Synthesis and characterization of pineapple leaf modified with diethylenetriamine solution

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Abstract. Pineapple is the third most consumed fruit in the world with an annual production of about 25 million tons. Usually, pineapple leaf (PL) becomes the waste after harvesting and most of the PL was burned to eliminate fungi, composted or just piled to rot. The aim of this study is to synthesize PL modified with diethylenetriamine (DETA) that contain amino groups (NH₂) which enhance the adsorption capacity via the impregnated method. In order to prove the presence of NH₂ groups on the surface of adsorbent after modification, the characterization analysis has been done. After the modification of PL with DETA (DETA-PL), the FTIR analysis shows the 2 peaks that attributed to the amino group. There also increased surface area, pore volume, pore size and the amount of N of DETA-PL as evidence of BET analysis and elemental analysis. The amount of N also increased after modification. The morphology of DETA-PL was smooth and crinkle after modification with DETA. The point of zero charges of DETA-PL was increased after the modification of PL. The finding obtained from all of the characterization analyses showed that there are presences of the amino group on the surface of DETA-PL adsorbent after modification. This suggested that DETA-PL is a promising adsorbent for an adsorption method of wastewater treatment.

1. Introduction

Recently, textile industries become one of serious environmental pollutant due to the large amount production of effluent that is not amenable to chemical or biological treatment and also containing highly toxic organic and inorganic contaminants [1, 2]. During the dyeing process, an estimation of about 1-10% loss of dyes and released directly into wastewater [3]. According to N.Wang et.al., (2019) [4], about 7 x 10⁸ kg of dyestuffs were produced every year around the world. The dye contains synthetic origin and complex molecular structures which are more stable and make it difficult to degraded once enter the water. Dyes also can be classified according to the basis of their solubility which is soluble dyes (acid, mordant, metal complex, direct, basic and reactive dyes) and insoluble dyes (azoic, sulfur, vat and disperse dyes) [5]. Reactive black 5 categories under an azo dye and this type of dye represent 60-70% of all synthetic dyes [6]. The azo dye provides bright, high intensity colors and good fatness characteristic which is cost effectivenes due to reduced production cost [7]. The presence of dyes into the wastewater even at low concentrations will exhibit high color, increased chemical oxygen demand (COD), and low light penetration and visibility. This situation can create serious threats to human health.
and marine organism [2]. Therefore, the effective treatment to remove dye from wastewater before they are released is of vital significance for environmental protection.

There are several methods and materials have been developed to reduce and eliminate pollutants in industrial wastewater such as co-precipitation, filtration, coagulation-flocculation, biological treatment and adsorption [8]. Among all treatment use for dye removals adsorption is considered as an effective water treatment technique due to cost-effective, straightforward, easy operation and efficient in removing pollutants [7, 2]. The other benefit of adsorption treatment is used at low concentrations in continuous or batch processes, regeneration, and reuse [7]. It is a suitable method for various pollutant removals in air and water. There are many types of adsorbent that had been investigated including activated carbon, resin and gel, graphene, metal oxide and polymer [4]. One of the most common adsorbents that used to adsorb dyes is activated carbon. However, the cost of activated carbon has been increasing due to the high demand for activated carbon in other purposed such as catalyst support, air filters and gas storage [10]. Therefore, the searches of non-conventional adsorbent or so-called low-cost adsorbent have been introduced and it generally refers to non-hazardous waste produced from industry, agriculture, and biosorbent [11]. The agriculture waste was chosen as one of the materials to produce adsorbent because of the adsorption characteristic that able to adsorb the dye molecules [12].

Pineapple (Ananas comosus) is one of fruit that consumed naturally or from processed product and it has been cultivated in Asia, Africa and America. Normally, after harvesting fruit, the pineapple leaf become residue and most of the time it will burn to eliminated fungi and other parasites, composted or just piled to rot [13]. Therefore, pineapple leaf can use as an adsorbent for adsorption treatment because it is abundantly available agriculture waste that is biodegradable. Pineapple leaf contains a high amount of cellulose, hemicelluloses, lignin and pectin. It’s also containing hydroxyl, carboxyl and carbonyl groups that have a potential for industrial application and can be the alternative way for existing synthesis adsorbents [14]. The aim of this study is to focus on the chemical, morphological and physical changes of pineapple leaf during the impregnated treatment. The structural and physicochemical properties of the pineapple leaf were studied by Fourier transform infrared (FTIR), Brunauer Emmett and Teller (BET), elemental analysis, scanning electron microscopy (SEM), and point of zero charges (PZC).

