

Application of Magnetic Coconut Shell-derived Biocarbon for Methylene Blue Removal

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Abstract: This study presents the preparation of magnetic biocarbon from coconut shell. The physicochemical properties of the prepared biocarbon was initially characterized by their iodine adsorptive capacity to estimate structure porosity and surface area. The comparative study was conducted between coconut shell-derived biocarbon (CSB), coconut shell-derived activated biocarbon (CSAB), and magnetic coconut shell-derived biocarbon (MCSB) to evaluate their adsorption efficiency towards methylene blue (MB) dyes in aqueous solution. The iodine number for CSAB showed greater difference compared to the CSB and MCSB. Meanwhile, the adsorption studies indicated that MCSB had higher adsorption value (68.83 mg/g) for methylene blue dye than the other biosorbents. This was due to abundant of Fe₃O₄ species and oxygen containing functional groups after the biocarbon was modified. The data of MB adsorption by MCSB reflected better adsorption efficiency overall. Hence, magnetization is suggested as a better option for biocarbon modification.

Keywords: Activated carbon, Coconut shell, Magnetic, Adsorption, Methylene blue.

1. Introduction

Malaysia is home to various types of industry such as agriculture, aquaculture, art and craft-based industry. Approximately, 70% of them are commonly function as small and medium entrepreneurs (SMEs), cottage and microenterprises (Akhir *et al.*, 2015). Rearing activity of freshwater prawn, catfish, tilapia and other species generate income to the villagers while batik making along the east coast of Peninsular Malaysia (Kelantan, Terengganu and Pahang) has become a national identity of Malaysia. However, running these activities can make some disadvantages as well where fish farming produce nitrogen and phosphorus waste meanwhile batik making which involves process of dyeing fabric generate wax, resin, silicates and dye waste (Rashidi *et al.*, 2013). Due to the recalcitrant nature of dyes and other chemicals, the release of effluent from batik industry will cause visible pollution because it interferes with light penetration resulting in reduced photosynthetic activity (Adegboyega *et al.*, 2015). However, since both industry involves small scale entrepreneurs, there are no proper treatment is applied to treat their effluent.

Biocarbon is a bio-product with high carbon content. Generally, burning biomass e.g. wood, manure and leaves in a fire creates ash that enriched with minerals such as calcium, magnesium and inorganic carbonates. In contrast, biocarbon is produced when these biomass

is heated in a closed container with little or no available oxygen is supplied (Saleh *et al.*, 2016). The thermal decomposition of organic materials occurring within this stage develops internal pore structure with various sizes of micro-, meso- and macroporous. The increased porosity, higher surface area, as well as diverse functional groups e.i. carboxyl, hydroxyl, phenolic hydroxyl and carbonyl groups present on the surface make biocarbon a versatile material for numerous application like remediation of wastewater, fertilization of agriculture soils, renewable energy source and many more (Han *et al.*, 2016).

Many methods are used for remediation of water contamination from organic as well as inorganic compounds in wastewater such as biological biodegradation (Al-Othman *et al.*, 2013), coagulation, chemical oxidation, and froth floatation (Zargar, Parham and Rezazade, 2011). However, due to high operating costs, these methods are limitedly used especially in small to medium scale industries. The most common mechanism widely used today is adsorption because it is simple to operate (Saleh *et al.*, 2016), low cost, uses less energy, less generation of toxic sludge, and higher removal efficiency (Mubarak *et al.*, 2016). Adsorption is defined as a process of molecules etc. gases, solute or liquids (adsorbate) depositing onto the porous structure of the adsorbent. Usually, modern activated carbon (AC) is used as adsorbent to purify wastewater of industrial effluent (Bhatnagar *et al.*, 2013). The used of AC as adsorbent in commercial systems is highly favourable but quite expensive due to the complex preparation and as materials are derived from non renewable sources of fossil fuel origin, i.e. bituminous coal, lignite, peat and petroleum coke which increase the production cost (Kamaruddin *et al.*, 2013). Hence, many research had been conducted nowadays to find cheaper and more abundant source. Biocarbon derived from agricultural biomass is increasingly recognized as materials to replace AC due to high porosity, large surface area, and less expensive due to simpler production process (Mubarak *et al.*, 2016). It is also reported that surface of the biocarbon is enriched with oxygen formed from various functional groups (Wang *et al.*, 2017) and influences the adsorption behaviour in addition to their porous structure (Mubarak *et al.*, 2016).

