



Preparation of chemically-activated high surface area carbon from waste vinasse and its efficiency as adsorbent material

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ABSTRACT

Herein, a chemically activated carbon (AC) has been prepared from molasses-to-ethanol-process waste (vinasse). The procedure involves the preparation of carbonaceous spheres (CS) from the hydrothermal carbonization of the vinasse followed by activation with KOH at 800 °C. The effects of sole thermal treatment (without KOH) and the chemical activation on the structure and morphology of CS were evaluated by means of TGA, FT-IR, XPS, Raman spectroscopy, SEM and BET techniques. The sole thermal treatment produced a carbonaceous material with equal micro-mesoporous contents and a specific surface area (189 m²/g). On the other hand, the KOH-based activation produced a mainly microporous AC ($V_{\text{micro}} = 0.574 \text{ cm}^3/\text{g}$, $V_{\text{total}} = 0.691 \text{ cm}^3/\text{g}$, $V_{\text{micro}}/V_{\text{total}} = 0.83$) with a high specific surface area (1042 m²/g). Batch adsorption efficiency of AC was determined by using Victoria Blue B as a model dye in aqueous solution as functions of several operation parameters. Based on the non-linear regression analysis, the Langmuir isotherm model with monolayer adsorption capacity of 713.254 mg/g was preferable. The obtained AC was reusable for at least five cycles of adsorption-desorption. All results showed that the prepared AC has potential usability for the treatment of water polluted by dye-stuffs.

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1. Introduction

Vinasse can be described as a liquid waste emerged from the ethanol production through the fermentation of sugarcane or sugar beet molasses. The total production of ethanol from both sugarcane and sugar beet all around the world in the year 2013 was estimated as 1.63×10^{11} L, which generated $(16\text{--}24) \times 10^{11}$ L of vinasse [1]. Although properties of the waste vinasses mainly depend upon their raw materials, they share similar characteristics involving a dark brown color, unpleasant smell, low pH (pH 3.5–5.0), high concentration of organic substances (organic carbon: 42–85 g/L, biochemical and chemical oxygen demand (BOD and COD): 35 and 50–150 g/L, respectively), potassium (2.3–5.1 g/L) and sulphate (1.1–4.2 g/L) [2–4]. The soil and water pollution may occur when the vinasse is discharged into the environment without a suitable evaluation approach or treatment technique [5]. Therefore, the studies should be continued to find out a suitable evaluation or treatment method for the waste vinasse.

The main techniques in order to handle with the vinasse involve its application to soil as fertilizer and treatment by means of anaerobic digestion [6,7]. The using vinasse as fertilizer not only increases the soil salinity but also causes several other problems, such as decreasing in

the redox potential of the soil and groundwater contamination as well as odor problem [1,6]. In case of the treatment of vinasse by anaerobic digestion, it is reported that the fluctuations in its quantity and composition as well as the existence of inhibitory substances often reduces the treatment efficiency [7]. The other disadvantages of this method are the requirement of long time and the formation of bad-smelling and corrosive gases [8]. There are also studies concerning to the preparation of biochar derived from vinasse so as to investigate the applicability to soil as a fertilizer [9] and as a material which prevents the loss of soil because of water erosion [10]. Recently, environmentally friendly approaches as alternatives to those mentioned above have been developed in our previous studies based on the preparation of activated carbon from waste vinasse by using a two-step pyrolysis process combined with oxidation stage, where the cold oxygen plasma [11] and H₂O₂ under hydrothermal process [12] were used as oxidizers. Both these approaches provided the activated carbon with microporous structure and high surface area (832.3 and 989 m²/g for the process using the cold oxygen plasma and hydrothermally H₂O₂ oxidation stages, respectively). It was reported that the adsorption efficiencies of both activated carbon materials, which were specifically evaluated on the methylene blue as a model cationic dye in the aqueous solutions, were superior than most of the carbonaceous materials in the literature.

In recent years, the popularity of adsorption technique has increased due to its high efficiency in the treatment of water and wastewater. The

