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Review

# Development of $CO_2$ activated biochar from solid wastes of a beer industry and its application for methylene blue adsorption

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ABSTRACT

An alternative activated biochar was developed from barley malt bagasse (BMB) through pyrolysis followed by $CO_2$ activation. The materials BMB, biochar and activated biochar ($CO_2$–biochar) were characterized and tested as adsorbents for the removal of methylene blue (MB) from aqueous solutions. Adsorption kinetics, equilibrium and thermodynamics were studied. It was found that BMB and biochar presented surface area values lower than 1 $m^2 g^{-1}$, while $CO_2$–biochar was a typical mesoporous material with surface area around 80 $m^2 g^{-1}$. As consequence, the adsorption potential for methylene blue was in the following order $CO_2$–biochar ≫ biochar > BMB. Adsorption kinetics of MB on $CO_2$–biochar followed the pseudo–second order model. Langmuir presented the best fit with the equilibrium adsorption isotherms. The maximum adsorption capacity was 161 mg $g^{-1}$. MB adsorption on $CO_2$–biochar was spontaneous, favorable and exothermic. Pyrolysis followed by $CO_2$ activation was a suitable route to produce an alternative mesoporous adsorbent from barley malt bagasse.

## 1. Introduction

Nowadays, the solid wastes management in food and beverage industries is a global concern (Girotto et al., 2015; Oliveira et al., 2017). The beer processing, for example, is composed by several unit operations, which in turn, generate a considerable amount of solid wastes. In the initial processing steps for the beer production, some operations transform the malt into "ready wort" for fermentation (Zarnkow, 2014). Consequently, solid and liquid fractions are obtained. The waste solid fraction is named barley malt bagasse (BMB). It is estimated that the production of 100 L of beer generates 20 kg of dry barley malt bagasse. This waste represents 85% of the total solid wastes in the beer processing, and in some cases, the industries need to pay for the correct management (Mello and Mali, 2014). Since Brazil is the third largest beer producer in the world (Mardegan et al., 2013), a considerable amount of BMB is generated. So, alternatives for the correct exploitation and management of the barley malt bagasse are required.

Pyrolysis is an alternative to exploit several types of organic solid wastes, including barley malt bagasse. The solid product of biomass pyrolysis is named biochar. Biochars can be used in several applications, including adsorption for wastewater treatment (Weber and Quicker, 2018). Sumalinog et al. (2018) prepared an activated biochar from municipal solid wastes using pyrolysis followed by KOH activation. The material was effective to remove contaminants from aqueous solutions. Jang et al. (2018) developed a NaOH activated biochar from *Pinus taeda*, and the material was an efficient adsorbent for tetracycline. As earlier demonstrated, the improvement of biochar properties can be obtained using an additional activation after the pyrolysis process. This activation can be performed by physical, chemical or physicochemical methods (Ahmed, 2017). Recent studies pointed out that the $CO_2$ activation provides an intensive improvement on the textural characteristics of the biochars (Jung and Kim, 2014; Liu et al., 2018).

It is know that the untreated colored effluents containing dyes are extremely harmful for animals, human beings and for the environment. In parallel, adsorption is one of the most suitable unit operations used to treat colored effluents before discharge. It is of simple implementation and operation, has low energetic requirements and low cost (Bonilla–Petriciolet et al., 2017). Adsorption is more attractive when alternative and low cost adsorbents like biochars are used. In this context, biochars and activated biochars have been used to adsorb dyes from aqueous media (Georgin et al., 2016; Sumalinog et al., 2018; Zazycki et al.,

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2018). Based on the best of our knowledge, there are few studies about the preparation and application of $CO_2$ activated biochar from barley malt bagasse.

The idea of this work is the development of an interesting material named $CO_2$ activated biochar, using solid wastes from a beer industry (barley malt bagasse) as precursor. The potential of $CO_2$ activated biochar as alternative adsorbent to remove methylene blue (MB) from aqueous media was investigated. Based on this idea, a synergistic effect on the wastes management field can be attained, i.e., an alternative material is produced using industrial solid wastes from a beer industry, and this material in turn, can be used to treat colored liquid effluents. The solid wastes (BMB) from a beer industry were pyrolyzed with $N_2$, generating a biochar and then, the biochar was activated with $CO_2$. The precursor, the biochar and the activated biochar were characterized. The potential of BMB, biochar and activated biochar to adsorb MB was evaluated in batch systems through kinetic, equilibrium and thermodynamics.

## 2. Material and methods

### 2.1. Beer industry wastes

Barley malt bagasse (BMB) was used as organic precursor for activated biochar preparation. BMB was selected since is largely generated in Brazilian beer industries and, some of these industries need to pay for the correct management of this waste. Wet BMB was donated from a beer industry located in the Brazil southern (Santa Catarina state). The material (particle size lower than 4 mm) was sun dried for 2 days, and after, oven dried at 40 °C for 6 h to attain moisture content of 2.24 ± 0.2% (wet basis). This material was named BMB.

