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Research article

Post-treatment of molasses wastewater by electrocoagulation and process optimization through response surface analysis

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ABSTRACT

Molasses wastewater is a high strength effluent of food industry such as distilleries, sugar and yeast production plants etc. It is characterized by a dark brown color and exhibits a high content in substances of recalcitrant nature such as melanoidins. In this study, electrocoagulation (EC) was studied as a post treatment step for biologically treated molasses wastewater with high nitrogen content obtained from a baker's yeast industry. Iron and copper electrodes were used in various forms; the influence and interaction of current density, molasses wastewater dilution, and reaction time, on COD, color, ammonium and nitrate removal rates and operating cost were studied and optimized through Box Behnken's response surface analysis. Reaction time varied from 0.5 to 4 h, current density varied from 5 to 40 mA/cm^2 and dilution from 0 to 90% (v/v expressed as water concentration). pH, conductivity and temperature measurements were also carried out during each experiment. From preliminary experiments, it was concluded that the application of aeration and sample dilution, considerably influenced the kinetics of the process. The obtained results showed that COD removal varied between 10 and 54%, corresponding to an operation cost ranging from 0.2 to 33 euro/kg COD removed. Significant removal rates were obtained for nitrogen as nitrate and ammonium (i.e. 70% ammonium removal). A linear relation of COD and ammonium to the design parameters was observed, while operation cost and nitrate removal responded in a curvilinear function. A low ratio of electrode surface to treated volume was used, associated to a low investment cost; in addition, iron wastes could be utilized as low cost electrodes i.e. iron fillings from lathes, aiming to a low operation cost due to electrodes replacement. In general, electrocoagulation proved to be an effective and low cost process for biologically treated molasses-wastewater treatment for additional removal of COD and nitrogen content and color reduction. Treated effluent samples with good quality were produced by EC, with COD, NH_4–N and NO_3–N concentrations of 180, 52 and 2 mg/l respectively. Response surface analysis revealed that optimized conditions could be established under moderate molasses wastewater dilution, (e.g. 45%), at 3.5 h treatment time and 33 mA/cm^2 current density.

1. Introduction

Molasses wastewater (MW) is a primary by-product of certain food industries such as cane-based sugar mills and distilleries. MW is characterized by dark brown color, extensive odor, and high COD (60,000 mg/l), while BOD values are in general lower (25,000 mg/l) (Chandra et al., 2008; Robles-Gonzalez et al., 2012) molasses wastewater may contain about 2% of melanoidins, a dark brown pigment, that result in the brown color of the wastewater. Melanoidins are polymeric substances, produced by non-enzymatic browning reactions between sugars and amino acids through the Mallard reaction; these compounds present poor biodegradability. Furthermore, molasses wastewater may contain other color compounds including phenols, melanin and caramel; the presence of these compounds is greatly affected by the raw material. As a result total nitrogen content of cane molasses wastewater is usually about 1–2 g/L while higher nitrogen content is observed in beet molasses wastewater, reaching up to 4 g/L; phenol compounds are more significant in cane molasses wastewater, while melanin is found in higher concentrations in beet molasses wastewaters (Satayawali and Balakrishnan, 2008). Due to the presence of poorly biodegradable compounds, such as

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melanoidins, the treatment of molasses wastewater has become a difficult task.

A typical management process of MW is based on biological treatment consisting in anaerobic digestion followed by aerobic treatment (Chandra et al., 2008; Robles-Gonzalez et al., 2012; Satyawali and Balakrishnan, 2008). Although BOD and COD values are reduced by these treatment steps, a high recalcitrant COD residue and a brownish color remain in the treated effluent. Therefore, a variety of techniques has been adopted for advanced MW treatment. Such techniques include ozonation (Robles-Gonzalez et al., 2012; Sangave et al., 2007; Pena et al., 2003), coagulation (Satyawali and Balakrishnan, 2008), membrane processing (Satyawali and Balakrishnan, 2008; Bilad et al., 2011; Nataraj et al., 2006), biocomposting (Satyawali and Balakrishnan, 2008), oxidation by Fenton's reagent (Robles-Gonzalez et al., 2012), enzymatic treatment (Sangave and Pandit, 2006a), ultrasound treatment (Sangave and Pandit, 2006b) and electrocoagulation (EC) (Krishna Prasad, 2010).

From the reported results in the literature, it is concluded that a single process is not effective for MW treatment. Thus, research is focused on the combination of two or more techniques. Usually biological treatment is combined with other techniques as pretreatment or post-treatment processes, such as ozonation (Sangave et al., 2007), ultrasound irradiation Sangave and Pandit, 2006b; (Sangave and Pandit, 2004), enzymes (Sangave and Pandit, 2006a), nanofiltration (Meihong et al., 2013) and coagulation (Liang et al., 2010). The combination of physicochemical methods not including biological treatment is less common, such as chemical oxidation by ozone combined with hydrogen peroxide and UV (ultraviolet) radiation (Beltran et al., 1997) or ozonation combined with EC (Asaithambi et al., 2012). All these methods exhibit certain advantages and disadvantages, such as high operation cost, formation of by-products etc. Nevertheless, a great variety of COD and color removal rates has been reported by these methods, depending on the quality and the composition of the raw effluent: in general, the higher the COD of the effluent, the less effective the treatment process appears (Asaithambi et al., 2012). Furthermore, pH greatly affects each process efficiency; pH and/or temperature adjustments have been adopted for improving the process effectiveness in few studies (Sangave and Pandit, 2006b; Krishna Prasad, 2010). However, utilization of pH or temperature adjustment on a large scale is an expensive method of low practical importance.

