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Performance of bioequalization-electrocatalytic integrated method for pollutants removal of hand-drawn batik wastewater

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ABSTRACT

Hand-drawn batik wastewater has the specific characteristics of intense color, alkaline pH, low COD and BOD contents (± 800 and ± 500 mg/L, respectively), and may pose environmental and human health risks. Chemicals used in dyeing and dewaxing processes (i.e., dye, wax, alum sulfate and starch) will influence chemical characteristics of wastewater generated. The integration of bioequalization and electrocatalytic was attempted in the present study as a feasible technology to treat these pollutants. Bioequalization tank of 18 m^3 was inoculated with 10% (v/v) seed sludge, equipped with four uniformly distributed feeding pipes and subsequently connected to an electrocatalytic reactor of 1.2 m^3 capacity. Ti/$RuIrO_2$ anode and stainless-steel cathode were used in the system with an electrode gap of 30 mm. The effluent was able to meet the discharge standard of local regulation at HRT of 48 h in bioequalization and electrolysis operating conditions: 5 V potential, pH 5, 4000 mg L^{-1} salt concentration and electrolysis time of 90 min. The electrode materials were potentially deactivated due to surface enclosure and metal decomposition, particularly ruthenium.

1. Introduction

Hand-drawn batik is an artistic commodity and one of the oldest cultural products of Indonesia. Batik industries are scattered across 38 regions in Java Island and are concentrated in several specific areas, i.e., Solo, Pekalongan, Tegal, Lasem, and Banyumas. Most of them are home-based and small-scale industries with no wastewater treatment plant. Batik has been recognized by UNESCO (United Nations Educational, Scientific, and Cultural Organization) as one cultural heritage of Indonesia [1]. This resulted in an increasing number of batik industries in other regions with their own signature patterns. Aside from its contribution to the rapid economic development, batik industries also have various negative environmental impacts due to wastewater generated. Batik wastewater is generally originated from soaking, boiling, and rinsing processes, most of which discharged into rivers or nearby streams without proper treatment, resulting in environmental and health problems [2]. Kant et al. [3] stressed the large volumes of wastewater and high content of pollutants contained such as dyes, starch, alum sulfate, and wax, resulting in characteristics of high pH, COD, TSS, and intense color. The presence of dyes in wastewater may cause severe damage to the aquatic environment [4,5]. This is because of their synthetic origin and complex molecular structure which make them more stable and difficult to be degraded [6].

The large amounts of wastewater with a high concentration of pollutants requires extensive treatment before being discharged into the environment. Physicochemical methods such as chemical precipitation, ultrafiltration, carbon adsorption, coagulation, flocculation, and ozone oxidation have been applied for batik wastewater treatment. However, those methods either are costly to be applied in a full-scale reactor or produce a considerable amount of sludge [7]. Rashidi et al. [8] utilized a baffle separation tank as an innovative pre-treatment method for batik wastewater treatment and succeeded in removing wax, sodium silicate, and dyes for 92%, 32%, and 2%, respectively. Advanced oxidation processes (photocatalytic) have been studied for textile wastewater treatment containing highly colored organic compounds [9–11], resulting in organic dyes removal. Another study also reported a complete decolorization of batik dye wastewater within three h and 80% COD reduction [12]. Subramaniam and Halim [13] employed electrochemical oxidation method and was able to remove COD up to 89.71%.

According to Mukimin et al. [14], electrooxidation advanced process (EOAP) was driven by oxidators generated at the anode, i.e., HClO, OH^o, and $S_2O_8{}^{2-}$. The reaction of this process is described as follows:

$$\text{Dyes} + HClO \rightarrow CO_2 + H_2O + Cl_2 \quad (1)$$

$$\text{Dyes} + {}^oOH \rightarrow CO_2 + H_2O \quad (2)$$

$$\text{Dyes} + S_2O8^{2-} \rightarrow CO_2 + H_2O + 2SO_4{}^{2-} \quad (3)$$

This pathway mechanism is known as indirect oxidation.

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Degradation of dyes by short-lived species (e.g., OH^o) may be restricted only to anode surface, and long-lived oxidants such as free chlorine (HClO) can diffuse away from the electrode surface to promote the bulk [15]. They also explained that oxidation mechanism was significantly affected by electrode material (active and non-active). When using an active anode, a strong interaction between the electrode (M) and the adsorbed OH^{oo} occur and the equation of electrodegradation is as follows:

$$M + H_2O \rightarrow M(OH^o) + H^+ + e \quad (4)$$

$$M(OH^o) \rightarrow MO + H^+ + e \quad (5)$$

$$MO + R \rightarrow M + RO^* \quad (6)$$

$$MO \rightarrow M + ½\ O_2 \text{ (side reaction)} \quad (7)$$

Meanwhile, non-active electrode participates in the electrooxidation as an inert material, in which the process is mediated by OH^o. It is also in competition with the reaction of oxygen evolution.

$$M(OH^o) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e \quad (8)$$

$$M(OH^o) \rightarrow M + ½\ O_2 + H^+ + e \quad (9)$$

The combined process of biology and advanced oxidation is a promising treatment system for specific wastewater such as batik. Therefore, this study aims to evaluate the efficiency of integrated technology of bioequalization and electrocatalytic for hand-drawn batik wastewater treatment. Equalization tank inoculated with microorganism as an innovative pre-treatment with numerous advantages, i.e., ability to achieve uniformity, degrade starch and separate wax and alum sulfate. Electrocatalytic reactor will be subsequently employed to degrade dye pollutant through an oxidation process. This integration system may become a reliable and attractive option to be applied in small industries with limited space. pH and retention time were determined as process variables investigated in the electrolysis process. The data of electrode morphology were thoroughly analyzed to inquire the stability of electrocatalytic reactor.

