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# Recovery of bioalcohols with potential as biofuels using an energetically sustainable separation strategy

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The recovery of ethanol and butanol in aqueous solutions using adsorption on bone char was analyzed. Adsorption kinetics and isotherms were quantified where the effect of initial concentration, pH and temperature on alcohol adsorption was evaluated. Results showed that butanol was preferably adsorbed than ethanol due to its higher hydrophobicity. In particular, the maximum adsorption capacities of bone char to ethanol and butanol adsorption were 7.58 and 8.78 mmol/g, respectively, at pH 6 and 30 °C. It was also observed that pH and temperature significantly affected the recovery of these potential biofuels.

**Keywords:** *adsorption, ethanol, butanol, bone char, bioalcohol recovery*.

## INTRODUCTION

Biofuels are classified as a green energy source. Liquid biofuels have been proposed to form a future leading supplier of energy to replace fossil fuels like gasoline, diesel and petrol [1]. These liquid biofuels cover a wide spectrum of options including several routes for their production [2]. In particular, bioalcohols can be applied as multipurpose chemical feedstocks including their use as an energy source [3]. Ethanol is an important renewable liquid fuel for motor vehicles [4-6]. On the other hand, butanol is a chemical feedstock that has also been considered as a promising liquid fuel [6-9].

These two alcohols can be obtained by fermentation processes. However, the fermentation employed to obtain ethanol and butanol can suffer some technical drawbacks such as a high substrate cost, low product yield and high recovery costs [10]. The low product concentration in the fermentation is associated with the presence of the alcohols themselves, which are toxic to the microorganisms that carry out the process. The content of butanol and ethanol in fermentation broths usually achieves a low concentration around 2 % along with other by-products [8]. Consequently, the recovery costs of bioalcohols are highly and strongly dependent on the required product purity [11]. This aspect could be a driving factor that defines the success and the potential commercialization of bioalcohols obtained from fermentation in a biorefinery context.

It is worth mentioning that distillation is the conventional strategy to separate the alcohols from fermentation broths [12]. However, this purification method is energy-intensive; besides, the alcohol separation from aqueous systems is challenging because the presence of azeotropes increases the difficulty of the separation by simple distillation. It has been estimated that a distillation process can consume 50 – 80 % of the total energy required for the alcohol production [13]. Alternative technologies to separate alcohols from fermentation broths include the adsorption, which appears particularly attractive since it requires low energy consumption, is environmental friendly, easy to perform and the adsorbents can be regenerated and reused. Adsorption constitutes an economical method of alcohol recovery from low-in-alcohol-concentration solutions, which could contribute to reduce the production costs of this type of liquid biofuels.

This study reports the adsorption of ethanol and butanol from aqueous solutions using commercial bone char as an adsorbent, and is the first step in the development of an effective and low-cost strategy for the recovery of these liquid biofuels. The efficiency of this bioalcohol recovery strategy was tested at different operating conditions detailed in the next section.

## EXPERIMENTAL

Experiments of ethanol and butanol recovery were performed using a commercial bone char supplied by the Brazilian company Bonechar Carvao ativado do Brasil Ltda. The adsorbent was produced from bovine bones via pyrolysis, and was washed with deionized water until obtaining a constant pH

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in the washing solution. Then, it was dried and sieved to obtain a mean particle diameter of 0.35 mm (i.e., 40 - 50 mesh fraction) and this raw adsorbent was employed for alcohol adsorption.

Adsorption kinetics and isotherms for the bioalcohols recovery were experimentally quantified at different operating conditions using agitated tanks with an adsorbent dosage of 5 g/L under constant stirring. Adsorption experiments were performed at pH 6 - 7 and 20 – 30 °C using aqueous solutions prepared with anhydrous ethanol and butanol (chemical of reagent grade and supplied by J.T.Baker with CAS 64175 and 71363, respectively) and deionized water. Ethanol adsorption kinetics was performed with initial concentrations of 130 and 650 mmol/L, while initial concentrations of 134 and 670 mmol/L were used for quantifying butanol adsorption kinetics. Samples were taken at operating times from 0.25 to 24 h. Alcohol adsorption isotherms were obtained using initial concentrations from 23 to 2200 mmol/L for ethanol and from 14 to 800 mmol/L for butanol, respectively. The equilibrium time was 24 h for both alcohols. The concentrations of these alcohols were determined via gas chromatography using a Thermo Scientific Trace 1300 GC equipped with a flame ionization detector (FID). The method for alcohols quantification was adapted from procedures reported in the literature [14,15]. A linear calibration curve was utilized for the quantification of each alcohol. All the adsorption experiments were conducted in triplicate and the average values were used for data analysis. The alcohol adsorption capacity of bone char ($q$) was calculated using a mass balance

$$q = \frac{C_0 - C_t}{m} V \quad (1)$$

where $C_0$ and $C_t$ are the initial and final alcohol concentrations of the adsorption experiments, $V$ is the alcohol solution volume and $m$ is the adsorbent mass, respectively.