EC has been proposed as a cheap and effective process alternative to chemical coagulation for wastewater treatment, including removal of heavy metals (Al Aji et al., 2012), treatment of wastewater of textile industry (Khandegar and Saroha, 2013), removal of dyes (Anantha Singh and Ramesh, 2013) and removal of boron (Isa et al., 2014). It is based on the *in situ* production of metal cation coagulants such as Fe^{+3} or Al^{+3}. The coagulant cations are produced by dissolution of a sacrificial metal by electrochemical reactions. Operation parameters affecting the process efficiency include current and voltage, electrode's material, shape and surface, and electrodes spacing.

EC is studied as an efficient method for the treatment of MW, with an increasing interest (Krishna Prasad, 2010; Yavuz, 2007; Ryan et al., 2008; Kannan et al., 2006; Krishna Prasad et al., 2008; Thakur et al., 2009; Prajapati and Chaudhari, 2014; Gadd et al., 2010a; Gengec et al., 2012; Susree et al., 2013; Kumar et al., 2009). One major inherent drawback of EC is the production of chemical sludge, requiring additional processes for adequate sludge treatment and/or utilization (Thakur et al., 2009; Prajapati and Chaudhari, 2014). During EC, pH alteration and temperature increase (due to ohmic heating) may occur (Ryan et al., 2008; Kannan et al., 2006). However, the issue of temperature and its consequences such as energy loss and acceleration of reactions is rarely discussed, most likely due to the fact that the effluents usually exhibit high conductivity. In addition, most of the studies are focused exclusively on COD, total carbon (TOC) and color removal while other parameters of the effluent such as nitrogen or phosphorous content are usually not considered (Ryan et al., 2008; Kannan et al., 2006; Krishna Prasad et al., 2008; Thakur et al., 2009; Prajapati and Chaudhari, 2014; Gadd et al., 2010a; Gengec et al., 2012; Susree et al., 2013; Kumar et al., 2009).

The operation of various EC reactor was evaluated in a recent study, for the assessment of COD removal as a function of energy consumption, residence time and current density, using three configurations: a batch reactor, a batch reactor with continuous recirculation and a continuous reactor with single pass (Susree et al., 2013). It was found that COD removal increased with the current density but this increase was related to an increased power consumption, in the batch reactor; lower COD removal rates were observed in the continuous system rather than the batch systems, due to the lower residence time obtained in the former reactor. However, under similar COD removal rates, a better utilization of power was measured in the continuous reactor than the batch one. Nevertheless, in most of the studies, the reactors are characterized by a large ratio of electrodes surface to volume of wastewater, which is associated to very high electrode surface or limited capacity of the treated volume. For example, typical values are 4 electrodes (2 anodes and 2 cathodes) with surface area 112 cm^2 each, and a treated volume of 1.5 l (Kumar et al., 2009) or 4 electrodes each one having surface 240 cm^2 and treated sample volume 0.8 l (Gengec et al., 2012). In large scale applications, such a ratio might be unattainable and/or could result to a high cost.

Nevertheless, the EC process is a rather complicated method, due to a number of available parameters affecting its efficiency (current, surface etc), providing a wide range of operating conditions; however certain optimum conditions have to be identified for maximum efficiency and minimum cost. Response surface analysis has been recently applied for data statistical analysis and for the determination of optimized solutions/conditions (Krishna Prasad, 2010; Krishna Prasad et al., 2008; Thakur et al., 2009; Gengec et al., 2012). Sufficient results were produced when the Box-Behnken design model was used (Krishna Prasad, 2010; Krishna Prasad et al., 2008), in particular when three design variables were considered, each one varying in three levels (Montgomery, 2001).

In this study, EC was evaluated as a post-treatment method of biologically treated MW, aiming to the optimization of operation parameters and the reduction of COD, color and nitrogen content of the effluent, using a low cost method.

2. Experimental

2.1. Materials

Sugar beet MW sample was collected from the outlet stream of the biological (anaerobic followed by aerobic process) treatment plant of a local baker's yeast industry. The average values of COD, pH, nitrogen in the form of nitrate ($N{-}NO_3$) and ammonium ($N{-}NH_4$), and BOD were 4150 mg/l COD, pH = 8.5, 44.7 mg/l $N{-}NO_3$, 820 mg/l $N{-}NH_4$ and 0 mg/l BOD_5. MW was diluted either by municipal wastewater sample, collected from the supernatant of the primary sedimentation tank of a municipal wastewater treatment plant, or by bottled water. Copper in the form of plate and massive cylinder of 99.9% purity was purchased from a copper manufacturing industry, while iron of purity >98% collected from the scrap of a local machine shop in various forms (plate, filings, massive cylinder and tube). Sodium sulfate (99% purity) was