Kinetics of wet air oxidation pretreatment and biodegradability enhancement of a complex industrial wastewater

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ABSTRACT

A kinetic study of wet air oxidation pretreatment and induced biodegradability enhancement of a model complex wastewater was studied in the temperature range of 150–200 °C, air pressure 6–12 bar (0.6–1.2 MPa), reaction time 15–120 min and agitation 150–500 rpm. Based on free radical mechanism, a kinetic model is postulated where the electron transfer from air (oxygen) to the substrate was assumed to initiate the free radical generation. According to the model, reaction orders for wet oxidation pretreatment (in terms of COD degradation rate) were found to be 1.0, 0.42 and 0.22 for COD and oxygen partial pressure respectively. The WAO pretreatment led to reorientation and/or breakdown of complex biologically recalcitrant molecules with 3–5-fold increase in biodegradability index. The kinetics of biodegradability index enhancement was successfully correlated with COD degradation kinetics.

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Introduction

Advanced Oxidation Processes such as wet air oxidation (WAO) has immense potential for the treatment of complex effluents containing high organic content (Chemical Oxygen Demand, COD 10–100 g L^{-1}), and/or toxic contaminants for which the conventional biological treatment approaches have severe limitations [15,6,9,17].

Highly concentrated, toxic as well as biorefractory wastewaters are generated from coking, chemical manufacturing, pharmaceutical operations, etc. [13,3]. The cane molasses-based distilleries generate one of such complex, troublesome and strongest industrial organic effluents with high COD (90,000–1,10,000 mg L^{-1}), dark brown colour and huge volume (8–15 L L^{-1} of alcohol produced) [11,18]. The biomethanated distillery wastewater (B-DWW, known as digested spentwash) after the conventional anaerobic digestion still retains a residual COD of more than 40,000 mg L^{-1}, intensified dark brown colour and becomes recalcitrant to further effective treatment by biological methods (BOD₅:COD ratio < 0.2). This residual COD represents complex organic molecular compounds which after wet air oxidation pretreatment breaks down into simpler lower molecular weight compounds. These lower molecular compounds are easily biodegradable, thus enhancing the BOD value

i.e. BI ratio. Hence, wet air oxidation of B-DWW results in significant COD reduction and BI enhancement as earlier reported by our group [17].

In the present investigation kinetics of wet oxidation based pretreatment of B-DWW as a model complex wastewater has been attempted. The sub-critical wet oxidation of phenol has been reported, based on free radical mechanism leading to formation of lower molecular weight compounds such as acetic acid, formic acid [20]. Catalytic wet air oxidation of phenol using aqueous copper nitrate catalyst was reported at various temperatures (40–50 °C), oxygen partial pressure (6–19 bar) and copper concentration (0–13 mg L^{-1}), the reaction orders were reported to be approximately 1, 0.5 and 0.5 with respect to phenol, oxygen and copper concentrations [21]. Gunale and Mahajani [9] have reported Fenton assisted wet air oxidation for aniline mineralisation in the temperature range of 200–240 °C, oxygen partial pressure 3.45–13.8 bar, they modelled the kinetic data using a power law rate expression in terms of COD.

It is often difficult to measure concentration of individual components in a complex effluent mixture such as B-DWW. Hence, the concept of lumped parameters to evaluate the wet air oxidation process (partial oxidation in present case) is of great significance [22,9]. In order to have a thorough understanding of the mechanistic approach of the WAO of B-DWW, the insights of the process kinetics is desirable for aiding the reactor design. Reports on the kinetic data available in the literature [19,9,5] mostly deal with WAO of individual compounds attempted

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towards substantial COD destruction, and kinetics of a complex effluent has been cited to a limited extent in the literature [22,10]. Keeping this in view, in the present investigation, WAO was investigated as a pretreatment option for complex effluent using a lab-scale reactor, with emphasis on enhancing the biodegradability index with limited COD destruction. Further, the kinetic data has been generated based on the process variables such as reaction time, temperature, pressure and speed of agitation of WAO. A kinetic expression for the WAO based pretreatment and induced biodegradability enhancement of model complex wastewater has been developed and presented in this study.

Materials and methods

Model complex wastewater and reagents

The biomethanated distillery wastewater (model complex waste water) was procured from the molasses-based distillery located in Central India (details not provided due to confidentiality issues). The wastewater was transported to the laboratory and was stored in tightly capped car buoys in cold storage (at 4 °C) for further use. The collected wastewater was analysed for its physico-chemical characteristics and the results are represented in Table 1. All the reagents and chemicals used in the study were of analytical grade.

