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Novel preparation of activated carbon by cold oxygen plasma treatment combined with pyrolysis

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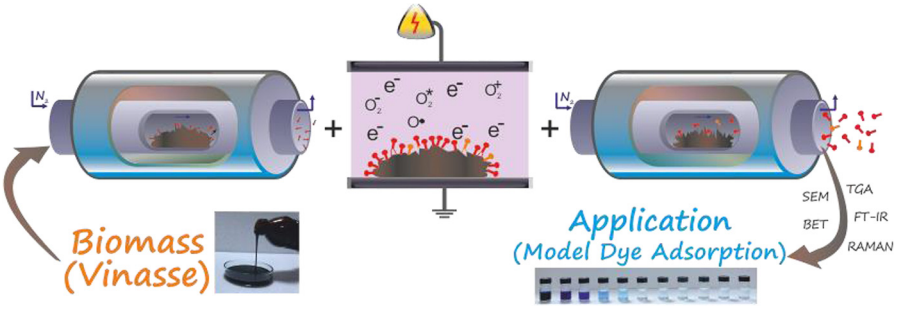
HIGHLIGHTS

- Vinasse has been used for the first time for the preparation of activated carbon.
- Oxygen plasma has been inserted for the first time between two pyrolysis processes.
- An activated carbon with mainly microporous structure has been obtained.
- Methylene blue adsorption capacity was higher than other carbonaceous materials.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports an original approach based on the inserting of a cold oxygen plasma treatment *as oxidation stage* between two pyrolysis processes for the preparation of an activated carbon from vinasse as a waste from the distillation of fermented sugar beet. The effects of pyrolysis temperature and plasma application time on the structural and morphological properties of the prepared carbon materials were investigated by Thermal Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) techniques and gas adsorption measurements (BET). The results of the different conditions indicated that the structure properties of the obtained activated carbon were significantly dependent on the pyrolysis temperature. As an optimum condition, the application of oxygen plasma for 5 min between pyrolysis processes at 1000 °C provided an eligible activated carbon with surface area (832.3 m^2/g) and mainly microporous structure. After preliminary examinations on various dyes, the adsorption performance of the activated carbon with highest surface area was specifically evaluated using methylene blue as a model dye in aqueous solution as functions of various operating parameters. Langmuir adsorption capacity (909.091 mg/g) of the prepared activated carbon toward methylene blue was superior than most of the other adsorbents.

1. Introduction

Vinasse is a liquid waste emerged from the distillation of fermented sugar beet or sugarcane molasses used for the ethanol production. 10–15 L of vinasse is averagely emerged from the production of each liter of ethanol. It is a dark brown acidic slurry

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(pH 3.5–5.0), which has high concentration of organic matter (organic carbon: 42–85 g/L, chemical oxygen demand: 50–150 g/L), unpleasant odor, potassium (2.3–5.1 g/L), sulphate (1.1–4.2 g/L) and others [1,2]. In the past, vinasse was directly discharged into the receiving water bodies, which resulted in serious environmental pollution problems. Therefore, various processes including fertirrigation, using as animal feed, anaerobic digestion and combustion in boilers have been reported for evaluation or treatment of vinasse [3]. However, all these processes have significant drawbacks. For example, the fertirrigation causes soil salinization, changes in the soil quality, odor problem, increasing phytotoxicity and dissolved salts in groundwater [3–6]. Usability of vinasse as animal feed is limited because of its high level of salts [7]. The main drawbacks of anaerobic digestion of vinasse are requirement of long detention and producing corrosive gases with unpleasant odor [3]. Apart from these processes, Sadeghi et al. [8] prepared a biochar from vinasse for application to a sandy clay loam soil to investigate the effects of vinassed-derived biochar on the soil loss, sediment amount, run-off time and volume due to water errosion at small-pilot scale. In another study, Melo et al. [9] applied a hydrothermal carbonization process to a mixture of sugarcane bagasse and vinasse for producing a hydrochar. They concluded that hydrochar has amorphous structure with similar composition to lignites and it has potential to be used as an agricultural fertilizer.

Herein, as an alternative to the current reuse/evaluation methods mentioned above, we described a novel process which converted the vinasse to a mainly microporous activated carbon by application of a cold oxygen plasma treatment combined with two-step pyrolysis process. In general, the physical and chemical processes are employed for the preparation of activated carbons [10] from different non-renewable precursors (i.e., petroleum based materials and lignite [11,12]) and renewable ones, including many different agricultural waste or lignocellulosic materials as reported in the review papers [13,14]. The physical treatment involves pyrolysis of precursor followed by activation using steam or CO_2 [15]. The chemical activation process includes impregnation of precurcors with a chemical activator (i.e., NaOH, KOH, H_3PO_4, $ZnCl_2$, H_2SO_4, K_2S, K_2CO_3, etc.) and application of heat treatment under inert atmosphere [16–22]. Although both physical and chemical activation processes provide activated carbon having a high surface area and a well-developed porosity [11], the latter process has some disadvantages such as requirement of removing the activator residue from product and being a less environmentally friendly method due to the use of chemical reagent [23].

