CHEMICAL REMEDIATION OF HIGH-B.O.D. AND DARK-COLORED EFFLUENT: EXPERIMENTAL AND COMPUTATIONAL STUDIES

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Abstract

Melanoidin is the main color pollutant from molasses and sugar-based factories. Its remediation is hampered by the persistence of its dark color due to its polymeric structure and its recalcitrance to microbial and chemical treatments. An anionic exchange resin method was used to decolorize melanoidin, which is also an ionic color pollutant. Several anionic exchange resins (DEAE Cellulose, DEAE Sephadex, Amberlite IRA-410, Dowex 1-X8 and chitosan) were evaluated and their ability to decolorize both the natural and the synthetic melanoidin were studied. Among the five anionic exchangers examined, DEAE-Cellulose showed the best performance for melanoidin decolorization. Three of these resins (DEAE Cellulose, DEAE Sephadex and Amberlite IRA-410) were further evaluated and characterized using Hyperchem and AUTODOCK. DEAE Sephadex was observed to have the lowest docking energy and Gibbs energy of binding. Furthermore, strong oxidizers such as ozone are needed in the chemical remediation of this important pollutant. The kinetics of ozonation of synthetic glucose-glycine prepared melanoidin was studied in unbuffered and buffered solutions (pH 3.5 -10). The reaction was found to obey first-order and half-order kinetics based on absorbance data at 475 nm and 280 nm, respectively. After two hours of ozonation, melanoidin decolorization was in the range 64–94%; decolorization was greater at lower pH values. Microbial decolorization was also performed. Synthetic glucose-glycine melanoidin, after partial purification by Sephadex G-100 chromatography, was ozonated and then used as culture substrate for Bacillus subtilis. Ozone treatment for 15, 30 and 60 minutes resulted in decolorization (reduction in absorbance at 475 nm) values of 21.4 %, 41.3 % and 65.3 %, respectively; corresponding molecular weight (MW) values were 18.8, 15.3 and 9.0 kDa compared with a MW of 51.6 kDa for raw melanoidin. The pH of the melanoidin solution decreased from an initial value of 6.4 to 5.3, 4.9 and 4.6 after 15, 30 and 60 minutes of ozonation, respectively. The 1-hour ozonated melanoidin showed further 23 % decolorization after bacterial treatment for 1 – 5 days. The final MW values after combined ozonation and bacterial treatment were 16.6, 13.2 and 7.8 kDa for 15, 30 and 60 minutes ozonation, respectively. Using computational chemistry, it showed that the melanoidin structure proposed by Yaylayan and Kaminsky (1998) had the least value (most negative) of heat of formation, both in vacuo and solvated system. Thermodynamically, this is the most stable among the Cammerer-Kroh (1995) and the Kato-Tsuchida (1981) structures of melanoidin.

Keywords: color pollutant, melanoidin, Maillard reaction, bacterial decolorization, computational chemistry, ozonation, Hyperchem, AUTODOCK, docking, solvation

Introduction

Melanoidin is a major color pollutant from molasses-based fermentation plants, alcohol distilleries and sugar processing factories. It collectively refers to dark-brown, high-polymeric compounds, which is formed by a non-enzymatic browning (Maillard) reaction between a reducing sugar and an amino compound upon heating. Melanoidin is found to be negatively charged because of the dissociation of carboxylic and hydroxylic groups (O'Melia, et. al., 1978) but the detailed molecular structure has not yet been established. Formation of this polymer is very complex and can be influenced easily by the change in reaction conditions (Cämmerer and Kroh, 1995). Concentration, pH, temperature, pressure, reaction time, water activity and inhibitors are some factors affecting the Maillard reaction.

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