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Application of CCD in RSM to obtain optimize treatment of POME using Fenton oxidation process

Mohamed Osman Saeed[a,*], Khairun Azizli[a,b], Mohamed Hasnain Isa[a,c], Mohammed J.K. Bashir[d]

[a] Sustainable Resource Mission Oriented Research (SUREMOR) Center, UTP, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia
[b] Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia
[c] Civil Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia
[d] Faculty of Engineering and Green Technology, University of Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia

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ABSTRACT

Post treatment palm oil mill effluent (POME) is typically non-biodegradable and contains high organic and inorganic matter. This study aims to optimize the operating parameters of the Fenton process in removing recalcitrant organics from POME by using a central composite design (CCD), which is a response surface methodology (RSM) module in the Design-Expert® software. Important parameters such as reaction time, H_2O_2 and Fe^{2+} ion concentrations, and pH were empirically determined and successfully optimized via RSM. Significant statistical quadratic polynomial for color and COD removal efficiency were obtained via regression analyses R^2, (0.81 and 0.70) for color and COD, respectively. The highest results were 97.36% removal for color and 91.11% removal for COD at pH 3.5 and 30 min of reaction time. Numerical optimization based on desirable functions was employed; 92.1% of color and 85.1% of COD were removed efficiently at pH (3.0–5.0) with a final pH of 2.85 (after reaction settlement), 4.57 g/L H_2O_2 and 1.88 g/L Fe^{2+} ions concentration, respectively, and 30 min of reaction time at 120 rpm agitation rate. The result showed that the Fenton process, at an accurate level, may be used as an effective technology for the post treatment of POME before final discharge into a nearby water body.

1. Introduction

1.1. Introduction

Palm oil mill effluent (POME) is the result of food oil industry operations. Malaysia has a large proportion of global crude palm oil production amounting to 19.9 million tons in 2011 [1] and results in the production of industrial wastewater, known as POME, which needs to be treated to reach the local authority's discharge standard levels to protect the environment [2]. POME is brownish in color because of the presence of lignin and its groups, tannin, humic acids, lipids, and fatty acids that are released during industrial steam extraction [3,4]. Currently, the elimination of POME's biodegradable and non-biodegradable organic compounds is a major concern faced by researchers. Karkare and Murthy [5] and Chang et al. [6] reported that biological processes (aerobic and anaerobic) are universally used in wastewater remediation; however, given its complex composition, conventional biological treatments are time consuming and usually insufficient in degrading high molecular weight fractions [7]. Najafpour et al. [8] reported that POME has been known as high strength industrial wastewater that is difficult to treat primarily because of its large variability of inorganic and organic contents.

Prior to aerobic treatment, anaerobic process should be used to reduce POME's organic strength [9]. In Malaysia, majority of palm oil industrial mills employ an anaerobic treatment process to treat high organic-loading wastewater, such as POME, at their primary stage [10–12] because of its low cost [13]. However, this anaerobic open tank digester have several drawbacks, such as long hydraulic retention time (HRT), large land areas, digester requirement, and methane collection and utilization difficulty, which cause a detrimental greenhouse effect to the environment [14]. In addition, integrated anaerobic-aerobic treatment followed by aerobic processes has been proven to have better performance in terms of removing POME organic compounds [15]. Thermophilic aerobic biological treatment for anaerobically treated POME was assessed for its COD, BOD, and TSS removal efficiencies [14].

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* Corresponding author. Tel.: +60 53687593; fax: +60 5365 6176.
E-mail address: osman.saeed@petronas.com.my (M.O. Saeed).

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The monitoring of POME has been recorded as a serious environmental problem; extensive studies of which have been reported and are still being conducted. A new biological treatment that uses bio-discs grown on a rotating biological contactor (RBC) with POME has been reported. After five days, 91% BOD was removed from a batch experiment; 88% COD removal efficiency was obtained at 55 h HRT [8]. Population balance model (PBM) for flocculation process was used to completely replace the inorganic coagulants with organic polymers in POME pretreatment by using dual and single polymer direct flocculation systems with applied shear [16].

Ultrafiltration (UF) membrane is one of the promising options for POME secondary treatment despite a major limitation, which is membrane fouling. Membrane-based industrial POME treatment was suggested as a solution in Malaysia, and several researchers proposed three different membrane designs and orientations, namely, designs A, B, and C [17]. Ahmad et al. [17] presented a pilot-scale ultrafiltration (UF) commercial membrane with ceramic and polyvinylidene difluoride (PVDF) to investigate the influences of trans-membrane pressure and cross-flow velocity on the performance of POME treatment. Hermia's mathematical model was recently suggested to investigate the effects of pressure, temperature, pH, and ionic strength on flux decline [19]. A novel technique, combined magnetic field and adsorption process activated carbon, was reported for removing color, TSS, and COD from biologically treated POME [20]. The adsorption capacity of natural zeolite for the removal of heavy metal ions, such as zinc (Zn^{2+}), manganese (Mn^{2+}), and iron (Fe^{3+}), which are found in POME, was investigated [21]. The low-cost natural zeolite was considered as an excellent candidate for the removal of metal ions in POME.