2. Experimental

2.1. Material

The reagent for modification including sodium chloride (NaCl), diethylenetriamine (C₄H₁₃N₃), potassium nitrate (KNO₃), hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.2. Preparation of modified pineapple leaf

The pineapple leaf (PL) got from ‘Pusat Pembangunan dan Teknologi Tamanan Nanas’ Pekan Nanas, Pontian, Johor were washed with tap water to remove dust, dried at 60 °C for overnight. After that, the PL was ground and filtered with a mesh screen to get 250 μm.

About 5 g of PL was mixed with 5 g of NaCl and 10 mL of distilled water in Scott Bottle and this mixture was placed into ultrasonication for 1 h. After that, the mixture was rinsed repeatedly with distilled water to remove untreated NaCl using vacuum filtration. The obtain PL-NaCl was treated with 20 mL of diethylenetriamine (C₄H₁₃N₃) and the mixture was agitated in a water bath shaker at 150 rpm at 90 °C for 4 h. Finally, the adsorbent was rinsed with deionized water for times until the pH was constant and dried at 60 °C for overnight [15].

2.3. Characterization

The raw PL and DETAPL were characterized by Fourier transform infrared (FTIR) using an IRTracer 100 spectrophotometer under spectrum 100 instruments in the scan range of 500-4000 cm⁻¹. The specific surface area, pore size and pore volume analysis of both adsorbents were measured using Brunauer Emmett and Teller (BET) instrument (Surfer Analyser Thermo Scientific) based on N₂ adsorption at 75°C. The elemental analysis of raw-PL and DETAPL- PL was characterized using elemental analyzer.
(Perker-Elmer Elemental Analyzer Vario EL (Germany) to identify contents of C, H, and N in the samples. The morphology of both adsorbents was analyzed by Scanning Electron Microscopy (SEM) using Variable pressure Scanning Electron Microscope (JEOL JSM-IT300LV, USA) and coated with platinum to avoid electron of the sample charging during analysis. The point of zero charges (PZC) of raw PL and DETAPL was performed as follows: 50 mL of 0.1 M KNO$_3$ solutions with defined initial pH in the range between 2 until 10 were prepared. The solution was adjusted by adding 0.1 M of hydrochloric acid (HCl) and sodium hydroxide (NaOH). After that 0.1 g of DETA-PL was added into the solution. The mixture was mixed on a shaker for 24 h at 30 rpm. After equilibration during 24 h, the mixture was filter and the final pH of the solution was measured.

3. Result and discussion

3.1. Functional group analysis

The FTIR spectrums of raw-PL and DETA-PL were shown in Figure 2. There are similar spectra that observed for raw-PL also can be seen at DETA-PL which is C-H stretching of CH$_2$ and CH$_3$ group (3000-2800 cm$^{-1}$), and aromatic carboxylic acid (2500-2400 cm$^{-1}$) [15]. There are 4 peaks as seen at the raw-PL spectrum which is 3393, 1639, 1156 and 1054 cm$^{-1}$. The peak 3393 cm$^{-1}$ was described as the hydrogen bonded –OH vibration of the cellulose structure of PL [16]. The peak 1639 cm$^{-1}$ was attributed to the primary OH groups and carboxyl group whereas the peak at 1156 cm$^{-1}$ assigned to the C-O-C vibrations in cellulose [15,18]. The present of C-O of a hydroxyl group can be seen at peak 1054 cm$^{-1}$ [19]. For the DETA modified PL, it can see that 5 peaks appear which is 3567, 1643, 1425, 1162 and 1054 cm$^{-1}$. The peak at 3567 cm$^{-1}$ indicated that the presence of the hydroxyl group (-OH) or amino group (N-H) on the adsorbent [19]. The appeal of a secondary amino group at bending vibration around 1643 cm$^{-1}$ is due to the shifted of the band at 1639 cm$^{-1}$ of raw-PL [12]. The peak at around 1425 cm$^{-1}$ was due to the symmetric stretching of the C-O group [20]. The peak 1054 cm$^{-1}$ also appears at raw-PL which indicates to C-O-C stretching of β-1,4-glycosidic bond ether groups [15]. From the FTIR analysis, it shows that the appeared of an amino group on the PL after modification with DETA (DETA-PL) indicated that the modification of adsorbent with DETA solution was successfully introduced into the adsorbent. The difference between raw-PL and DETA-PL shows that the interaction of diethylenetriamine molecules to the cellulose which shows in Figure 1.