Even though agricultural biomass derived as biocarbon is an ideal absorbent due to lower cost but it faces the same difficulty as AC when separating from an aqueous solution as they are produced and used in powdered form. Therefore, modifying this biocarbon by loading magnetite, Fe_3O_4 particles will add magnetic effect to the adsorbent and making it easier to be separated using magnetic technique (Ruthiraan *et al.*, 2014). The modification method of biocarbon have been studied extensively by different researchers for removal of heavy metals and other organic contaminants from wastewater like chromium (Han *et al.*, 2014), cadmium (Ruthiraan *et al.*, 2014), acid orange 7 dye (Wang *et al.*, 2017) and 4-nitrotoluene (Saleh *et al.*, 2016).

The goal of this present study is to prepare magnetic biocarbon material from coconut shell. Comparative kinetic studies of raw biocarbon, activated biocarbon and coconut shell based magnetic biocarbon had been carried out to determine the most efficient adsorbent to be employed for the removal of methylene blue dye in aqueous solution.

2. Materials And Method

2.1 Adsorbent Preparation

Coconut shell based biocarbon were obtained from local supplier, Green Impiana Brothers Solution (GIBS), at Melor, Kelantan. They were crushed and sieved to attain particle sizes of less than 150 μm and labelled as CSB. Coconut shell activated biocarbon (CSAB) were prepared by using chemical activation; CSB was impregnated with sodium chloride

$$S_{BET} = \left(\frac{IV \times 10^{-3}}{\text{Atomic mass of iodine}} \right) \times N_A \times \omega$$

(NaCl) as dehydrating agent at 1:1 ratio (wt/wt) overnight. The mixtures were introduced into the muffle furnace at specific temperature and holding time. After cooled down in furnace, they were extensively washed with distilled water until the pH became neutral. Finally, the samples were oven-dried at 105 °C overnight. The samples were designated as CSAB. To prepare MCSB, CSB samples were added into the aqueous solutions of FeCl₂ (2 M) and FeCl₃ (1 M). Then, NH₄ solution (0.7 M) was added dropwise into the mixture under vigorous mechanical stirring. The resulting biocarbon (labelled as MCSB) were washed until the filtrate reached pH 7 and dried in the oven at 110 °C overnight. Finally, the samples were stored in a tightly closed container.

2.2 Adsorbent Characterization

The general properties of the samples such as biocarbon yield (%) by mass, moisture content (%) by mass, ash content (%) by mass, pH, and volatile matter were studied according to standard procedure (Anisuzzaman *et al.*, 2015). Meanwhile, determination of iodine number was analysed according to ASTM prescribed method (ASTM, 2006).

2.3 Solutions Preparation

All reagents used were of analytical grade. A stock solution (1000 mg/L) was prepared from MB dye (molecular weight = 319.87 g/mol). Subsequent experimental solutions were prepared by diluting the stock solution with distilled water. The concentration of MB was determined at 660 nm by UV-visible spectroscopy. Meanwhile, 0.1 N iodine solution was prepared by dissolving the sublimed iodine in the potassium iodide, and 0.05 N sodium thiosulphate was standardized with pure potassium iodide.

2.4 Determination of iodine value

A 40 ml of standard iodine solution is treated with 0.2 g of carbon samples. The solution was shaken for 50 min and filtered after equilibrium. Ten ml of the filtrate is titrated with 0.05 N sodium thiosulphate solution, using starch as the indicator. Similarly, the quantity of thiosulphate to titrate 10 ml of the blank solution was determined. Each titration was carried out in triplicates and the average titre used in calculating the iodine number (IV) using equation (Equation (1), (2), (3)) below:

$$IV = C \times \text{Conversion factor } (C_f) \quad (1)$$

$$C_f = \frac{\text{atomic mass of iodine} \times N \times 40}{w \times B} \quad (2)$$

$$C = B - A \quad (3)$$

where, atomic mass of iodine is 127, N is the normality of iodine solution used, w is the mass of biocarbon used (g), V is the volume (ml) of thiosulphate for biocarbon free aliquot, and B is the volume of thiosulphate for blank solution. Iodine number is calculated as the amount of iodine adsorbed (mg) by the biocarbon material (g). Calculation of surface area based on iodine number is as follows (Equation (4)):

$$(4)$$

where, IV is iodine number obtained in Equation (1), N_A is $6.02 \times 10^{23} \text{ mol}^{-1}$ and ω is 0.2096×10^{-18} .

