of $R_L$ obtained from the slope of the Freundlich plot equation can be used to indicate adsorption intensity. When the value is more than 1, it indicates the domination of chemisorption taking place. In this research, it is found that the $n_F$ value is 1.402, indicating the possibility of chemisorption-dominant adsorption. In order to determine whether the MO adsorption falls into the chemisorption or physisorption category, kinetics studies are conducted.

$$R_L = \frac{1}{1+KLC_0} \quad (7)$$

$R_L$ value closing to 0 indicates the unlikelihood of Langmuir isotherm model, the otherwise is when the value is close to 1 [22]. As can be seen in Table x, $R_L$ is keep getting close to 0, indicating that the adsorption fitting to Langmuir isotherm is due to the low adsorbate concentration. Therefore, for MO adsorption on CA-PU sheets is suggested to fit the multilayer Freundlich isotherm model.

Figure 5. Plots of: (a) Langmuir; (b) Freundlich; (c) Halsey; and (d) Harkin-Jura Isotherm models for MO adsorption on CA-PU sheets

3.3.4 Kinetics studies
Experimental data of MO adsorption in this research are examined with pseudo-first-order and pseudo-second-order equations. Pseudo first-order modeling is based on the assumption that physical diffusion determines the adsorption rate. While, pseudo-second-order model describes the strong relationship between chemisorption and adsorption rate [23]. The equations of both pseudo-first-order and pseudo second-order can be seen as follows:
Where, $k_1$ (1/h) and $k_2$ (g/mg h) are the adsorption rate constants for pseudo first-order and pseudo second-order, respectively.

Solid thick lines in Fig. 6 represent the theoretical data while the thin lines with dots represent the experimental data. Pseudo first order plots give no agreement between the theoretical data and experimental data. Meanwhile good agreement between experimental and theoretical data is obtained in pseudo second-order plots. It suggests that chemisorption is the limiting-rate steps for MO adsorption on CA-PU sheets. Therefore, the adsorption is greatly affected by the presence of functional groups interaction of CA-PU surface and MO molecules. The process might involve the valency covalent [23] and π-π stacking forces [12], ascribing to the presence of C=O and aromatic rings of CA-PU sheets, which also contribute to its hydrophilic property.

**Figure 6.** Plots of: (a) pseudo-first-order; and (b) pseudo-second-order models for MO adsorption on CA-PU sheets

4. Conclusion

The addition of urethane linkage through copolymerization of PU and CA is suggested to change the chemical properties and morphology of the material. This copolymerization is made possible due to the reaction of hydroxyl groups from CA and diisocyanate from MDI, confirmed by the absorbance peak change and formation in the FTIR spectrum. Surface morphology analysis also proves the improvement of the material properties, where the dispersion of CA molecule and the formation of porous space are found. Nevertheless, the increase of MDI percentage more than 15% adversely affects the adsorption capacity of MO. Evaluation of isotherm models for MO adsorption on CA-PU sheets suggests the applicability of Freundlich isotherm ($R^2 = 0.9722$). This adsorption also fits with pseudo second-order kinetics model, which suggests the chemisorption-dominant adsorption. Therefore, the adsorption of MO on CA-PU sheets is majorly induced by the presence of functional groups that can form covalent and π-π stacking interaction with the adsorbate.

5. Acknowledgement

We would like to express our deep gratitude to Universitas Syiah Kuala for their valuable grant, under PRUUPD program Number: 860/UN11/SPK/PNBP/2019.
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