![Figure 1. Reaction scheme of the synthesis process](image)
3.2. Specific surface area, pore size and pore volume analysis

The specific surface area for raw-PL and DETA-PL was determined using BET and BJH methods. According to the BET result (Table 1) show that the surface area and pore volume of raw-PL was 0.7919 m$^2$/g and 0.0126 cm$^3$/g. The surface area and pore volume increase after modification with DETA which is 3.9658 m$^2$/g and 0.0283 cm$^3$/g. This is due to the surface functionalization of DETA on the surface area of DETA-PL [21]. According to the BJH method, pore size under range 2 to 50 nm is categories as mesopores [11,18]. Table 1 shows the pore size of DETA-PL (2.0365 nm) was greater than raw-PL (1.4116 nm). This indicated that modified with DETA solution increases the pore size of the adsorbent.

Table 1. Surface area, pore size and pore volume analysis of Raw-PL and DETA-PL

| Adsorbent | Surface area (m$^2$/g) | Pore volume (cm$^3$/g) | Pore size (nm) |
|-----------|------------------------|------------------------|----------------|
| Raw-PL    | 0.7919                 | 0.0126                 | 1.4116         |
| DETA-PL   | 3.9658                 | 0.0283                 | 2.0365         |

3.3. Elemental analysis

The chemical composition of raw-PL and DETA-PL was determined using elemental analysis and the results are shown in Table 2. The amount of carbon and hydrogen after modified with DETA solution was slightly decreased from 42.82 % to 41.90 % (C) and 6.90 % to 5.50 % (H) [23]. The important chemical composition after modification with DETA solution is the nitrogen content was increased to 2.52 % and suggested that the amino groups incorporation on the DETA-PL surface [15]. Figure 1 shows the reaction scheme of the synthesis process and it proved that the presence of the amino group after the modification.

Table 2. Elemental analysis of Raw-PL and DETA-PL

| Samples   | N (%) | C (%) | H (%) |
|-----------|-------|-------|-------|
| Raw-PL    | 1.70  | 42.82 | 6.90  |
| DETA-PL   | 2.52  | 41.90 | 5.50  |
3.4. Morphology analysis
The morphologies of raw PL and DETA-PL were evaluated from the SEM images at 1000X magnification (Figure 3). The surface of raw PL was rough with the appeared of patches indicating the presence of some organic materials like lignin or tannin [24]. After modification with DETA, the surface of PL was become smooth and crinkle due to the impregnated of DETA [25]. There also the presence of irregular pore on the surface of DETA-PL [26].

![Image of variable pressure SEM of a) raw PL (1000x) b) DETA-PL (1000x)](image)

3.5. Point zero charge
The point zero charges (pHpzc) is used to determine the pH at which the net surface charge of the adsorbent is zero and cation exchange and anion exchange capacity are equal on the adsorbent surface [27]. The result of this study (Figure 4) shown the pHpzc of the DETA-PL was observed at 8.13. From the graph show that the proton retention decreases gradually start from initial pH 4 until reach pHpzc. The DETA-PL tends to release protons to the solution when at above pHpzc and occur the decrease of final pH values. This due to the modification of pineapple leaf with diethylenetriamine (DETA) which changing the charge balance onto the adsorbent surface and adsorption properties of DETA-PL [15].
4. Conclusion
In this study, DETA-PL has been synthesized successfully via the impregnated of DETA solution with pineapple leaf which has the ability to absorb anionic dyes due to the presence of the amino group. The presence of an amino group on the DETA-PL was getting from FTIR analysis. The increased of surface area, pore volume and pore size after modification with DETA as evidenced from BET analysis and categories as mesopore adsorbent. The increased of N (%) after modification also is shown the presence of amino groups on the DETA-PL. This result was supported with morphology analysis which there is change on the surface of adsorbent after modification. The modification of PL with DETA also increased the point of zero charges of the adsorbent. This study has confirmed that the presence of the amino group on the adsorbent surface after modification with the DETA solution.

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