Wet air oxidation reactor and operation

The studies were carried out in a wet air oxidation reactor, having 1.8 L capacity (Model – 4578, Floor Stand HP/HT Reactor, Parr Instruments, IL, USA) made of SS-316. The reactor (ID 95 mm) was equipped with a four bladed turbine type impeller (ID 50 mm). The agitation speed was varied between 150 and 500 rpm using a variable speed motor. The gas inlet, gas release valve, cooling water feed line and pressure valve were mounted on top of the reactor. The reactor was also equipped with rupture disc and a non-return valve at gas inlet. 500 mL of the wastewater was used for pretreatment (equivalent to working volume of 0.5 L). The reactor was properly sealed, ensuring absence of any leakage. The reaction mixture was then heated to a desired temperature and air was sparged, using a gas sparger situated beneath the impeller, to the predetermined level (6–12 bar). The total pressure is the sum of air (applied) pressure and liquid vapour pressure. The B-DWW stored at 4 °C was allowed to attain the room temperature. The wastewater was then used as such for pretreatment using WAO.

The B-DWW was subjected to WAO as a pretreatment in batch experiments. As no pH adjustment was made, the original wastewater pH was the initial pH for the pretreatment step. Wet air oxidation was carried out at different conditions in the temperature range of 150–200 °C, pressure 6–12 bar and time 15–120 min and agitation speed 150–500 rpm. After every run, the reactor was put in a cooling mode. The pre-treated samples were analysed for pH, COD, BOD, total organic carbon (TOC), volatile fatty acids (VFA) and biodegradability index (BOD:COD ratio). The details of process and mechanism of WAO has been described earlier by various workers [19,9,5,17].

Analysis

All samples were analysed for COD, BOD and VFA as per the standard methods (American Public Health Association, APHA [1]). Control dynamics make pH meter was used for monitoring pH of the samples during investigation. FTIR analysis of WAO untreated and treated samples was carried out using Fourier Transform Infrared Spectrometer (FTIR Model: Vertex 70-Bruker). For H NMR analysis samples were extracted with D_2O under N_2 inert atmosphere (5 mm NMR tube). The samples were analysed using BRUKER AV III 500 MHz FT NMR Spectrometer and chemical shift were recorded in ppm (δ) with TMS at 0.0 as an internal standard. To minimise the block effect each WAO run was repeated three times by a single operator in succession.

Biodegradability index

The biodegradability index (BI) is a measure of the extent to which a waste is amenable to biodegradation. BI can be expressed as ratio of BOD_5:COD [16]. The COD and BOD of the WAO pretreated wastewater were evaluated as per the Standard Methods [1] and compared with the B-DWW without WAO pretreatment.

Results and discussion

Diffusion mass transfer considerations

The WAO process and mechanism has been described earlier by various workers [19,9,5,17]. The overall wet air oxidation mechanism incorporates two steps. One is the physical step i.e. the transfer of oxygen from the gas to the liquid phase and the transfer of carbon dioxide to the gas phase from the liquid phase. The second one being a chemical reaction between the organic matter and oxygen dissolved in the liquid phase, producing carbon dioxide. While operating a wet air oxidation reactor, it is usually considered that gases diffuse rapidly within the gas phase. The only significant transfer resistance is located at the gas–liquid interface and the actual conditions within a reactor will depend on its hydrodynamics. For high mixing efficiencies, the oxygen concentration within the bulk liquid is close to the interface (or equilibrium) concentration and the overall rate is close to the chemical rate.

Owing to the high diffusivity of O_2 in the gas phase and its low solubility in water, the gas phase mass transfer resistance was estimated to be negligible in the range of operating temperatures used for present studies. To get a representative kinetic data, the reaction must take place in the slow-reaction regime with substantial kinetic control (in which case the overall rate is determined by the reaction rate in the bulk liquid) or in the fast-reaction regime (in which the reaction is complete in a very small region close to the interface). In order to ascertain the true kinetics of the reaction, it is necessary to eliminate diffusion resistance for which the effect of agitation was also accounted for in this investigation, studies were conducted in the range of 150–500 rpm. The results are presented in Fig. 1. It was observed that the liquid side mass transfer resistance was eliminated at 200 rpm. Therefore all the further experiments were conducted at this rpm to ensure a kinetically controlled regime.

Table 1
Characteristics of complex wastewater (biomethanated distillery wastewater).

Parameters	Value
pH	7.61
Colour	Brown
COD (mg L^{-1})	40,000
BOD (mg L^{-1})	6744
TOC (mg L^{-1})	18,700
Total solids (mg L^{-1})	31,000
Total suspended solids (mg L^{-1})	1600
Biomass (%)	1
VFA (mg L^{-1})	180
BOD:COD ratio	0.17

The values given in the table are average of 3 sets of observations with S.D. < 5.