1.2. Background

Additional chemical oxidation processes are necessary for the pre or post-treatment of POME. Recently, advanced oxidation processes (AOPs) have attracted great attention as alternative methods to reduce industrial wastewater organic loads. AOPs are capable of transforming non-biodegradable pollutants into non-toxic biodegradable substances [22]. They can rapidly oxidize a wide range of organic pollutants by generating very reactive groups such as hydroxyl radical ($OH^{\bullet}$). The H_2O_2 oxidation alone has been found ineffective for the removal of particular refractory contaminants at high concentrations because of low reaction rates at low H_2O_2 concentrations. Transition metal ions (e.g., Fe^{2+}), UV-light, and ozonation can naturally activate H_2O_2 to form the important groups of hydroxyl radicals [23].

Fenton's reagent, a member of the AOPs oxidation family, has been considered to be a promising and attractive treatment technology for degradation and discoloration of industrial oily wastewater pollutants. In recent years, there has been an increasing focus on the mechanism of Fenton's reagent which can produce $OH^{\bullet}$ radical groups in different ways [24]. Nasr et al. [18] found effectual 86% COD removal when Fenton's reagent method was applied in decomposing non-compliant organic components in olive oil mill wastewater. Meanwhile, Aris et al. [19] obtained highest removals of COD (75.2%) and color (92.4%) at ambient-Fenton.

The use of Fenton reagent in treating industrial wastewater has received great interest because of its high capability to generate hydroxyl radicals group through the decomposition of H_2O_2 by metal ions at acidic conditions [21,25]. Moreover, it can be applied to a wide range of organic pollutants because of its ease in implementation and operation at mild conditions. The efficiency of this process can be greatly enhanced by integrating it with other water treatment methods, such as electricity (E-Fenton) [29], coagulation [19], and membrane [24] to generate additional hydroxyl radicals. E-Fenton process has the combined advantages of electrochemical and Fenton treatment methods, each a powerful treatment method. The oxidizing power of H_2O_2 can be strongly enhanced using the Fenton method in a low pH medium, where a small quantity of Fe^{2+} ions catalyst is added to the contaminated solution to generate $OH^{\bullet}$ and Fe^{3+} ions from Fenton's reaction. Generally, the reaction of hydroxyl radicals and organic compounds produce water, carbon dioxide, and salts [30]. However, the attack of the $H\dot{O}$ radical in the presence of oxygen generates a complex series of oxidation reactions. The exact reaction routes to complete the mineralization of the organics are still not clear. Chlorine-containing organic compounds, for example, are oxidized first to intermediates, such as aldehydes and carboxylic acids, and then to carbon dioxide and water, and finally to chlorine ions [22].

In organic pollutant treatment, the Fenton process can be progressed in the presence of one or more oxidizing agents (mostly O_3, O_2 or H_2O_2) and a metal salt or oxide catalyst (usually iron) by the following reaction chains (Group A includes Eqs. (1)–(7)) [23,27–29,31,32]. Hydroxyl radical ($HO^{\bullet}$) is one of the most active oxidant agents that can be rapidly reacted with most organic molecules at a constant rate. Based on the nature of the organic compound, denoted here by (R), the newly generated $HO^{\bullet}$ can attack organic radicals by one of the following chemical reaction chains (Group B includes Eqs. (8)–(11): additive radical (Eq. (8)), hydrogen abstraction (Eq. (9)), electron transfer (Eq. (10)), and radical combination (Eq. (11)). The hydroxyl radicals produced react rapidly with most of the organic compounds either by addition to a double bond or by abstraction of a hydrogen atom from aliphatic organic molecules. The resulting organic radicals then react with O_2 to initiate a series of oxidation reactions leading to the mineralization of the organics to produce CO_2 and H_2O. AOPs have these advantages. As such, investigating parameters such as pH, H_2O_2, Fe^{2+}ions, and reaction time is important.

Normal Fenton in an acidic medium, Group A Eqs. (1)–(7)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \tag{1}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2 + H^{+} \tag{2}$$

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{3}$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2{}^{\bullet} + H_2O \tag{4}$$

$$HO_2{}^{\bullet} \leftrightarrow O_2{}^{\bullet} + H^{+} \tag{5}$$

$$Fe^{3+} + HO_2{}^{\bullet}/O_2{}^{\bullet -} \rightarrow Fe^{2+} + H^{+}/ + O_2 \tag{6}$$

$$Fe^{2+} + HO_2{}^{\bullet}/O_2{}^{\bullet -} \rightarrow Fe^{3+} + H_2O_2 \tag{7}$$

Organic compounds reaction in an acidic medium, Group B Eqs. (8)–(11)

$$R + HO^{\bullet} \rightarrow ROH \tag{8}$$

$$R + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \tag{9}$$

$$R^{n} + HO^{\bullet} \rightarrow R^{n-1} + HO- \tag{10}$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \tag{11}$$

In multivariable analyses, the traditional optimization technique of changing one variable at a time to study the variable response effect is impracticable and does not represent the interaction effect between different factors [29]. Therefore, experimental statistical design considers one of the most useful methods in obtaining valuable and statistically significant models of a phenomenon by performing a minimum number of calculated experiments. It also considers interactions among the variables and can be used to optimize the operating parameters in multivariable analyses. RSM was used for the modeling and analysis of problems in which a response of interest is influenced by several variables to optimize the same response [33]. A favorite model in RSM is the central composite design (CCD), which is efficient and flexible in providing adequate data on the effects of variables and overall