Study of pyrolysed acid and based treated coconut coir as green photocatalyst substrate

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Abstract. This study investigates the possible contribution to sustainable development by utilizing agriculture waste materials to prepare a substrate for photo-catalysis application. The photocatalytic performance of impregnated TiO2 on acid and base-treated coconut coir (CC) and their pyrolysed form have been studied. The photocatalytic performance of impregnated TiO2 on acid treated CC improved compared to bare TiO2. However, the pyrolysed samples showed higher thermal stability and porosity compared to only treated CC, their catalytic performance was decreased. It seems that impregnated TiO2 undergo interaction with treated CC during pyrolysis. More investigations to reveal exact reason of this behavior is in progress.

1. Introduction

Although theoretically all carbonaceous material with a high percentage of carbon in their composition could produce activated carbon (AC), only coal and lignocellulosic materials have been used for commercial production of activated carbon (ACs). Many researchers are investigating utilizing of agricultural by-products and residual wastes as resource materials for preparing the AC [1, 2]. It is well known that prepared activated carbon composition, structure, qualities and characteristics determine by the physical and chemical properties of the starting materials, the activating agent, and the preparation procedure [3]. Our previous studies on chemical treatment of agricultural wastes have been revealed that desirable changes in their structure are occurred which lead to higher water absorbency because of increasing of OH groups on their surfaces [4]. With this in mind, we decided to explore the possibility of using physical and chemical activation and treatment to prepare green substrate from the agricultural waste for catalytic application. Coconut coir is a natural fiber obtained from the coconut husk, a waste biomass readily available and a cheap material resulting in from the coconut fiber industry. Its fibers are bound together through lignin, cellulose and hemi-cellulose natural polymers [5]. In this study, nano TiO2 has impregnated on the surface of coconut coir when it is chemically treated. Later, the prepared samples are pyrolysed and the photocatalytic behavior of them is studied.
2. **Materials and Catalysts Preparation**

After washing the coconut coir (CC) with distilled water and drying in the oven at 50 °C, they were soaked in NaOH (QReC) 1.6M and nanoTiO₂ (Aldrich, 21 nm) (5% W/W CC) and mixed in room temperature for 60 min. Later, it was washed with plenty of water till neutralized and dried at room temperature (RT) (hereafter denoted as sample CC(NaOH)). The dried materials were pyrolysed at 450°C for 1 hour under N₂ gas flow (heating rate 10 °C/min) thereafter prepared sample was utilized as catalyst in photocatalytical performance evaluation with methylene blue under UV light. For second try, the washed and dried coconut coir soaked with the H₂SO₄ (R&M Chemicals) solution 0.4 M and nano TiO₂ (5% W/W CC) and mixed at room temperature (RT) for 40 min. After washing with plenty of water till neutralized, it was let to dry at RT (hereafter denoted as sample CC (H₂SO₄)), the dried sample was pyrolysed at 450°C for 1 hour under N₂ gas flow (heating rate 10 °C/min).

3. **Results and Discussion:**

Figure 1 shows the scanning electron micrographs of the prepared samples’ surface (Carl Zeiss Merlin Compact). As shown in pictures, the Pyrolysis of both acid and base treated CC, makes porous honey comb shape in CC.

![SEM images](image)

**Figure 1** SEM images (a) CC (H₂SO₄) before pyrolysis, (b) CC (H₂SO₄) after pyrolysis, (c) CC (NaOH) before pyrolysis and (d) CC (NaOH) after pyrolysis, respectively.

TGA analysis (Figure 2) of prepared samples revealed that thermal stability of pyrolysed CC in both acid and base treated forms are much higher than CC without pyrolysis.
Crystallinity analysis of the prepared CC samples were conducted with a Bruker DB-Advance X-ray diffractometer (Figure 3). The peaks of impregnated TiO$_2$ nanoparticles could be seen in the XRD patterns of CC samples which treated with acid and base before pyrolysis while surprisingly, the peaks become wider and weaker after pyrolysis. This indicated that TiO$_2$ nanoparticles have the intercalation with treated CC during pyrolysis which caused the TiO$_2$ lattice structure to collapse and the intercalated product is relatively poorly crystalline.

