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Effect of Initial pH for the Decolouration of Methylene Blue in Aqueous Solution Using Nanocellulose From Durian Husk

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ABSTRACT

An effective strategy for ensuring the long-term availability of accessible resources involves the utilisation of green technology that integrates plentiful resources like cellulose. Cellulose has numerous qualitative advantages, such as being biodegradable, eco-friendly, biocompatible, and rich in hydroxyl (OH) groups. Consequently, cellulose supplies are plentiful and may be replenished in the environment. Thus, cellulose is commonly employed in the packaging, healthcare, and textile sectors. An investigation was conducted to examine the impact of the initial pH on the process of decolorizing methylene blue. The data reveals that a pH level of 44.4% exhibits worse performance compared to a higher pH level. Specifically, a pH level of 7 achieves a maximum decolouration of up to 98%. The study employed methylene blue (MB) as a model for the adsorption investigation. The results of this study suggest that cellulose nanofibrils (CNF) obtained from durian husk possess favourable characteristics as an adsorbent material or as a framework for the immobilisation of nanoparticles for use in nanoelectronics applications, which is a subject of interest.

Keywords: *Cellulose nanofibril (CNF), decolouration, durian husk, initial pH, methylene blue*

1. INTRODUCTION

Agricultural products play a significant role in the national economy, particularly in emerging countries and ASEAN regions [1]. Agricultural activities typically involve the processes of seeding, fertilising, planting, and harvesting, which have a direct impact on the quantity and quality of the products [2]. Hence, agricultural waste constitutes a fundamental element of this activity. Due to the progress in technological understanding, this agricultural waste has been extensively studied and recognised as a novel source of prosperity within the framework of the "Circular Economy" paradigm.

Utilising agricultural waste components has been observed to decrease disposal maintenance expenses and mitigate the environmental impact caused by the incineration of agricultural waste [3]. The agricultural waste consists of carbohydrates, proteins, and micro and macro-nutrients. However, the most important components in solid form are hemicellulose/cellulose and lignocellulosic compounds, which are challenging to handle using traditional methods [4].

The Malaysian agricultural industry received a contribution of 448,271.51 metric tonnes of durian in 2021, with a transaction value of RM8.4 billion [5]. Consequently, 60% of the garbage is discarded and transforms into agricultural waste, which can give rise to diverse pollution issues. Consequently, in recent years, researchers have initiated investigations into the potential inherent in durian husks to address the aforementioned issues. For instance, Balram et al. (2016) discovered an antifungal characteristic in the durian husk (DH) [6].

Cellulose is an abundant and readily available resource present in the environment. Scientists globally have devised various effective techniques to expand the applications of cellulose, including the conversion of cellulose into cellulose nanofibril (CNF) and cellulose nanocrystal (CNC) forms [7].

Cellulose nanofibrils (CNF) exhibit excellent adsorption properties, making them a highly effective natural adsorbent. Cellulose pulp is subjected to mechanical or chemical procedures to extract CNF. Usually, the procedure starts with readily available bleached kraft pulp or sulphite pulp. Afterwards, the pulp needs to undergo further defibrillation procedures, including high-pressure steam explosion, homogenization, and chemical treatments [8]. Researchers have extensively studied several applications of CNF, such as reinforcement in composites, thickening agents in food and paint, electronic devices, and scaffolds for tissue growth [9].

The efficacy of CNF as a cationic dye adsorbent has not been definitively proven, in contrast to cellulose nanocrystal (CNC) which has exhibited encouraging outcomes in this aspect. The objective of this study is to examine the influence of the initial pH value on the process of removing colour from water, specifically focusing on the decolorization of dyes. Methylene blue (MB) will be used as a representative dye in an aqueous solution.

2. MATERIALS AND METHODS

2.1. Materials

The DH was bought from local street vendors and consisted of a variety of durian species. The chemicals used in the experiment were sodium chlorite (80% purity, Acros Organics, US), glacial acetic acid (95% purity, R&M Chemicals, MS), methylene blue, and sodium hydroxide (99% purity, Merck). Hydrochloric acid (32% purity, JT Baker, India) was also utilised without any additional purification.

2.2. Methods

2.2.1 Delignification and Defibrillation of Durian Husk

The DH, seen in Figure 1(a), had several rinses with distilled water to eliminate contaminants introduced during the manufacturing stage. Subsequently, it was subjected to vacuum drying to attain a moisture content of less than 10%. The DH was subsequently pulverised to obtain powdered forms.

