Preparation of *Cyperus diffusus* Vahl cellulose–polyaniline composite for dye removal

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**Abstract.** *C. diffusus* Vahl cellulose was used as an alternative in the preparation of cellulose–polyaniline composites. This involved the use of sodium hydroxide, hydrogen peroxide, and sulfuric acid as reagents for the isolation of *C. diffusus* Vahl cellulose. The isolated material was analysed using Fourier Transforms Infrared (FTIR) and the results showed the it has similar peaks pattern with the original cellulose as observed with 3333 cm⁻¹ for OH stretching, 2889 cm⁻¹ for C–H vibration, and several other indicators. The powder produced was used as a reaction partner for *in-situ* synthesis of *C. diffusus* Vahl cellulose-Polyaniline (*C. diffusus* Vahl cellulose-PANI) in dimethyl sulfoxide (DMSO) using ammonium persulfate (NH₄)₂S₂O₈ as the oxidator. The solid material product was effective in metanil yellow adsorption from the corresponding solution up to 99%.

1. Introduction

The use of polymer is familiar to mankind from the past up to the present moment. In recent times, several developments have been made and one of the useful polymers is polyaniline. Despite its strength, this polymer has a weakness caused by its rigid-rod macromolecular chains [1]. Therefore, several studies have been conducted to increase its processability by forming composites with other polymers such as the popular cellulose [2]. For instance, cellulose fiber was impregnated with polyaniline under *in-situ* reaction by a common procedure using ammonium persulfate as polymerization reagent. The composites produced were able to adsorb meloxicam effectively compare to independent cellulose fiber and polyaniline [3]. Moreover, water hyacinth was also used as a natural source of cellulose and later modified with polyaniline using a blending method. The composite formed was further applied as a sensor for humidity measurement in the room. These findings provide further information on the usefulness of cellulose-PANI as a polymer composite [4]. Furthermore, even though it is possible to use bacterial cellulose purely because it was produced by specific bacteria, it was also modified using PANI under some varied conditions and the results showed the characteristic of the blended materials was affected by the attributes of the matrix and the conditions of the reaction [5].

Surfactant such as cetyltrimethylammonium bromide (CTAB) was also discovered to have effects on the morphology and other characteristics of cellulose-PANI composites. The condition of the reaction provides a soft template to introduce reactants with lamellar structure into the connection between surfactant and anion of APS [6]. Moreover, some composites were synthesized via *in-situ* chemical
oxidation polymerization through the use of certain aniline precursor derivatives such as polyaniline (PANI), poly (N-methyl aniline) (PNMANI), and poly (N-ethyl aniline) (PNEANID) combined with cellulose. The capacity of the composites as adsorbent of AR4 and DR23 dyes was tested and the best result was found with PANI/cellulose [7]. In addition, the synthetic method of in-situ polymerization of aniline to coat the bacterial cellulose (BC) using interfacial polymerization was also reported, for example, on isolated bacterial cellulose in water and organic phase [8]. Other results showed BC/PANI nanocomposite membranes with both conductive and electrode resistant sides were easily obtained. The concentration of the oxidant also provided a significant effect on their microstructures [9]. Further developments showed Imperata cylindrica L. cellulose was isolated and used in a cellulose-PANI composite under some variations of HCl concentration. In this case, K2Cr2O7 was used as an oxidizer instead of the common ammonium persulfate and the desired product was obtained with good properties while the electrical conductivity was observed to be depending on the HCl concentration. Finally, the best condition was found at 3 M HCl as indicated by its production of the highest electrical conductivity [10].

These reported efforts toward the production of cellulose-polyaniline composites with high adsorbent capacity showed there is a need for further research, especially on the sustainability of the materials. This research was, therefore, conducted to provide new information on the utilization of local material, C. diffusus Vahl, as a natural cellulose resource and the composite produced was applied as an adsorbent on metanil yellow dyes in synthetic waste.

