Facile preparation of a magnetic carbon adsorbent via simultaneous magnetization and activation of sugarcane bagasse and Fe$^{2+}$ and Fe$^{3+}$ ions

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Abstract. Magnetic carbon materials have attracted lots of interests as novel adsorbents for removal of toxic substances from aqueous solution. However, so far the preparation of those materials has relied on multi-step procedures, leading to high costs of production in the large scale. Therefore, a facile method to produce magnetic carbon adsorbents via simultaneous magnetization and activation process in a single step has been developed. Sugarcane bagasse is the abundantly primary solid waste of sugar industries in Thailand. To best and economically use such sugarcane bagasse, a novel separable magnetic carbon composite (SM-BG-0.2NaOH-800) was successfully prepared via the purposed process. Raw sugarcane bagasse was used as a carbon precursor and Fe$^{2+}$ and Fe$^{3+}$ ions as a source of magnetic particles in the carbon composites. NaOH is used as both precipitating agent for the magnetite (Fe$_3$O$_4$) particles and activating agent to develop the porosity. The resulting material was characterized using N$_2$ sorption analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Vibrating Sample Magnetometry (VSM).

1. Introduction
Water contaminated with toxic dyes, for example, methylene blue (MB) causes serious harm to humans and ecosystems [1]. The treatment techniques for removing these pollutants include coagulation and flocculation, oxidation, and adsorption [2]. Adsorption is considered to be one of the most effective methods as the result of its simplicity of the design and low costs. Porous carbon materials are a class of excellent adsorbents due to their large specific surface area, developed porosity and chemical stability widely used for dye adsorption in a wastewater system. However, their use in the fine powder form makes the whole process slow due to the sedimentation process. For this reason, magnetic carbon adsorbents have attracted lots of interests owing to their fast and simple separation ability by using an external magnet after completed adsorption [3,4,5].

In this work, the facile single step method for fabricating a magnetic carbon adsorbent via simultaneous magnetization and activation process was demonstrated. Sugarcane bagasse is the
abundantly primary solid waste of sugar industries in Thailand. Therefore, it has been selected as a precursor and Fe\(^{2+}\) and Fe\(^{3+}\) ions as a source of magnetic particles in the carbon composite. NaOH is used as both precipitating agent for the magnetite iron oxide (Fe\(_2\)O\(_3\)) particles and activating agent to develop the porosity. Furthermore, methylene blue (MB), a toxic and carcinogenic compound, which has been used in actual textile industry was chosen as a synthetic dyes model for adsorption study.

2. Methodology

First, sugarcane bagasse was collected, washed to remove impurities, and then dried in an oven at 100°C for 48 h. The dried sugarcane bagasse (BG) was ground into 200-325 mesh size. In a typical synthesis, 15.00 g of BG was soaked with 1:2 M ratio of Fe\(^{2+}/Fe^{3+}\) for 1 h. Then, 100 mL of distilled water and 38 mL of 0.2 M NaOH solution was added into the mixture subsequently. The resulting mixture was further stirred at ambient temperature for 2 h. Subsequently, it was heated in an oven at 80 °C for 3 days to evaporate the water (SM-BG-0.2NaOH), followed by pyrolysis at 800 °C under nitrogen atmosphere for 1 h. The resulting sample was collected, washed and then labeled “SM-BG-0.2NaOH-800”. The magnetic carbon adsorbent was characterized using N\(_2\) sorption analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Vibrating Sample Magnetometry (VSM).

To investigate the adsorption performance of the adsorbent towards MB, adsorption isotherm experiments were performed with 0.05 g of the magnetic carbon material and 20 mL of various concentrations of MB solutions. The mixture was shaken for 48 h at room temperature to reach equilibrium. The adsorption kinetics experiments were performed with 0.05 g of the magnetic carbon material and 20 mL of 100 mg L\(^{-1}\) of MB solutions, at room temperature (30±2°C) for 0–24 h. After complete adsorption, adsorbent material was separated from the solution using a magnet.

