Dielectric barrier discharge ionization (DBDI) technology combined with coagulation–flocculation for wastewater treatment of pulp and paper industry

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ABSTRACT

Dielectric barrier discharge ionization (DBDI) and a mixture of coagulants (poly aluminum chloride (PAC) and chitosan) in this study were combined for liquid waste treatment of pulp and paper industry. A coagulant was added as a pre-treatment of liquid waste that contained total suspended solids (TSS). The effect of coagulant and time on the reduction of TSS, reduction of chemical oxygen demand (COD), and color were investigated in this study. The coagulant was a combination of PAC and chitosan with amounts of 0.1, 0.2, 0.3, 0.4, and 0.5 g/L. DBDI process was conducted at 10, 20, 30, 40, and 50 min. A combination of DBDI and coagulants was performed to investigate the reduction of TSS, COD, and color. The initial liquid waste characteristics in this study were 3,929.40 mg/L of COD, 4,185 mg/L of TSS, and 17,140 Pt-Co of color. The efficiency of COD removal was significant at 89.81% using 0.3 g/L coagulant mixture and 40 min of DBDI operation time with a power input of 75 W. The highest TSS removal reached 99.14% and 99.22% color removals. The highest TSS and color removals were observed at 0.4 g/L coagulant and 50 min DBDI operating time. It can be concluded that the combination of DBDI with a mixture of coagulant (PAC and chitosan) is significantly effective in treating liquid waste pulp and paper industry.

Keywords: DBDI; Coagulation–flocculation; Pulp and paper; Wastewater; Contact time

1. Introduction

Water pollution of pulp and paper industry is generated from the coating and sizing process. Paper and pulp industry pollutants contain chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), and color [1]. A recent study found that wastewater of pulp and paper industry contains 6.354 mg/L of COD and a high concentration of color from the coating process [2]. Wastewater from the pulp and paper industry contains chlorinated compounds, resinous acids, tannins, fatty acids, phenols, and their derivatives, lignin and their derivatives, and sulfur compounds. All of these compounds caused a high concentration of COD, color, total organic carbon (TOC), and low biodegradability index (<0.4) [3,4]. Most pulp and paper industries apply synthetic coating containing azo compounds which are characterized by the presence of one or more azo (–N=N) groups attached to two substituents: benzene or naphthalene derivatives [5]. Azo compounds are the most dominant source of environmental pollution.
High solubility of azo in water may result in contamination of the river.

Various advanced oxidation processes have been investigated for reducing color pollutants in wastewater such as. Oxidation process of wastewater aimed to oxygen-based in-situ oxidation which creates mineralization or partial degradation that meets the quality standard of effluent. Mineralization is a conversion process of compounds to carbon dioxide, water, and inorganic ion. The oxidation process is required for wastewater treatment to remove persistent molecular structures, reduce toxicity, and increase the solubility of wastewater. The oxidation process based on the release of electricity in wastewater or at the gas–liquid interface for diminishing various organic compounds, including coating has been investigated.

A dielectric barrier discharge (DBD) reactor is utilized for the ionization process of ambient mass spectrometry [6]. DBD has also been applied for testing contaminants in the environment [7] and specifically implemented for wastewater [8,9]. Ionization is a physical process of converting atoms or molecules into ions by increasing or reducing charged particles such as electrons [10]. The ionization produces electrons that could be utilized as an active species to reduce wastewater pollutants.

A study has proven that the implementation of active species in DBD reactors was able to reduce COD and color of textile wastewater by 68% and 71%, respectively [11]. Another study had shown that DBD technology was also able to reduce 74% of COD of waste rubber [12]. The advantages of DBD technology compared to other technologies are requiring less land and fewer chemicals, as well as generating less mud.

The development of DBD reactor is required to optimize TSS reduction [13]. Flocculation coagulation can be used to reduce TSS by applying coagulants such as aluminum sulfate and poly aluminum chloride (PAC) [14]. However, a high concentration of suspended aluminum in the water influences human health. Several studies found that aluminum salts such as aluminum chloride or aluminum sulfate are the cause of Alzheimer’s disease [15,16]. It also affects respiratory and cardiovascular, hepatobiliary, and reproductive systems [17]. Therefore, several studies have been conducted to produce natural coagulants (bio coagulant) that replace synthetic coagulants. Bio coagulant is safe for human health, biodegradable, and more effective to reduce pollutants [18]. The use of chitosan as a primary coagulant resulted in a good performance in acidic solutions of high turbidity waste. Hence, it needs pH adjustment to wastewater. Chitosan combined with PAC coagulant resulted in higher turbidity reduction and considerable turbidity reduction at pH 7.5. In this regard, this study addresses to diminish COD, TSS, and color levels of wastewater produced in pulp and paper industry by implementing coagulation with a combination of synthetic biochemicals through the use of DBD ionization process [19].