**Figure 2.** TGA results for prepared samples

**Figure 3.** XRD pattern for CC prepared samples
4. Catalytic Evaluation

The photocatalytic activity of the prepared catalyst was tested by methylene blue (MB) degradation under a set of conditions. The degradation of MB dye was observed by UV/vis spectrophotometer (Shimadzu, Model 2450). MB dye solution was used as an objective pollutant because having made it possible for the UV-Vis spectroscopy to monitor the degradation of MB dye. The calibration curve of MB dye was recorded at a wavelength 665 nm. The MB dye solution was irradiated using UV-lamp (PHILIPS-15 Watt), and was held in a closed box. The irradiation source is placed on the top at a distance of 12 cm from the glass beaker containing photocatalyst samples. The photocatalytic degradation of MB for all photocatalyst samples was done using an initial concentration of 0.05 mM for MB suspension. Prior to illumination, 20 mg photocatalyst was added to the MB aqueous solution (20ml). The photocatalyst mixture was stirred in a dark place for 30 minutes in order to reach MB absorption-desorption equilibrium needed for the commencement of the photocatalytic reaction. After that, the photocatalyst mixture was exposed to a UV-lamp for a maximum irradiation time of 120 minutes. The photocatalyst mixture was withdrawn and filtered in order to separate the photocatalyst powder from the MB dye solution. The MB degradation was calculated according to the Beer-Lambert Law [6]. The concentration of MB is proportional to absorbance of MB. Hence, the degradation efficiency of MB can be calculated by following equation (1):

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

(1)

Where, \(C_0\) is the initial concentration of MB solution and \(C_t\) is concentration of MB after 120 minutes’ irradiation time. The percent (\%) of MB degradation calculated by the above equation is an important value that can be used to measure the catalyst performance for each sample (Table 1).

Table 1. The photocatalytic performance result for prepared samples in different weight ratio

| sample                  | TiO2  | TiO2 | CC(H2SO4) Before pyrolysis | CC(H2SO4) After pyrolysis | CC(H2SO4) After pyrolysis | CC(NaOH) Before pyrolysis | CC(NaOH) After pyrolysis |
|-------------------------|-------|------|----------------------------|---------------------------|---------------------------|--------------------------|--------------------------|
| Degradation             | 97.52 | 97.36| 99.73                      | 98.2                      | 94.94                     | 94.2                     | 92.78                    | 97.16                    |

The result revealed although the photocatalytic performance of impregnated TiO\textsubscript{2} on acid treated CC is improved compared to bare TiO\textsubscript{2}, the pyrolysed acid and base treated samples exhibit lower performance. According to XRD results, decreasing of catalytic performance of pyrolysed samples could likely be attributed to the interaction of nanoTiO\textsubscript{2} and treated CC during pyrolysis which leads to lower crystallinity of TiO\textsubscript{2}. Intercalated nano TiO\textsubscript{2} with lower crystallinity decrease the active sites for photocatalytic reaction and decrease catalytic performance.

5. Conclusion:

Although the initial investigation of utilizing the modified coconut coir as green substrate showed better performance compared to bare nano TiO\textsubscript{2}, further investigation is needed to reveal the reason
behind lower performance of pyrolysed samples which showed higher porosity and higher thermal stability. Applying impregnation procedure after pyrolysis of treated CC could be better option for increasing the photocatalytic performance of samples. Currently, further studies for improvement of CC as green substrate in catalytic application is in progress.

References:
[1] Gawande, P.R., Preparation and activation of activated carbon from waste materials-A review. IJRASET International Journal for Research in Applied Science and Engineering Technology, 2016. 4(XII): p. 1-4.
[2] Yahya, M.A., Z. Al-Qodah, and C.W.Z. Ngah, Agricultural bio-waste materials as potential sustainable precursors used for activated carbon production: A review. Renewable and Sustainable Energy Reviews, 2015. 46(Supplement C): p. 218-235.
[3] Sreńcsek-Nazzal, J., et al., Production, characterization and methane storage potential of KOH-activated carbon from sugarcane molasses. Industrial Crops and Products, 2013. 47: p. 153-159.
[4] Emdadi, Z., et al., Chemically Treated Rice Husk Blends as Green Desiccant Materials for Industrial Application. Chemical Engineering & Technology: p. n/a-n/a.
[5] Suhas, P.J.M. Carrott, and M.M.L. Ribeiro Carrott, Lignin – from natural adsorbent to activated carbon: A review. Bioresource Technology, 2007. 98(12): p. 2301-2312.
[6] Afifah, N., et al., Photodegradation of methylene blue by LaFeO₃/ZnO nanocomposites under visible and UV light irradiation. J. Phys. Conf. Ser. Journal of Physics: Conference Series, 2017. 820(1).