## RESULTS

Ethanol and butanol adsorption kinetics on bone char at different operating conditions (i.e., initial concentration and pH) are shown in Figure 1. Overall, more than 80 % of the amount of both alcohols was recovered during the first 6 h of the experiments at the operating conditions tested. These kinetic profiles indicated that the alcohols adsorption occurred on the external surface of bone char. Results given in Figures 1b and 1d showed that the higher the alcohol concentration in the aqueous solution, the faster the mass transfer and the higher the adsorption capacity. Figures 1a and 1c show that the adsorption of ethanol and butanol was significantly affected by solution pH, with the lower pH increasing substantially the adsorption capacity for either of the two alcohols. In particular, the solution pH affected the alcohol recovery because the surface charge of the adsorbent changed [16].

Figure 2 displays the adsorption isotherms of ethanol and butanol on bone char at two different pH values and two different temperatures. These isotherms were L-type according to the Giles classification, which corresponded to a favorable adsorption process [17]. The maximum adsorption capacity for ethanol was 6.36 mmol/g at 30 °C and pH 7, which increased up to 19.18 % at pH 7 and 20 °C and 19.65 % at pH 6 and 30 °C. The maximum adsorption capacity for butanol was 7.40 mmol/g at 30 °C and pH 7 and it increased 12.86 % at pH 7 and 20 °C and 16.37 % at pH 6 and 30 °C. Results showed that the adsorption capacities of butanol were higher than those obtained for ethanol. This adsorption performance can be the result of the more hydrophobic nature of butanol as opposed to that of ethanol. It is worth mentioning that longer chain alcohols show a greater adsorption capacity due to their increasingly hydrophobic nature [16]. Similar trends for the adsorption of ethanol and butanol have been reported in previous studies when polymeric resins, zeolites and activated carbon F-400 were used as adsorbents [9,18,19].