2. Experimental setup and method for analysis

The coagulant used was aluminum sulfate (Al₂(SO₄)₃·18H₂O) (Merck, Germany). The material used to test COD has pro analysis quality (p.a) (Merck, Germany). COD and color testing were conducted using UV-Vis Spectrophotometer (Genesys 10S, Thermo Fisher Scientific, USA). TSS testing was measured using analytical balance (Mettler Toledo ME204T, Switzerland) and Oven (Memmert UN55, Germany). The coagulation–floculation process was carried out using a jar test tool (VELP Scientifica, Italy). This study was conducted for six months. The independent variable in this study was coagulation–floculation and time for the DBD ionization process, while the dependent variables were COD, TSS, and color. Four levels of coagulation–floculation implemented during the experiment were 0.1, 0.2, 0.3, 0.4, and 0.5 mg/L. The DBD ionization process was observed at 10, 20, 30, 40, and 50 min. The control variables during the coagulation–floculation process were reduction speed and stirring time. Meanwhile, the control variable during of DBD ionization process was the voltage. Meanwhile, the DBD ionization reactor of the experimental setup is shown in Fig. 1.

The next step was pre-treatments by coagulation–floculation process. The coagulant in this study was a combination of PAC and chitosan with a ratio of 90:10. The sedimentation process was conducted for 3 h. The samples of sediment were obtained for measuring TSS, COD, and color.

The sediments obtained from pretreatment then would be processed in DBD through ionization reactor. This study applied 15 kV for ionization voltage. A previous study conducted by Sucipta [20] applied 13 kV in ionization, stated that the higher voltage increased pollutant removal of liquid waste. The duration of exposure time in this study refers to Affif [12] study that implemented five variations of treatment time: 10, 20, 30, 40, and 50 min. The volume of wastewater initially exposed to the ionization reactor was 50 mL. As a final result, after the DBD ionization reactor process, the wastewater samples were obtained and TSS, COD, and color were measured.

The experiment results were analyzed using a non-parametric statistical test called Kruskal–Wallis for testing the reduction significance among the k-treatments experiment. This analysis was applied due to small samples involved and non-repetitive the experiment during the limited budget and time of the experiment. The small sample leads to unjustifying the normality assumption.

3. Results and discussions

3.1. Characteristics of wastewater of pulp and paper industry

Prior to processing, the COD, TSS, and color of liquid waste samples were tested. The results of the initial measurement of COD, TSS, and color and quality standards based on Central Java Regional Regulation are presented in Table 1. The initial measurements of COD and TSS of pulp and paper industry were much higher than the wastewater quality standard determined by Central Java Province regulation. Hence, pulp and paper industry wastewater should be processed...
In this study, all wastewater samples were processed with coagulant and flocculation. The results of COD, TSS, and color in wastewater before and after processed with coagulant-flocculation are presented in Figs. 2–4. Fig. 2 shows that COD concentration in wastewater dropped in 0.1 and 0.2 mg/L coagulants. In this observed that COD concentrations increase to 593.81 and 607.01 mg/L at 0.4 and 0.5 mg/L coagulants after reaching the lowest COD concentration of 566.2 at 0.3 mg/L coagulant. Kruskal-Wallis test was used in this study to prove the coagulant significant to pollutant changes of pulp and paper wastewater. Summary of non-parametric statistical test for the reductions of COD, TSS, and color shown in Tables 2 and 3. According to the test presented in Table 2, there is a significant reduction of COD in wastewater among the amount of coagulant in pulp and paper wastewater. Table 3 presents a pairwise comparison between the amounts of coagulants. It proves the reduction significant of COD in wastewater occurred after adding 0.1 and 0.2 mg/L coagulants. The higher concentrations of coagulant, that is, 0.3–0.5 mg/L, do not significantly reduce the COD in wastewater.