2. Material and Methods

2.1. Materials

Aniline as a precursor for synthesis of polyaniline was purchased from Merck (98% purity) and used as purchased. HCl, NaOH, H2SO4, DMSO, H2O2, (NH4)2S2O8 (ammonium persulfate, APS), acetone, and metanil yellow were used as received. Demineralized water was used for preparing some solutions and for cleansing the solid materials prior to further steps. C. diffusus Vahl was collected from coastal area in Bengkulu city.

2.2 Procedure

The cellulose was extracted from C. diffusus Vahl by modifying a previously applied procedure [10-12]. The pieces of dried sample were ground to powder and placed in a round bottom flask after which 1 M NaOH was added at a ratio of 10 g/120 mL. The mixture was heated at 80 °C for 1.5 h and the solid material produced was cleansed using demineralized water. The cleansed solid materials in 50 mL H2O2 5% heated at 80°C for 20 minutes, cooled to room temperature followed by filtration. Furthermore, the solid material residue was added to 60 mL H2SO4 (2 N), stirred at room temperature for 30 minutes, then the solid material obtained was rinsed using demineralized water and later dried using an oven at 50 °C for 24 h for further analysis.

The in-situ synthesis of C. diffusus Vahl cellulose-polyaniline also followed the modifications of a standard procedure [3]. Typically, 0.5 g as-prepared cellulose was added to 25 mL dimethyl sulfoxide (DMSO) and stored at room temperature for 1 h followed by the addition of 0.5 g aniline and stirring for another 1 h. Moreover, 80 mL of 1 M hydrochloric acid was added to the mixture after which 4.86 g of APS was slowly added for 30 minutes [13]. The mixture was further stirred for 1 h and stored at room temperature for 24 h. It was later rinsed with 100 mL of 0.2 M HCl and 100 mL acetone. The solid material was dried at 60°C for 24 h and stored in a desiccator for further analysis and application. In order to identify the functional group of cellulose and C. diffusus Vahl cellulose-PANI, a Fourier transform infra-red (FTIR, Bruker) analysis was performed. The surface areas of the materials were measured using Brunauer, Emmett and Teller (BET) method (Quantachrome® ASiQwin™ analyzer).

The application of the material obtained for adsorption started with the preparation of the calibration curve by measuring the absorbance of standard solutions of 2, 4, 6, 8, and 10 mg/L metanil yellow using UV-Vis spectrophotometer (Cary 60 UV-Vis - Agilent). The adsorption ability of the
polymers was evaluated by adding 10 mL of 10 ppm metanil yellow to 10 mg of the cellulose-PANI composite. After 90 minutes, the aliquot’s absorbance was measured using a UV-Vis spectrophotometer. Furthermore, a control experiment was conducted using cellulose as an adsorbent following a similar procedure. All the experiments were repeated three times.

3. Results and Discussion

Figure 1 shows the natural cellulose was isolated from the *C. diffusus* Vahl which are grown in the coastal area and with limited reports showing their utilization for polymer development. The extraction processes involved the use of some chemicals such as sodium hydroxide, hydrogen peroxide, and sulfuric acid to remove lignin, bleaching, and hemicellulose hydrolysis, respectively as shown in Figures 1a-c [14]. The processes were conducted easily in every step and the material obtained was in yellow-white powder form. Moreover, *in-situ* polymerization of aniline was conducted in the presence of *C. diffusus* Vahl cellulose and a desired black sticky composite material was produced as shown in Figure 1d.

![Flow chart of extraction of *C. diffusus* Vahl cellulose from the raw material to the final composite product: (a) *C. diffusus* Vahl growth location, (b) *C. diffusus* Vahl powder, (c) final product of *C. diffusus* Vahl cellulose, and (d) *C. diffusus* Vahl cellulose-PANI composite.](image)

Further investigation was conducted to identify the functional group changes of the cellulose after it was treated with aniline under *in-situ* polymerization and the results are shown in Figure 2. Some specific peaks are shown in Figure 2(a) with $3333 \text{ cm}^{-1}$ found corresponding to O-H group, $2889 \text{ cm}^{-1}$ to C-H stretching vibration while the sharp peak at $1026 \text{ cm}^{-1}$ was corresponding to –C-O- bonding in the cellulose structure. These peaks are almost similar to the patterns of the reported cellulose [15]. However, Figure 2(b) shows a peak at $3226 \text{ cm}^{-1}$ corresponding to N-H of polyaniline as well as $1666 \text{ cm}^{-1}$ and $1436 \text{ cm}^{-1}$ assigned as an aromatic chain for the double bond (C=C). In addition, the peak at $796 \text{ cm}^{-1}$ was the area showing the C-H bonding of the cellulose and aniline aromatic rings.