2.5 Adsorption of Methylene Blue

In this assay, 0.025 g of biocarbon material is placed in contact with 25 ml of a MB solution at different concentrations (10, 20, 40, 60, 80, and 100 mg/L) for 24 h at room temperature. The remaining concentration after 24 h was analysed by UV-visible spectroscopy at 660 nm. In this research, the amount of MB adsorbed in mg/g from each solution is calculated as Equation (5) meanwhile adsorption efficiency (% removal) is calculated according to Equation (6):

$$q_e \text{ (mg / g)} = \frac{(C_o - C_e) \times V}{m} \quad (5)$$

$$\% \text{ removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (6)$$

where, C_o is the initial concentration of MB solution in mg/L, C_e is the concentration of MB solution at equilibrium time (mg/L), V is the volume of solution treated in L, and m is the mass of adsorbent in g.

3. Results And Discussion

Table 1 shows the result of proximate analysis conducted on sample biocarbon and activated biocarbon derived from coconut shell, known as CSB and CSAB respectively. The study was conducted according to American Society of Testing and Materials (ASTM, 2006). The fixed carbon content obtained from this study is higher than other biomass precursor reported before such as rice husk biocarbon (17.34%) (Kizito *et al.*, 2015), tamarind seed biocarbon (28.89%) (Mopoung *et al.*, 2015), and *Leucaena leucocephala* bark (18.10%) (Anupam *et al.*, 2011). This may be due to the structural compositional difference in terms of cellulose, hemicellulose and lignin that build up the cell wall of the precursor used (Hodgson *et al.*, 2016). Hence, higher carbon content of coconut shell precursor may indicate suitability of this precursor as candidate for industrial waste water treatment application. The data also revealed that the fixed carbon content of CSAB is relatively higher than CSB. This could be attributed to the ability of NaCl to retain carbon and avoid loss of volatile matter. Thus, indicate the successful activation process by using of NaCl as dehydrating agent to replace other more corrosive chemicals reported before i.e. H_3PO_4 , H_2SO_4 , ZnCl , NaOH , and KOH . NaCl may promote redistribution of carbon structure and increase the yield of fixed carbon.

Table 1. Proximate analyses of coconut shell derived biocarbon and activated biocarbon.

| Sample | CSB | CSAB |
|--------------------------|-------|-------|
| Ash content (%) | 5.62 | 3.74 |
| Moisture content (%) | 6.27 | 3.24 |
| Volatile matter (%) | 46.92 | 31.25 |
| Fixed carbon content (%) | 41.19 | 61.17 |
| pH | 7.25 | 7.78 |

Iodine adsorption number or iodine number is one of the most important parameters to characterize carbon performance (Itodo *et al.*, 2010). Iodine number is expressed in mg/g. It is also the measurement of micropore (0-20 Å) content of carbon samples by adsorption of iodine molecules from a solution. Iodine number is also depicted as an indication of total surface area. The typical range for iodine number required for waste water application is 500-1200 mg/g (Mopoung *et al.*, 2015).

Table 2. Iodine number and surface areas of CSB, CSAB, and MCSB.

| Sample | IV (mg/g) | Surface area (m ² /g) |
|--------|-----------|----------------------------------|
| CSB | 321.47 | 316.97 |
| CSAB | 816.00 | 804.58 |
| MCSB | 159.57 | 157.34 |

The results of iodine number determination is shown in Table 2. It was revealed that CSAB has higher iodine number as compared to CSB. It is worth to mention here that simple pyrolysis produced biocarbon with limited porosities (IV = 321.47 mg/g) and smaller surface areas (316.97 m²/g) whereas further treatment with salt (NaCl) demonstrated higher porosities (IV = 816.00 mg/g) and larger surface area (804.58 m²/g). Salts may have incorporated into the interior of the biocarbon and influenced development of internal porosity. Activation process also inhibits particle shrinkage and volume contraction (Guo *et al.*, 2007). This result is in agreement with previous study where BET surface area of palm shells biocarbon (206 m²/g) is lower than activated palm shells biocarbon treated with H₂SO₄ (1014 m²/g) (Guo *et al.*, 2005). On the other hand, MCSB gave lower iodine number (159.57 mg/g) compared to both CSB and CSAB. This may be due to the magnetic particles or magnetite (Fe₃O₄) deposited onto the porous structure of the biocarbon hence the reduced iodine value (159.57 mg/g) with smaller surface area (157.34 m²/g). This data was supported by the SEM-EDX analysis of magnetic sludge-derived biochar (MSDBC) conducted in the previous work where iron components was found distributed not only on the surface of biochar but also in the interior of MSDBC (Wang *et al.*, 2017).