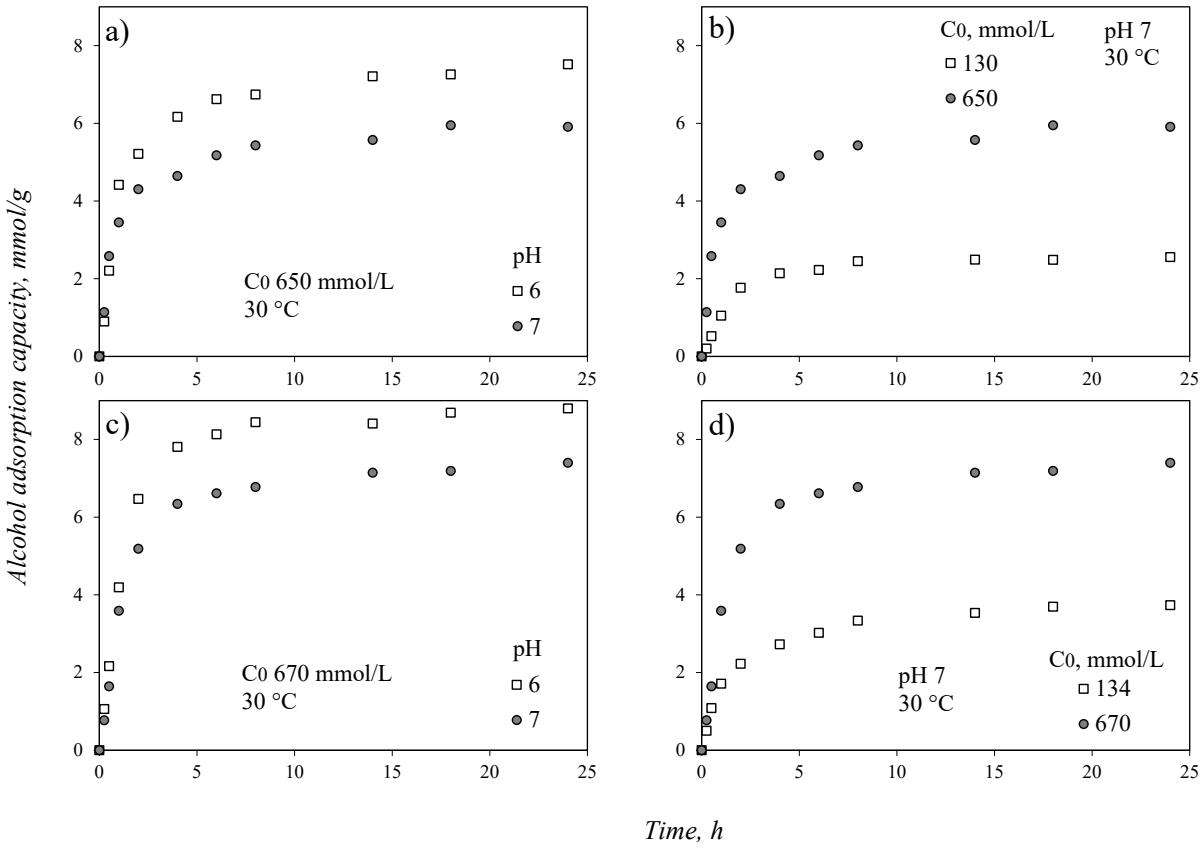


**Fig. 1.** Adsorption kinetics of a, b) ethanol and c, d) butanol at 30 °C.

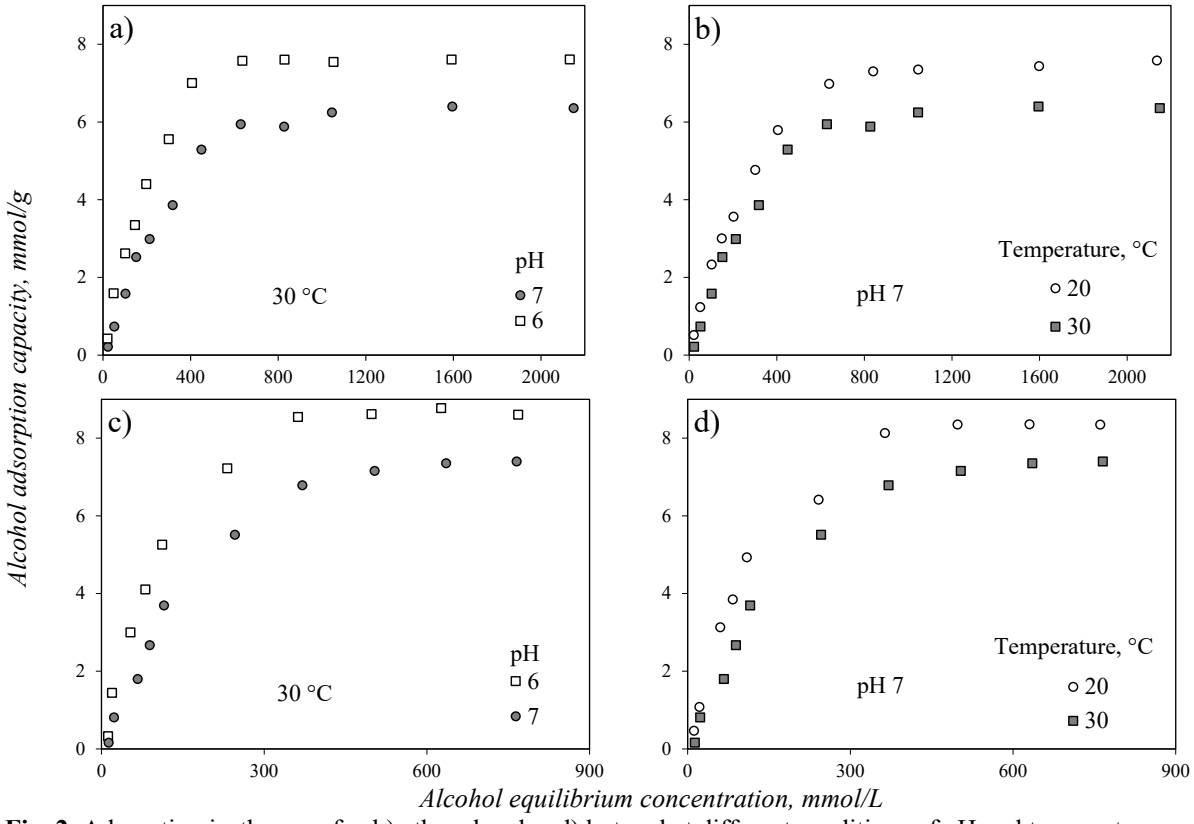


**Fig. 2.** Adsorption isotherms of a, b) ethanol and c, d) butanol at different conditions of pH and temperature.

## CONCLUSIONS

In this study, the analysis of ethanol and butanol adsorption on bone char was performed at 20 and 30 ºC and at pH 6 and 7 in a batch system. Results showed that ethanol and butanol adsorption on bone char was significantly affected by solution pH and temperature. The maximum uptake of ethanol and butanol was obtained at pH 6 and 30 °C where butanol adsorption was higher than that of ethanol. Recovery of ethanol and butanol via adsorption on bone char appears to be a feasible and low-cost process.

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