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activated carbon is one of the most suitable adsorbent material for the removal of pollutants from water [13]. Particularly, the large surface area and chemical nature of the activated carbon provides the high removal efficiency towards a wide variety of dye-stuffs from wastewater [14–17]. The recent studies have shown a trend to the utilization of low-cost and renewable agricultural wastes as precursors for the preparation of activated carbon [18,19]. In this study, the development of a high surface area activated carbon obtained by KOH-based activation of carbonaceous spheres produced from the hydrothermal carbonization (HTC) of vinasse has been reported for the first time. The schematic presentation of the procedure is illustrated in Scheme 1. The reason why HTC process was chosen as a first step of this procedure is because of the fact that it is considered as an efficient way for the conversion of many different biomass groups, such as wood and woody biomass, herbaceous and agricultural biomass, aquatic biomass, animal biomass waste, industrial biomass and their mixture, into the valuable carbonaceous products for promising application in many areas including carbon fixation, water treatment, fuel-cell catalysis, energy storage and so on [20–22]. Additionally, a recent review [23] and some research papers [24,25] have reported that many different hydrothermally carbonized biomass wastes can be successfully activated by means of a chemical process using different activation reagents, i.e., KOH, NaOH, ZnCl₂, H₃PO₄, etc. in order to increase their surface area, hence their performances as adsorbent materials. The KOH-based activation is one of the most widely used method for various carbonaceous starting materials, including coal, biomass or carbonized biomass by HTC process, graphene and so on, because it mostly ensures the ultra-high surface areas [26–28]. On the basis of this background, herein, the procedure by the combination of HTC step with KOH-based activation process is described to prepare activated carbon originated from vinasse. The temperature used in the activation step was determined by considering thermal gravimetric analysis of the carbonaceous spheres from the HTC process of vinasse. Further techniques covering FT-IR, XPS, Raman Spectroscopy and SEM as well as the determination of specific surface area, pore volume and pore size distributions were performed to characterize all the materials. Then, the adsorption performance of the obtained activated carbon was specifically determined on the Victoria Blue B (VB) as a model basic dye in the aqueous solution. The VB is a widely used dye-stuff in the textile industry especially for coloring anionic fabrics, i.e., cotton, silk and nylon [29]. Moreover, it has toxicity to aquatic life and chronic effect on the respiratory system [30]. The influences of solution pH and contact time on the adsorption efficiency were examined and the results were discussed. The isotherm analysis and reusability of the obtained activated carbon were presented.

2. Material and methods

2.1. Material

Ethanol, hydrochloric acid, sodium hydroxide and sodium chloride were supplied from Merck Co. (Darmstadt, Germany). The VB used as a basic model dye was purchased from Sigma-Aldrich. Fig. 1 depicts the chemical structure of VB, whose dimensions were estimated by using ACD/ChemSketch freeware (Canada).

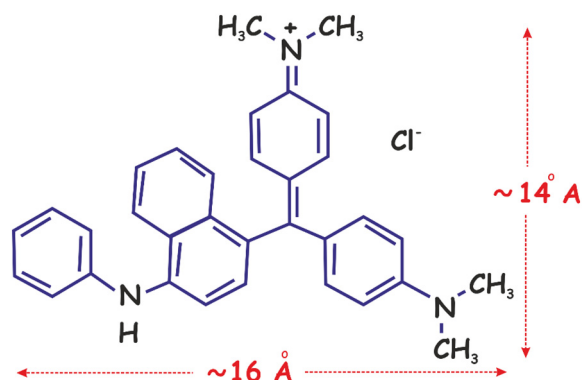


Fig. 1. Chemical structure of Victoria Blue B.

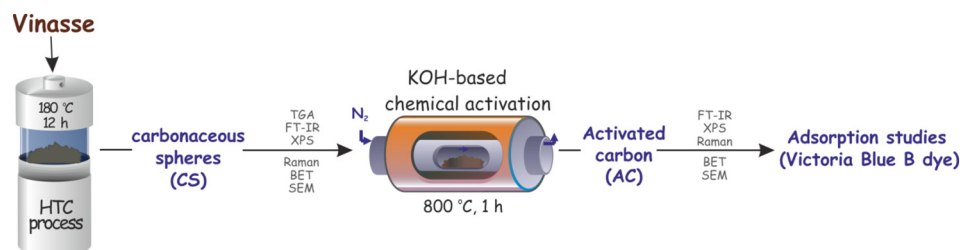
The waste vinasse was supplied from a distillation unit of bio-ethanol production process in a sugar beet factory (Konya, Turkey) and it was kept in the dark at 4 °C. The main properties of vinasse determined by means of the standard methods of APHA, AWWA, WEF were recorded as follows [31]: pH: 5.3, COD: 152 g/L, BOD: 90 g/L, conductivity (electrical): 24 ms/cm, total solids: 126 g/kg, volatile solids: 121 g/L, metal content (K: 19.4 g/L, Ca: 5.15 g/L, Zn: 0.17 g/L and Ni: 0.04 g/L).

2.2. Preparation of carbonaceous spheres by HTC process

The liquid waste vinasse was converted into the carbonaceous spheres by means of a modified HTC process described in our previous studies [32,33]. Namely, 5 mL of vinasse was put into a 50 mL capacity Teflon-lined stainless steel autoclave. It was heated to 180 °C and maintained at this temperature for 12 h. After cooling down the autoclave to room temperature, the black precipitate was washed with distilled water and finally dried in an oven at 100 °C overnight. The obtained carbonaceous spheres were identified as CS.

2.3. KOH-based activation procedure

The chemical activation was carried out by mixing 1 g of CS with KOH at a ratio of (1:1, w:w). This mixture was heated up to a temperature of 800 °C at a heating rate of 5 °C/min by using a horizontal furnace (Protherm, Turkey) containing a stainless steel tube, heating for 1 h under N₂ flow atmosphere (200 mL/min). After the obtained activated carbon was cooled to room temperature, it was washed with hot distilled water until the pH of the washing solution reached 7–7.5. Finally, it was dried at 100 °C overnight and stored in a desiccator for further characterization and adsorption studies. This final activated carbon was coded as AC. In order to determine the influence of the chemical activation on the structure and morphology of the CS, they were also pyrolyzed under the same conditions of the chemical activation process described above without using KOH. The obtained material was signed as CS-Pyrolyzed.



Scheme 1. The schematic illustration of all experimental procedure.

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