Figure 1 shows the effect of initial dye concentration (10 to 100 mg/L) on MB adsorption capacity of CSB, CSAB, and MCSB. Equilibrium adsorption capacity (mg/g) increased with increase in MB initial concentration. The results suggested a high MB adsorption efficiency in all samples. It was observed that the adsorption capacity of CSAB was higher than CSB samples but lower than MCSB (CSB < CSAB < MCSB). The results supported the iodine value data where activated carbon material has a larger surface area and porosity compared to biocarbon coconut shell. From the results obtained it was revealed that when salt treatment is applied, the generation of internal porosity provide more sites for MB molecules to be adsorbed.

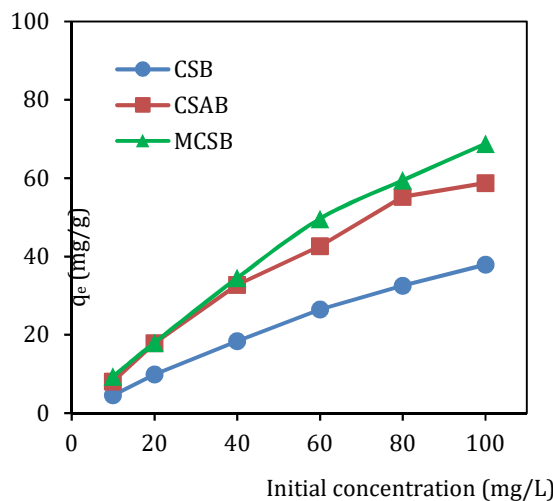


Fig.1. Effect of initial MB concentration on adsorption efficiency.

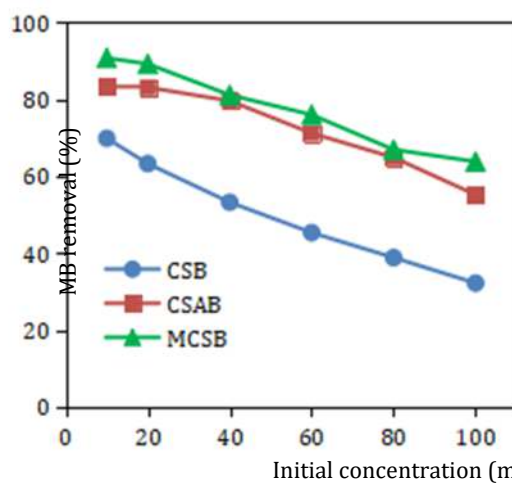


Fig.2. Effect of initial MB concentration on MB removal.

As shown in Figure 1, the data also demonstrated that loading magnetic Fe_3O_4 loading increased the adsorption efficiency of MCSB even albeit lower presence of porous structure (seen from lower iodine value). This may be due to abundant Fe_3O_4 particles and oxygen containing functional groups as biocarbon was modified. Drastic increase can be seen with q_e (mg/g) under all initial concentration as both MCSB and CSB is compared. At initial concentration of 100 mg/L, MCSB adsorbed (68.83 mg/g) MB, higher than CSB (37.94 mg/g) and CSAB (58.79 mg/g). Similarly, at the same condition (100 mg/L) MCSB removed (63.78%) more MB dye efficiently than CSB (32.24%) and CSAB (55.18%) as shown in Figure 2. The higher efficiency can be attributed to the combination of available porosity and due to the distribution of various functional groups that promoted chemical bonding reactions with the MB molecules within MCSB.

4. Conclusions

This manuscript reports experimental data on physical characteristics of simple biocarbon pyrolysis and salt activated biocarbon (CSB and CSAB). The results clearly showed that both CSB and CSAB produced higher fixed carbon content, 41.19% and 61.17%, respectively which makes it as potential candidates to treat batik manufacturing's effluent. In addition, high adsorption efficiency of CSAB (55.18%) to remove MB dye from aqueous solution (100 mg/L) can be correlated to higher surface area (804.58 m²/g). Meanwhile, the higher removal (63.78%) using MCSB is most likely due to the abundance of Fe₃O₄ species and oxygen containing functional groups. Hence, magnetization of biocarbon samples can greatly increase adsorption capacity.

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