2. Materials and methods

2.1. Materials

Batik wastewater was collected from soaking, boiling dan rinsing processes of a batik industry located in Sragen, Central Java, Indonesia. It was then fed to bioequalization tank of 18 m^3 capacity (dimension 4 × 2 x 2.25 m). Four pipes (3 in) were installed at the bottom of the tank to evenly distribute wastewater. Bioequalization tank was started up at an HRT of 48 h and inoculated with immobilized anaerobic sludge up to 10% of tank volume. The characteristics of seed sludge are summarized in Table 1.

Electrocatalytic reactor (1,2 m^3) consisted of six vertical tubes (capacity of 200 L), each was equipped with a mixer and a pair of electrodes (30 mm of electrode gap), was applied as a secondary treatment unit. The integration system was depicted in Fig. 1.

Ti/$RuIrO_2$ cylinder anodes (ø: 100 mm, ℓ: 850 mm) were obtained from Baoji Changli Special Metal Co., Ltd. The electrodes were of the same material as those used in our previous application [14], in which the metal oxide layers were of rectangular shapes with a fairly similar size of 10 μm and amorphous. pH value was adjusted using technical grade sulphuric acid. Domestic grade salt was supplemented to supply chloride in the electrolysis process.

Table 1
Characteristics of seeding sludge used in experiment.

Parameter	Value (%)
TS	14.45
VS	63.02
FS	36.98

2.2. Experimental procedure

Wastewater was fed to inoculated bioequalization tank to ensure its uniformity and reached desired retention time. Pollutant reduction efficiency was determined based on the comparison of wastewater quality before and after treatment. Concentrations of COD, BOD, TSS, ammonia, sulfide, phenol and oil were used as indicators of process efficiency. Pre-treated wastewater was then pumped to feeding tank by means of a water pump (Shimidzu PS 230 BIT) to achieve hydraulic retention time of 60, 90, 120, 150, and 180 min, and then subsequently supplemented with salt (4000 mg/L) and sulphuric acid to achieve desired initial pH (3, 5, 7, 9). Effluents were collected and measured continuously.

2.3. Analysis

For TSS, BOD, NH_3, H_2S, phenol and oil determination, standard method was used (APHA AWWA 2540D; 5210B; 5220 B; 4500-NH3 F; 4500-S^{2-} D; 5530C; 5520C). Chemical oxygen demand (COD) was determined using a modified method for samples with high salinity according to Vyrides and Stuckey [16]. Decolorisation process was studied using spectrophotometer UV–vis (Shimadzu U 1800) at a wavelength of 617.5 nm. Physical and chemical properties were monitored regarding composing element and surface morphology by SEM-EDX (JEOL JSM-6360LA dan Carl Zeiss EVO 10).

3. Results and discussion

3.1. Waste removal in bioequalization tank

Characteristics of wastewater processed in this research are shown in Table 2. High biodegradability index (BOD/COD ratio of 0.63) was due to the presence of starch and dissolved wax in wastewater. Based on the biodegradability index of wastewater processed, it is clear that pre-treatment employed in this research is more favorable, as supported by literature reporting that complete biodegradation may be reached when the effluent shows a biodegradability index of at least 0.4 [17]. Higher concentration of COD to BOD is attributed to non-biodegradable components, such as dyes and other components used in batik making process. Whereas, total suspended solids were dominated by either alum sulfate or sodium silicate and undissolved wax.

As it is observed in Table 1, all pollutants contained in batik wastewater decreased significantly after biological treatment. The result indicates the occurrence of biodegradation process in bioequalization tank. Significant BOD and COD removal efficiencies of 76% and 67%, respectively, were observed at an average organic loading rate (OLR) of 0.9 kg COD m^{-3} d^{-1}. It implied an effective degradation by active microorganisms at a hydraulic retention time (HRT) of 48 h. It was possibly due to the presence of starch contained in wastewater which was previously reported as readily degradable carbohydrate and easily converted into CO_2 and H_2O [18]. It is also in accordance with the finding of another study reporting that starch was easier to be used as carbon source in anaerobic microbial cell metabolism and biomass growth [19]. Araujo et al. [20] also mentioned that starch is a biodegradable hydrocarbon compound composed of two major components, i.e., amylose (a mostly linear α-D-1-4-glucan) and amylopectin (a α-D-1-4-glucan).

A drastic reduction of total suspended solids (72%) was also observed. It was possibly due to the separation of settleable components such as alum sulfate, sodium silicate, and floatable wax. Based on these findings, it is evident that bioequalization tank was able to function as biodegradation and equalization tank simultaneously. It was presumed that at HRT of 48 h, anaerobic degradation and settling processes