

Melanoidin removal in multi-oxidant supplemented microwave system: Optimization of operating conditions using response surface methodology and cost estimation



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ABSTRACT

Melanoidin removal in a microwave (MW) coupled with persulfate (PS) and/or hydrogen peroxide (H_2O_2) system was investigated. As a precursor, batch-mode MW-PS experiment was conducted at 250 mg/L of melanoidin concentration. The removal was observed to be 100% in 20 min of MW irradiation at PS dose of 2500 mg/L and it was found that the rate constant increased with PS dosage. On the other hand, the MW- H_2O_2 process has shown 31% removal at 6000 mg/L H_2O_2 dosage in 20 min. A central composite design (CCD) was used to identify the interaction between melanoidin concentration (500–10000 mg/L), pH (2–12), H_2O_2 (0–6000 mg/L) and PS (0–5000 mg/L) dosages on melanoidin removal in MW system. The basic condition (pH > 7) has shown higher melanoidin removal in the presence of H_2O_2 /PS; however, proportionate decrease in removal was observed with increase in melanoidin concentration. The addition of H_2O_2 and PS has amplified the removal of colour induced by melanoidin, which was modeled by quadratic ($R^2=0.87$) and cubic ($R^2=0.98$) regression models. A set of validation experiments were carried out under model predicted optimum conditions. The experimental observations were in good correlation with the cubic model predicted values. Alcohol scavenging experiment shows that both sulfate and hydroxyl radical are responsible for melanoidin removal. The generation of hydroxyl radicals was estimated. A simple first-order kinetic equation-based model was developed to calculate the cost per kg of melanoidin removal in MW-PS/ H_2O_2 system. Overall, MW-PS/ H_2O_2 system seems to be a better alternative for high-rate melanoidin removal.

1. Introduction

The treatment of wastewater from agro-based industries like distillery, winery, and brewery has become a serious challenge at present due to the high organic content and the presence of recalcitrant and refractory compounds like melanoidin, phenolics, etc. Melanoidins are dark brown coloured, high molecular weight polymers formed as the end-products of Maillard reaction. They have antioxidant, anti-hypertensive, and antimicrobial activities [1]. Maillard reaction occurs when a carbohydrate reacts with an amino acid or an amine at a temperature higher than 40 °C. Therefore, these melanoidins are common constituents in the wastewater of agro-based industries that process organic food materials at high temperatures. Due to the presence of melanoidins as high as 2–20 g/L, biological treatment is not feasible for wastewater from such industries. Aerobic and anaerobic treatment systems can easily remove sugars, volatile organics and other easily biodegradable compounds that constitute COD and BOD but the colour

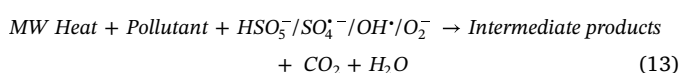
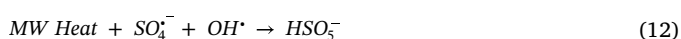
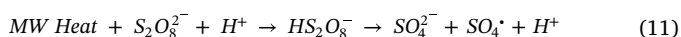
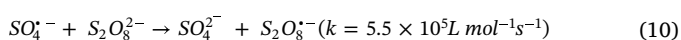
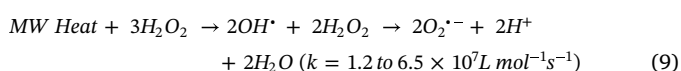
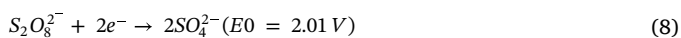
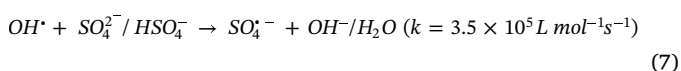
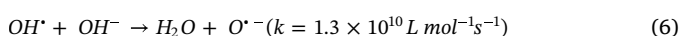
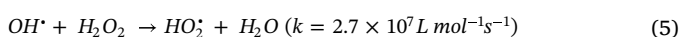
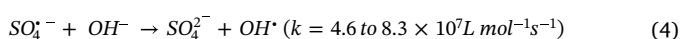
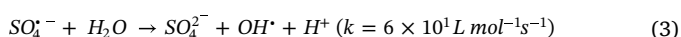
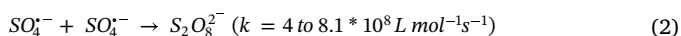
and COD constituted by melanoidin remain unchanged after treatment. Biological treatment systems could remove only 6–7% of melanoidin and therefore, reverse osmosis and/or advanced oxidation processes (AOPs) have been used to concentrate or degrade melanoidins [2–4].

Microwave (MW) technology has been used for various applications including preparation of catalysts [5–7], sludge management [8,9], biogas production [10], heating and enhancement of different catalytic oxidation and reduction processes [11,12]. MW systems are coupled with other AOPs and oxidants such as persulfate (PS) and hydrogen peroxide (H_2O_2) for the treatment of wastewaters containing various organic pollutants. [13–21]. MW creates hotspots and favors free radical generation, which in turn reduces the activation energy [22]. The mechanism of sulphate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals (OH^{\bullet}) reaction under MW irradiation is explained based on Eqs. (1–9). Under acidic conditions, the addition of PS to MW system accelerates the generation of $\text{SO}_4^{\bullet-}$ as shown in Eq. (1). Subsequently, the generated $\text{SO}_4^{\bullet-}$ can lead to the formation of OH^{\bullet} (Eqs. 3,4). Similarly, the

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presence of H_2O_2 under MW environment can generate OH^\bullet and superoxide ion ($O_2^{\bullet-}$) (Eq. 9) whereas under combined PS/ H_2O_2 , peroxymonosulfate (HSO_5^-) can be generated as shown in Eq. 12 [23,24]. The efficiency of HSO_5^- is higher compared to PS, which can result in enhancement of pollutant removal [19,23]. On the other hand, the presence of HSO_5^- , $SO_4^{\bullet-}$, OH^\bullet and $O_2^{\bullet-}$ could accelerate the rate of pollutant removal and better mineralization of the organics. However, high concentration of radicals may result in self-quenching effect (Eq. 2,10) and in turn could reduce the rate of oxidation [25–27]. The generation of radical has been quantified in the past with alcohol quenching experiments [27,26]. In addition, the removal rate also depends on the nature of pollutant, type of bonding between molecules and structure of the target compound.