Further experiment involved the application of extracted *C. diffusus* Vahl cellulose and *C. diffusus* Vahl cellulose-PANI composite as an adsorbent for metanil yellow solution. This is important because metanil yellow is widely used in many industries such as textiles and cosmetics. Unfortunately, they produce wastes that have an environmental impact due to their carcinogenic nature and inability to degrade naturally [16].
Figure 2. FTIR spectra of (a) C. diffususVahl cellulose, (b) C. diffususVahl cellulose-PANI Composite.

This metanil yellow standard solution has a specific absorbance at 437 nm and a linear regression was obtained from the aforementioned peaks. This was further used to easily determine the amount of metanil yellow absorbed by C. diffusus Vahl cellulose and C. diffusus Vahl cellulose-PANI. The adsorption efficiency was calculated using equation (1) and the amount of metanil yellow adsorbed (mg/g adsorbent) was calculated using equation (2).

\[
\text{Adsorption efficiency} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \\
\text{Adsorption capacity} = \frac{(C_0 - C_t) \times V}{W}
\]

Where \(C_0\) is the initial concentration of metanil yellow and \(C_t\) is the final concentration after it has been treated with the adsorbent, \(V\) (L) is the volume of the solution, \(W\) (g) is the mass of absorbent used. The results are shown in Table 1.

| Repetition | Adsorption efficiency of C. diffususVahl cellulose (%) | Adsorption capacity of C. diffususVahl cellulose (mg/g) | Adsorption efficiency of C. diffususVahl cellulose-PANI (%) | Adsorption capacity of C. diffususVahl cellulose-PANI (mg/g) |
|------------|--------------------------------------------------------|-------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| 1          | 0.548                                                  | 0.055                                                 | 97.648                                                   | 9.765                                                    |
| 2          | 3.078                                                  | 0.308                                                 | 99.103                                                   | 9.910                                                    |
| 3          | 2.720                                                  | 0.272                                                 | 99.461                                                   | 9.946                                                    |
| Average    | 2.115 ± 1.369                                         | 0.212 ± 0.137                                         | 98.737 ± 0.960                                           | 9.874 ± 0.096                                           |

Table 1 clearly shows the presence of PANI increased the adsorption efficiency of cellulose from 2.115% to an extremely high adsorption capability > 99%. The adsorption capacity of the C. diffusus Vahl cellulose-PANI composite (9.874 mg/g) was also higher than the corresponding C. diffususVahl cellulose in the absence of PANI (0.212 mg/g). This was further confirmed by visually differentiating between the results of both materials as shown in Figure 3. Although BET analysis show that the C. diffusus Vahl cellulose has higher surface area (40.108 m²/g) than the C. diffusus Vahl cellulose-PANI composite (25.918 m²/g), the C. diffusus Vahl cellulose-PANI composite has higher adsorption
efficiency due to the higher porous matrix than the *C. diffusus* Vahl cellulose. The other possibility is the presence of specific chemical interaction between metanil yellow with *C. diffusus* Vahl cellulose-PANI could increase the adsorption efficiency. This research showed it is possible to use *C. diffusus* Vahl cellulose-PANI composite as an alternative adsorbent for metanil yellow and other dyes.

![Figure 3. Visual differentiation of metanil yellow treated with (a) *C. diffusus* Vahl cellulose, (b) *C. diffusus* Vahl cellulose-PANI.](image)

4. Conclusion

*C. diffusus* Vahl from the Bengkulu coastal area has the potential to be used as an alternative cellulose source for manufacturing natural-based composites. It was found that *C. diffusus* Vahl cellulose-PANI to have an average of >99% efficiency which is higher than the cellulose precursor.

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