3. Results and Discussion

The XRD patterns of SM-BG-0.2NaOH and SM-BG-0.2NaOH-800 are shown in Figures 1a,b respectively. A relatively broad typical XRD pattern for SM-BG-0.2NaOH proves that the uncalcined sample possessed no crystalline iron particles (Figure 1a). In contrast, the XRD pattern of SM-BG-0.2NaOH-800 shows sharp peaks at \(2\theta = 18.3^\circ,30.1^\circ, 35.5^\circ, 37.1^\circ, 43.1^\circ, 53.5^\circ, 57.0^\circ, 62.6^\circ\) and 74.1° which could be indexed to the crystalline magnetite particles (Fe\(_3\)O\(_4\) (Figure 1b). This could confirm a successful conversion of iron ions into the iron magnetite phase by simple precipitation coupled with a subsequent pyrolysis.

![Figure 1. XRD patterns of SM-BG-0.2NaOH (a) and SM-BG-0.2NaOH-800 (b)](image)
The elemental composition and bonding relationship of SM-BG-0.2NaOH-800 were analyzed by XPS, as shown in Figure 3. Three typical peaks corresponding to the binding energies of C 1s (284.5 eV), O 1s (532.0 eV), and Fe 2p (710.38 eV) could be seen in the survey spectra (Figure 3), and the Fe 2p peak of SM-BG-NaOH-800 was not very conspicuous due to a low Fe content. XPS analysis determined the C, O and Fe contents to be 89.90, 11.75 and 3.34 %wt, respectively. The high C content and detailed analysis for the XPS (data not shown here) confirms the existence of abundant C sp² structure, which is a typical behaviour for the carbons obtained by pyrolysis of biomass at temperature >700°C. Even though the Fe content in the form of Fe₃O₄ for the whole sample (3.34 %wt) is not large, the magnetic properties of SM-BG-NaOH-800 are satisfactory. The good magnetic behavior of the resulting magnetic carbon composite is shown in Figure 4. The hysteresis loop evaluated by VSM measurement of SM-BG-0.2NaOH-800 is illustrated in Figure 4a. The VSM measurement shows a very high hysteresis and symmetric magnetization curves, suggesting a high super paramagnetic property, which is consistent with the presence of Fe₃O₄ in the XRD results. The saturation magnetization value of the sample was found to be 17.971 emu g⁻¹. As shown in Figure 4b, SM-BG-0.2NaOH-800 was easily separated from water by an external magnet and the entire sample particles could completely attracted within 5 minutes.

The adsorption performance toward methylene blue on SM-BG-0.2NaOH-800 was studies by using 0.05 g of carbon composite in 20 mL of MB solution containing various concentrations for 48 h. The results from adsorption isotherm (Figure 5a) demonstrated that the maximum adsorption capacity of MB on SM-BG-0.2NaOH-800 is as high as 58.26 mg/g. The determination coefficient (R²) of the Langmuir model equal to 1, indicating the isothermal data was well fitted to the Langmuir model, as shown in Figure 5b. The adsorption kinetics results are shown in Figures 6a,b. In Figure 6a, the adsorption amount of MB onto SM-BG-0.2NaOH-800 increased gradually in the first 300 min and reached adsorption equilibrium around 400 min, illustrating a fast adsorption kinetic. The linear fitting curve of pseudo-second-order models for MB adsorption can be observed in Figure 6b, exhibiting a good linear correlation with R² of 0.9984. The adsorption performance of the sample shown here is
relatively comparable to or even higher than that of many magnetic adsorbents reported in the literature [5,6,7].

Figure 5. Adsorption isotherm (a) non-linear and (b) linear plots towards MB dye on SM-BG-0.2NaOH-800.

Figure 6. Adsorption isotherm (a) non-linear and (b) linear plots towards MB dye on SM-BG-0.2NaOH-800.

4. Conclusion

A magnetic carbon adsorbent (SM-BG-0.2NaOH-800) was successfully prepared using sugarcane bagasse as a carbon source and Fe$^{2+}$ and Fe$^{3+}$ ions as a magnetic precursor via a facile, one-pot synthesis and simultaneous magnetization/activation process. The adsorbent can be used to adsorb methylene blue dye from aqueous solution, exhibiting adsorption capacity (58 mg g$^{-1}$) with very high saturation magnetization value (17.971 emu g$^{-1}$).

5. References

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