The delignification process used acid-chlorite bleaching, which was carried out six times. In each cycle, 1.125 g/g of sodium chlorite and 1.25 g/g of acetic acid were used. Following the treatment, the sample underwent multiple rinses with distilled water, as depicted in Figure 2(c), prior to the nano-fibrillation process. The nano-fibrillation method involved utilising a high-speed blender, with the addition of 0.7wt% of NaCl as a counter ion.

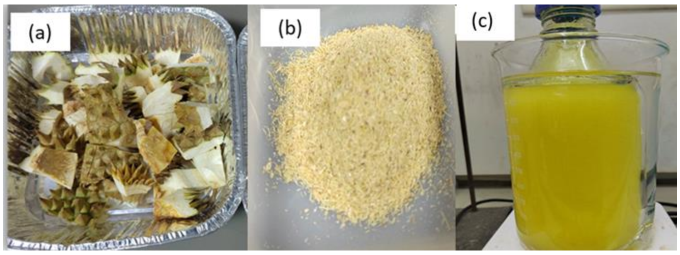

Figure 1. a) Durian husk (DH) before treatments, b) DH powder after vacuum-drying and grinding into powder, and c) delignification; acid chlorite delignification process.

2.3. Drying Methods

Two drying procedures, vacuum-dry and freeze-dry, were selected for pre-treatment and storage purposes.

2.3.1 Vacuum-drying

The vacuum-drying procedure was conducted utilising a vacuum oven (Model V-200, Memmert, Germany) at 40°C and a vacuum pressure of 50 millibars. The samples were subjected to heat using a heating plate located in the drying chamber of a vacuum oven measuring 550 × 600 × 400 mm and operating at a power of 1200 W. The heating process was conducted until the samples achieved a moisture content of less than 10%.

2.3.2 Freeze-drying

The freeze-drying process was conducted at a temperature of -110°C utilising the Scanvac and Coolsafe 110-4 equipment, after the freezing of all the samples at -80°C. This requirement is necessary to ensure that all samples have completely solidified prior to the lyophilization procedure.

2.4. Effect of initial pH

The starting pH of MB was adjusted to the target pH values (2, 4, 7, 9, and 11) by utilizing 0.1 M NaOH and 0.1 M HCl. An investigation on the kinetics of adsorption of methylene blue (MB) onto cellulose nanofibril (CNF) derived from durian husk. A 100 mL solution of MB with a concentration of 10mg/L was placed in a 250 mL flask. The solution was then mixed with 0.1 g of adsorbent, as depicted in Figure 1. At regular 10-minute intervals, a volume of 0.1 mL of MB solution was extracted, and the present concentration of MB was measured using a spectrophotometer. The percentage of the decolorization was then estimated based on the amount of colour degradation.

$$\%\,Decolouration = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_0 and C_t are the initial concentration and concentration of the dye at a time, t (mg/L) respectively.

Concurrently, the determination of the amount of dye absorbed per unit mass of adsorbent at a specific time t, represented as q_t (mg/g), was conducted using the following equation.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

Where C_0 and C_t are the initial concentration and concentration of dye at time, t, (mg/L), while m and V are the mass of adsorbent (g) and volume of dye solution (L).

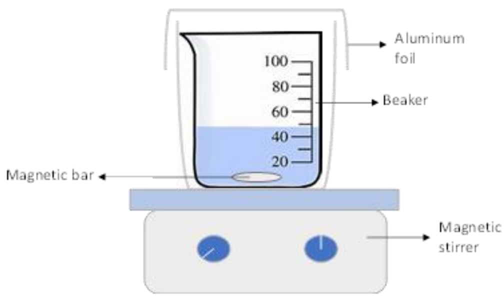

Figure 2. The setup for catalytic measurement decolouration of methylene blue using CNF from durian husk.

3. RESULTS AND DISCUSSIONS

The fibres undergo defibrillation by applying the force of a high-speed blender, resulting in a smooth texture as depicted in Figure 3(a). Cellulose is an organic substance that is prone to fungal infestation. Hence, it is important to undergo a drying procedure for preservation to preserve the quality and nanostructure achieved. The freeze-drying method was selected due to its capacity to generate a light and airy texture, resembling cotton, as illustrated in Figure 3(b), which will aid in future investigations.

