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Research article

Activated carbon from sugarcane bagasse ash for melanoidins recovery

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ABSTRACT

This work investigates the value added utilization of two sugar-distillery wastes: (i) melanoidins, which are complex Maillard reaction products in molasses distillery wastewater, and (ii) unburnt carbon in sugarcane bagasse ash. Activated unburnt carbon (AUC), prepared by deashing and steam activation, had properties comparable to commercial activated carbon (CAC). Both carbons are suitable for melanoidins adsorption followed by desorption using 25% pyridine solution. For AUC, the equilibrium adsorption data is well described by Langmuir isotherm up to 35 °C while Freundlich model fits better at higher temperature. Adsorption using CAC followed Freundlich isotherm at all temperatures. Both carbons followed pseudo second order kinetics and displayed endothermic physisorption. Recovery of melanoidins from AUC (78%) was close to that observed with CAC (80%).

1. Introduction

Melanoidins are dark coloured complex Maillard reaction products formed by reaction between carbonyl groups of reducing sugars and compounds with free amino groups. They exist in dietary products like honey (Brudzynski and Miotto, 2011), coffee (Rufian-Henares et al., 2009) and beer (Kuntcheva and Obretenov, 1996) and possess potential physiological benefits like antioxidant, antimicrobial and antihypertensive activity (Rufian-Henares and Morales, 2007). Melanoidins are a significant constituent (nearly 2%) of wastewater (spentwash) generated from sugarcane molasses based alcohol distilleries (Martins and Van Boekel, 2004). Owing to their structural complexity, melanoidins are difficult to bio-degrade and pass through the conventional anaerobic digestion step without breaking down. Moreover, the colour intensifies during biological treatment leading to issues in disposal of the biologically treated effluent. Removal of melanoidins prior to biological treatment could thus offer a solution, especially if the recovered melanoidins could be utilized.

Several routes have been followed for recovering melanoidins from different sources. Melanoidins have been concentrated using different ultrafiltration membranes (100 and 10 kDa respectively) in order to explore their physiological benefits (Rufian-Henares and Morales, 2007). Solvent extraction studies were conducted with post biomethanated distillery wastewater for melanoidins extraction at different pH using isopropanol. Maximum melanoidins extraction was obtained at pH 11 (2.87% w/v) (Kalavathi et al., 2001). Different waste based adsorbents have also been investigated for recovery of melanoidins. Modified zeolites achieved 90% removal of synthetic melanoidins with maximum adsorption capacity increasing from 823 mg/g to 1157 mg/g as temperature was raised from 25 °C to 45 °C (Onyango et al., 2011). Chitin nanofibers showed adsorption capacities between 131 mg/g to 353 mg/g at different temperatures (Dolphen and Thiravetyan, 2011). Activated carbon from bagasse bottom ash achieved more than 90% reduction in synthetic melanoidins concentration with maximum adsorption capacities ranging from 200 mg/g to 235 mg/g as temperature increased from 5 °C to 60 °C (Simaratanamongkol and Thiravetyan, 2010). Melanoidins were desorbed after physisorption in these studies using distilled water or a combination of distilled water, NaOH, ethanol, and methanol. Overall, melanoidins adsorption capacity of these materials was low.

Sugarcane bagasse ash from Indian sugar factories contains 16%–33% unburnt carbon, which translates to an estimated annual generation of approximately 0.97 million tonnes of unburnt carbon (Gupta et al., 2003; Batra et al., 2010). This unburnt carbon can be readily separated and converted to adsorbent for recovery of small molecules like phenols (Bajwa et al., 2015). Utilization of unburnt

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carbon would not only result in alternative use of erstwhile waste material but would also lead to economic and environmental gains.

The novelty of the work lies in the recovery of melanoidins by adsorption-desorption process using waste from the same industry. Sugarcane bagasse ash, which is another sugar-distillery process waste, was used to prepare activated carbon from its unburnt carbon fraction. Details of the carbon properties and adsorption-desorption studies are presented. The present study investigates recovery of melanoidins using prepared activated unburnt carbon and that procured commercially. The activated carbons have been characterized and equilibrium, kinetic & thermodynamic adsorption studies were performed to obtain the melanoidins adsorption potential. Different desorption solvents have been examined and the most suitable conditions for melanoidins recovery has been identified.

2. Materials and methods

2.1. Materials

Bagasse ash was collected from Simbhaoli Sugars Limited, Uttar Pradesh, India. Commercial activated carbon and chemicals used for desorption studies were supplied by Qualigens, Delhi. D-Glucose and glycine were obtained from Sigma Aldrich, Delhi. Cerium nitrate hexahydrate was purchased from HiMedia Pvt Ltd Mumbai, India. Reverse osmosis (RO) water (conductivity 0.016 mS) was used to prepare the required solutions.