In recent years, ozone oxidation and cold oxygen plasma techniques have been widely used in order to improve the reactivity, number of oxygen containing functional groups and hidrophilicity of the biochar and activated carbons for applications as an adsorbent material or a catalysis support [24–26]. Itoh et al. [27] reported that ozone could be efficiently used for the oxidation of carbon at temperatures up to 300 °C and beyond this temperature oxidation efficiency started to decrease because of thermal decomposition of ozone. The cold oxygen plasma treatment is considered as an environmentally-friendly process because it takes very short time and no chemical activators are needed [28]. During the cold oxygen plasma treatment on a carbon-based material, chemically active oxygen radicals, ions and molecules are produced and they attack the sp^2 hybridized graphite like C = C bonds. This attack causes defects in the prime sites of carbon-based material, which plays an important role in the functionalization of surface with oxygen [29]. Various papers reported that activated carbon derived from some precursors and treated with air and/or cold oxygen plasma processes can be efficiently used as adsorbent material for removing various pollutants, such as pentachlorophenol [25], lead [26], acid orange-II dye [30], anilin [31], dibenzothiophene [32] etc. from aqueous solutions and mercury [33] from gas phase.

Literature survey shows that so far the plasma treatment has been applied to the activated carbons as a final surface functionalization process. On the basis of this knowledge, another point which makes our study different from previously reported ones is that cold oxygen plasma treatment is used for the first time *as oxidation stage* between two pyrolysis processes during the preparation of an activated carbon. In order to prepare this novel activated carbon from sugar beet vinasse, it was dired at 230 °C in an oven. After the first pyrolysis of dried vinasse under nitrogen atmosphere, the cold oxygen plasma treatment was applied to the pyrolyzed materials *as oxidation stage* followed by a final pyrolysis. The temperatures (600, 800 and 1000 °C) for the first pyrolysis were selected by means of thermal gravimetric analysis (TGA) of the dried vinasse. These materials were then oxidized by means of 5 min of plasma treatment, followed by a final pyrolysis under same condition of the first one. The obtained materials from each stage were characterized by using Thermal Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX) techniques and gas adsorption measurements (spesific surface area, pore volume and pore size distribution). The effect of oxygen plasma on the characteristics of the materials was examined at different time between 1 and 10 min. The adsorption performance of the activated carbon having the maximum surface area, pore volume and their size distribution was spesifically evaluated by using methylene blue as a model cationic dye in aqueous solution. The effect of the operating parameters including solution pH, contact time, adsorbent dosage and temperature on the adsorption efficiency were studied. Isotherm analysis and reusability of the prepared activated carbon were presented. The adsorption capacity of the activated carbon toward methylene blue was also compared with others in the literature.

2. Material and methods

2.1. Material

Hydrochloric acid, sodium hydroxide, sodium chloride, ethanol and methylene blue were obtained from Merck Co. (Darmstadt, Germany). Bromophenol blue, Rhodamine B, Congo red, Victoria blue B and Lissamine green B were obtained from Sigma-Aldrich.

The liquid vinasse was obtained from ethanol distillation unit in a sugar beet processing company (Konya Şeker Co.) located in the city of Konya (Turkey) and it was stored in dark at 4 °C. The vinasse was characterized on the basis of standard methods of APHA, AWWA, WEF [34] and the results were as follows: pH: 5.30, chemical oxygen demand:152 g/L, biochemical oxygen demand: 90 g/L, electrical conductivity: 23.9 ms/cm, total solids: 126.4 g/kg, volatile solids: 120.5 g/L, potassium: 19.4 g/L, calcium: 5.15 g/L, zinc: 0.17 g/L and nickel: 0.04 g/L.

2.2. Drying and pyrolysis of vinasse

Firstly, 1 L of the liquid vinasse was placed into a silicon mould and dried in an oven (Nabertherm, Germany) with a temperature program including a heating rate of 5 °C/minute until 230 °C and hold at 230 °C for 6 h. The dried vinasse was ground and sieved to obtain a particle size less than 100 μm. The first pyrolysis of pretreated vinasse was carried out in a tubular furnace (Protherm, PZF 12/50/500, Turkey) using a stainless steel reactor under nitrogen atmosphere (flow rate: 200 mL/minute). The temperature program of the pyrolysis was a heating rate of 5 °C/minute until the desired