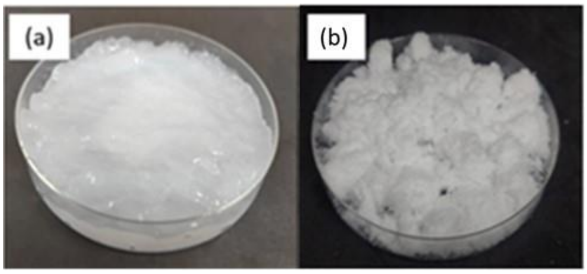

Figure 3. a) Nanocellulose before the storage drying process, and b) nanocellulose after freeze-drying for storage.

Figure 4(a) illustrates the correlation between the starting pH and the percentage of MB decolouration. The analysis of decolouration efficacy demonstrates that the pH level of the medium has an impact on the surface charge of the adsorbents. The surface charge of cationic dye adsorbents diminishes as the pH falls. This demonstrates the effectiveness of adsorption and the feasibility of regeneration through desorption at low pH. The CNF adsorbents exhibit optimal performance, achieving a 44.4% increase in decolouration at pH 7 compared to pH 2, resulting in a 98% decolouration rate. The adsorption efficiency decreases at low pH levels because there is increased competition between H^+ ions and dye molecules, resulting in the formation of electrostatic attraction [10]. This response also indicates the restoration of adsorbents at a lower pH.

Additionally, the maximum capacity (q_t) was examined, as depicted in Figure 4(b). The data revealed that the adsorbent demonstrates optimal performance in solutions with an acidic to neutral pH. Specifically, the q_t value exceeds 10 mg/g at pH 4 and pH 7. Like the impact of MB decolourization, a pH of 2 has been found to have the lowest adsorption capacity. This is because the high concentration of H^+ ions affects the adsorption of MB onto the adsorbent [11]. Hence, the presence of an acidic solution can facilitate the desorption process, enabling the adsorbent to be reused for multiple cycles. The adsorption capacity began to decline at a pH of 9, with a qt value of 8.9 mg/g, and continued to drop at a pH of 11, with a qt value of 8.5 mg/g.

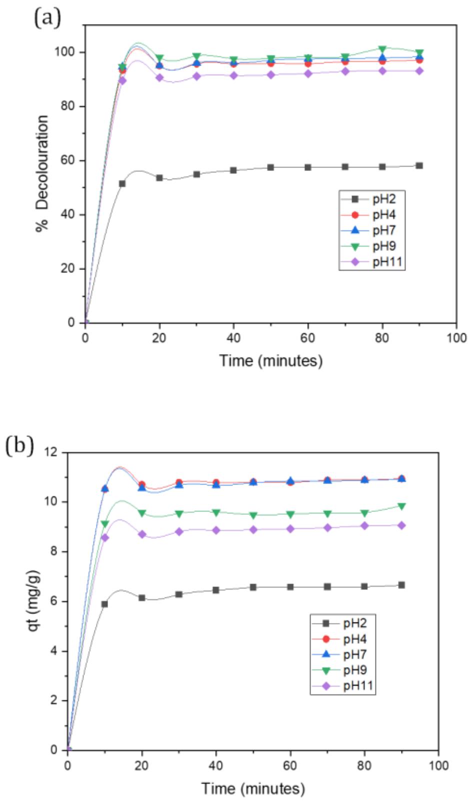

Figure 4. a) Kinetic study on the decolouration of MB and b) DH powder after vacuum-drying and grinding into powder, c) DH powder after oven-drying and grinding into powder and d) delignification; acid chlorite bleaching process.

4. CONCLUSIONS

Following a series of procedures, such as pre-treatment, production of cellulose nanofibers (CNF), and storage treatment, CNF derived from durian husk has been effectively generated. Hence, the adsorption effectiveness of the adsorbent was determined by considering the maximum absorption efficiency and the initial pH effect on decolorization. According to the acquired data, it was found that an extremely acidic pH, like pH 2, facilitates the process of de-absorption rather than absorption. Therefore, the range of pH 4 to pH 7 demonstrates a more pronounced absorption pattern, resulting in a 98% achievement in decolorization. This illustrates the influence of H^+ ion competition in the decolorization process. Although the overall association between pH and maximal absorption efficiency shows a similar pattern, there is a tendency for absorption efficiency to decline between pH 9 and pH 11.

This study proposes a viable paradigm for using cellulose nanofibers (CNF) derived from dissolved hemicellulose (DH) as a source of affordable and high-quality material. Therefore, it also provides a more environmentally friendly option for several sectors such as mechanical, energy, construction, and medical. This has the potential to open up new opportunities and possibilities for researchers to maximise the use of agricultural waste, so improving the general quality of life.

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