2.2. Preparation and characterization of activated carbons

The procedure provided in Batra et al. (2010) was followed. Carbon-rich fraction (>425 μm), obtained by sieving bagasse ash, was further separated by flotation. The separated carbon was dried and deashed with acid (15% HCl, followed by 25% HF) before washing thoroughly with RO water and drying. The separated carbon (UC) and the deashed carbon (D-UC) were steam activated at different carbon: water ratio of 1:3, 1:5 and 1:7 at 800 °C for 3 h in stainless steel containers (Subramanian et al., 2013). To increase mesoporosity, D-UC was impregnated with aqueous cerium nitrate solution (0.5% and 1.0% cerium nitrate loading on carbon) for 8 h at room temperature (Shen et al., 2003). The impregnated carbon was oven dried at 120 °C for 5 h and then steam activated at varying carbon: water ratio, activation temperature (680 °C-870 °C) and time (1.5–6 h). All carbons were provided codes to indicate the activation conditions. For example, 3D-UC-680-0.5 indicates deashed unburnt carbon, steam activated at 1:3 carbon: water ratio at 680 °C after impregnation with 0.5% cerium nitrate.

Physical characterization of commercial and prepared activated carbons was done using standard (ASTM-American Society for Testing and Materials) methods. pH for activated carbons was measured as per the procedure mentioned (Ahmedna et al., 1997). Selected samples were analyzed for pore size (in Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Gujarat using PASCAL 440 Porosimeter, Thermo Quest) and CNH (in SICART, Gujarat using CHN/S/O analyzer Perkin Elmer, series 11, 2400, USA). Surface functional groups were analyzed using Fourier Transform Infrared (FTIR) spectra (Perkin Elmer, USA). BET surface area measurements were obtained from nitrogen adsorption isotherms at 77 K by using a SmartSorb surface area analyzer.

2.3. Adsorption-desorption studies

Melanoidins, prepared using D-glucose and glycine (Dahiya et al., 2001), was dialyzed (>12 kDa cellulose dialysis membrane, procured from Sigma-Aldrich, USA) to remove low molecular weight compounds. The dialyzed stock was used to make 5% v/v solution that was subsequently used in all adsorption experiments. The pH of the solution was 7. Melanoidins content in both adsorption and desorption studies was estimated at 475 nm using *UV–Vis* spectrophotometer (Aquamate, India).

Adsorption was carried out by mixing 50 mL of melanoidins solution with known amount of adsorbent (2 g/L-16 g/L) in 100 mL conical flasks. The mixture was kept in a shaker (Orbitek, Scigenics Biotech, India) at 160 rpm for 24 h at different temperatures (15 °C-45 °C) and was vacuum filtered through 0.45 μm filter paper before analysis. One set of flasks without carbon addition was kept as control. All the experiments were done in duplicate. The difference in the data was calculated as relative difference [Relative difference (%) = (difference of replicate 1 and replicate 2) x 100/Average of two replicates]. Adsorption capacity (q_e, g/g) at equilibrium was calculated as follows (eqn. (1), Simaratanamongkol and Thiravetyan, 2010).

$$q_e = \{(C_o - C_e) \times V_o\}/m \quad (1)$$

where, C_o and C_e are the initial and final concentration of adsorbate solution (g/L) respectively, V_o is the volume of adsorbate (L) and m is the adsorbent mass (g).

Adsorption kinetics was studied over 30 min–240 min at optimum dosage at varying temperature (15 °C–45 °C) and the thermodynamic parameters were determined. Different solvents namely distilled water at varying pH (2, 7 and 11) and temperature (25 °C and 90 °C), NaCl (0.5 M, 1 M), pyridine (25%), acetone, 10% ethanol, brine at 84 °C and pH 12, and new regeneration solution (5% NaOH, 0.2% H_2O_2, 25% ethanol) were screened for melanoidins desorption. Post adsorption, the activated carbon was separated from the supernatant by settling and vacuum filtration and mixed with 50 mL of desorption solvent. The mixture was agitated in a shaker at 25 °C for 24 h at 160 rpm and the supernatant analyzed by spectrophotometer at 475 nm. Desorption percentage was calculated as follows (eqn. (2), Bertin et al., 2011).

$$D\ (\%) = \{(C_d \times V_d) \times 100\}/(C_o - C_e) \times V_o \quad (2)$$

where, C_d is concentration of melanoidins obtained after desorption,V_d is volume of desorption solvent, C_o and C_e are the initial and final concentration of adsorbate solution (g/L) respectively, V_o is the volume of adsorbate (L).

The most suitable desorption solvent was selected, its concentration optimized (20%–35%) and the desorption kinetics analyzed over a duration of 30 min–240 min.

3. Results and discussion

3.1. Activated carbons characterization

The physical and surface characterization of different steam activated unburnt carbons has been studied (Supplementary sheet, Table S.1). The unburnt carbon is alkaline, which is related to its high ash content, mainly due to presence of calcium salts, alkali carbonates and silica (Hapazari et al., 2011). Increase in ash content upon steam activation may be attributed to higher burn off at 800 °C thereby increasing the pH of the carbons. Deashing of UC decreased the ash content from 23% to 2.2% leading to consequent reduction in pH. Steam activation led to appreciable increase in the surface area and methylene blue number, especially if the carbons were deashed.

To enhance the mesoporosity of the activated carbons by catalyzing the steam activation reaction, D-UC was impregnated with cerium nitrate and steam activated at varying temperatures and