The presence of melanoidin produces deep brown colour and therefore, AOPs that are not dependent on photochemical activation are generally preferred. As a result, ozonation, ultrasound, and other similar hybrid systems have been adopted for melanoidin removal [28–30]. It was reported that coupled multi-oxidant systems are capable of producing synergistic effects [31]. Thus far, melanoidin removal in coupled MW-multi-oxidant system has not been investigated in detail. Moreover, the interactions of oxidant dosage with pH and initial melanoidin concentration are difficult to be predicted in traditional experimental design under MW-multi-oxidant systems. Central composite design (CCD) is an effective tool used for design of experiment, optimization of system parameters, analysis of variance and error analysis. Therefore, this investigation is focused to study the (a) melanoidin removal between MW-PS, MW- H_2O_2 and MW-PS/ H_2O_2 systems, (b) melanoidin removal rate constants under different systems, (c) interaction between initial melanoidin concentration, pH and oxidant dosage by CCD, (d) generation of free radical species with alcohol scavenging experiments, and (e) cost for melanoidin removal in the MW-multi-oxidant system.”.

2. Materials and methods

2.1. Chemicals

Sodium persulfate (98% w/w) and hydrogen peroxide (30% w/w) were purchased from AVRA Chemicals, India and Fischer Scientific,

India, respectively. Premium grade ethanol (EtOH) and analytical grade tert-butanol (TBA, 99% purity) was purchased from Hayman, UK, and Merck, India, respectively. Analytical grade Dimethyl sulfoxide (DMSO) and 2,4-Dinitrophenylhydrazine (DNPH) were purchased from Cisco research laboratory ltd., India. Acetonitrile (HPLC grade) was purchased from Rankem, India. Dextrose, glycine, NaOH, and H_2SO_4 used for the experiments were procured from Merck, India. Distilled water (DW) was used for all experimental purpose.

2.2. Preparation of melanoidin solution

A stock melanoidin solution of $210 \pm 20 \text{ g/L}$ (COD $\sim 240 \pm 10 \text{ g/L}$) was prepared by mixing dextrose (1 M), glycine (1 M) and sodium carbonate (0.5 M). Subsequently, the solution pH was adjusted to 7 by adding 1 N H_2SO_4 , stirred for 30 min and incubated in a hot air oven at 95°C for 7 h. The dark brown solution obtained was cooled and stored at 4°C in the refrigerator.

2.3. MW reactor set-up

A customized MW reactor, as used previously [14], of frequency 2450 MHz and capable of operating at 1000 W with an inbuilt magnetic stirrer and temperature sensor was used for the experimental work (Ragatech Pvt. Ltd., India). A reaction vessel of 1 L volume was used and 500 W power and 80°C was maintained throughout the experiment. The MW reactor was operated in batch mode with 100 mL working volume. A counterflow heat-exchanging condenser was housed to collect the vapour which was circulated back into the reaction vessel to maintain a constant working volume.

2.4. Experimental techniques

2.4.1. Melanoidin removal batch experiments

In order to evaluate the effect of pH, dosage and irradiation time on melanoidin removal, MW- batch experiments were conducted with 250 mg/L of melanoidin and under different combinations of pH (2–12), PS dosage (100–5000 mg/L) and H_2O_2 dosage (100–6000 mg/L). The experiments were conducted for 20 min and the samples were withdrawn from the reactor at various time intervals to determine melanoidin removal. The batch study was divided into three phases: 1) MW-PS, 2) MW- H_2O_2 and 3) MW-PS/ H_2O_2 . The effect of PS and/or H_2O_2 dose, MW irradiation time and pH on melanoidin removal observed in these experiments are used to evaluate boundary condition for CCD experiments with MW-PS/ H_2O_2 system.

Alcohol quenching experiment was conducted for melanoidin degradation with MW-PS/ H_2O_2 process in presence of scavenging agent to stop radical generation during the reaction. The scavengers used were TBA and EtOH for quenching OH^\bullet and $SO_4^{\bullet-}$, respectively. The concentration of each scavenging agent added during the experiment was 0.4 M to compare effect of scavengers on melanoidin removal. The OH^\bullet was estimated by trapping with DMSO and converting into formaldehyde by adding DNPH. The DNPH-HCHO concentration was detected and calibrated in HPLC (Dionex, USA) fitted with C18 silica-based reverse phase column and UV-vis detector. The mobile phase was acetonitrile: water (60:40) with a flow rate of 1 mL/min. The retention time of DNPH and DNPH-HCHO derivatives were found at 4.8 and 7.4 min, respectively. For HPLC analysis, 2.5 mL of sample was added to 2.5 mL of 25 mM phosphate buffer and 0.2 mL of DNPH. Subsequently, the sample was mixed well and kept for 30 min in room temperature. Finally, the resultant mixture was diluted 20 times and injected into HPLC for analysis.

2.4.2. Experimental design for melanoidin removal

The response surface methodology was used to optimise experimental parameters of MW-PS/ H_2O_2 system for better melanoidin removal at different initial concentrations. A 2^4 full factorial design with

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