### 2.2. Development of biochar and $CO_2$ activated biochar

The samples of biochar and $CO_2$ activated biochar were prepared through $N_2$ pyrolysis followed by $CO_2$ activation. The experiments were carried out in a tubular reactor (Sanchis, Brazil) operating in batch system, according to the scheme presented in Fig. 1. Zazycki et al. (2018) have recently described this apparatus. It is a furnace containing a quartz reactor coupled internally. The reactor dimensions are: 98.1 cm length, 49 mm outside diameter and 43 mm internal diameter. The reactor was heated electrically by two resistors, each one with a 1900 W power. Two type K thermocouples were positioned inside the reactor.

The cylindrical quartz reactor was charged with approximately 120 g of BMB sample and the system run under nitrogen gas ($N_2$) at 0.25 L min$^{-1}$ (the $N_2$ flow rate effect on the pyrolysis was evaluated by preliminary experiments, from 0.10 L min$^{-1}$ to 0.50 L min$^{-1}$, being the best performance attained at 0.25 L min$^{-1}$. The value of 0.25 L min$^{-1}$ was sufficient to avoid heat ad mass transfer resistances). The temperature was increased at a heating rate of 10 °C min$^{-1}$ until 800 °C, being held at 800 °C for 60 min, and allowed to cool under $N_2$ flow until room temperature (the temperature effect on the pyrolysis was evaluated by preliminary tests, from 500 °C to 850 °C, being the best performance attained at 800 °C. This temperature was sufficient to eliminate the volatile compounds of the sample). The pyrolysis vapors condensation was conducted in accordance with CEN BT/TF 143 standard (CEN, 2004) using ten bubblers. In each experiment, 100 mL of isopropyl alcohol were added in each bubbler, except for the first and last (empty). All the bubblers were kept in a cold box (ice bath, salt, and isopropyl alcohol). The aim was to keep the bath bubblers at low temperature (around −10 °C). A gas meter was used to measure the volume of gas produced in the pyrolysis experiments. The bio–oil and the biochar were collected and their masses were determined for yield computation. The solid material obtained in this step was named biochar. The percentage yields of biochar, pyrolytic liquid and uncondensed gases were determined as follows:

$$\text{Biochar Yield}(\%) = \frac{m_{\text{biochar}}}{m_{\text{BMB}}}100 \tag{1}$$

$$\text{Liquid Yield}(\%) = \frac{m_{\text{liquid}}}{m_{\text{BMB}}}100 \tag{2}$$

$$\text{Gas Yield}(\%) = 100 - \text{Biochar Yield} - \text{Liquid Yield} \tag{3}$$

where $m_{\text{BMB}}$ (g) is the mass of precursor material inserted into the reactor, $m_{\text{biochar}}$ (g) is the mass of solid in the reactor after the pyrolysis process and $m_{\text{liquid}}$ (g) is the mass of liquid that was stored in the collector of the reaction system after the pyrolysis process.

Subsequently, the reactor was charged with approximately 25 g of biochar, and the system run under carbon dioxide ($CO_2$) at 0.15 L min$^{-1}$. The temperature was increased at a heating rate of 10 °C min$^{-1}$ until 900 °C, being held at 900 °C for 60 min and allowed to cool under $CO_2$ flow until room temperature. The material obtained after this step was named $CO_2$ activated biochar ($CO_2$–biochar). The $CO_2$–biochar was collected and its mass determined for yield computation. The percentage of mass loss of the samples due to activation (burn–off %) and yield of activated biochar were calculated as follows:

$$\text{Burn - off}(\%) = \left(\frac{m_{\text{biochar}} - m_{CO_2\text{ - biochar}}}{m_{\text{biochar}}}\right)100 \tag{4}$$

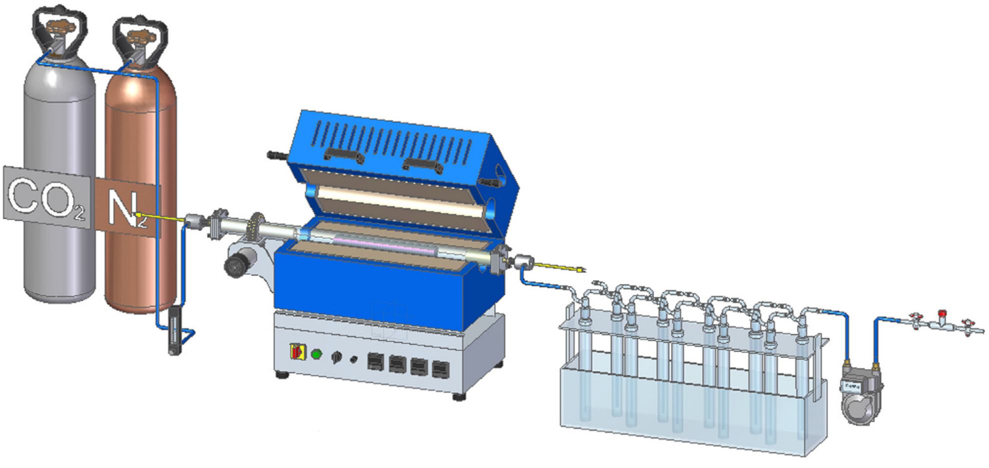

**Fig. 1.** Experimental setup used for the preparation of biochar and $CO_2$ activated biochar.