There is an argument that the use of a combination of PAC and chitosan as coagulant creates the bridge between particles in wastewater that influence the effectiveness of forming flocculation [21]. However, the reduction of COD was not significant because an excessive coagulant covered colloidal particles that inhibited the formation of flocs [21]. Colloidal particle improves COD, because it may create flocs (suspension) when coagulant is added. The suspension produces sediment due to gravitational force. On the other
hand, the formation of suspension will be inhibited when coagulant exceeds. Hence, in this study, the suspension was unable to be formed at 0.4 and 0.5 mg/L. The reduction had also occurred for TSS concentration in wastewater which showed a reduction at all amounts of coagulant. Fig. 3 presents the reduction of TSS reached the lowest of 44 at 0.4 mg/L coagulant and rebounds to 264 at 0.5 mg/L. Tables 2 and 3 show a significant TSS reduction at all amounts of coagulants.

TSS particles in wastewater are attached by a coagulant, that is, PAC and chitosan. TSS particles have negative charges. It turns into colloidal particles that are difficult to create sediment in wastewater. Meanwhile, PAC has a positive charge of destabilized colloidal particles in the wastewater. Chitosan that was diluted using acidic liquids will be cationic. This led chitosan chains to be able to bind particles in the wastewater. The chitosan, which is a polymer, has a long bonding chain as presented in Fig. 5. This long chain is able to bind some particles. It is also able to bind flocs produced from the destabilization of PAC into larger floc bonds.

When the coagulant is increased to 0.5 mg/L, the TSS concentration rebounds to 264 mg/L. This is because of the increased amount of coagulants produces restabilization [22]. It also may be caused by resuspension of solids at a high concentration of coagulants redispersing the particles due to the creation of positive charges on the particle surface [23].

Meanwhile, the initial color of the liquid waste was red. The initial color concentration measured using a spectrophotometer was 17,139.76 Pt-Co. It is shown in Fig. 4 that after treatment with coagulation–flocculation the concentration of wastewater color decreases significantly at 0.1 and 0.2 mg/L coagulant. At 0.3–0.4 mg/L the reductions of color are low. It also proved by the Kruskal–Wallis test in Tables 2 and 3 that the changes of color change at all amounts of coagulant are significant.

This may due to reagents between Al in coagulants with acids in color molecules form salts that difficult to dissolve [24]. This property causes the creation of sedimentation and degrades the color concentration in the liquid waste. Chitosan containing many amine groups improves performance in coagulation and flocculation with PAC [19].

Table 3
Summary of non-parametric statistical test (Kruskal–Wallis) for the reduction of COD, TSS, and color in wastewater by coagulant

<table>
<thead>
<tr>
<th>Pairwise comparison</th>
<th>Kruskal–Wallis test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COD</td>
</tr>
<tr>
<td>0 vs. 0.1 mg/L</td>
<td>−2.402 (0.016)*</td>
</tr>
<tr>
<td>0.1 vs. 0.2 mg/L</td>
<td>8.308 (0.004)*</td>
</tr>
<tr>
<td>0.2 vs. 0.3 mg/L</td>
<td>3.103 (0.078)</td>
</tr>
<tr>
<td>0.3 vs. 0.4 mg/L</td>
<td>0.103 (0.749)</td>
</tr>
<tr>
<td>0.4 vs. 0.5 mg/L</td>
<td>0.641 (0.423)</td>
</tr>
</tbody>
</table>

*Significant at α = 0.05.
It is seen in Fig. 4 that the color of wastewater continues to be much lighter in 0.4 mg/L coagulant, but increases more than double after coagulant increase to 0.5 mg/L. This study provides evidence that the more coagulants are added, the more particles cause the bound colors. However, Bolto and Gregory [25] argues that the more coagulants used covers the surface of pollutant particles. This prevents the restabilization–formation of large flocs, due to the unavailability of an empty space for bonding of pollutant particles.

3.3. Processing with DBD ionization technology

Figs. 6–8 show the result of COD, TSS, and color after adding coagulant and processed with DBD ionization technology. Among COD, TSS, and color, it is apparent that time DBD ionization reduces the concentration of COD, TSS, and color. The significant reduction of COD, TSS, and color occurred without coagulant (control) and 0.1 mg/L coagulant. Gradual reduction of COD, TSS, and color are observed at 0.2, 0.3, 0.4, and 0.5 mg/L coagulants. Table 4 presents Kruskal–Wallis test for coagulant-based significant changes of pollutant and then processed by DBD ionization.

As shown in Fig. 6, COD of wastewater at 0 and 0.1 mg/L coagulants reduced gradually by the time of DBD ionization. A small reduction of COD occurred when the coagulant was equal to 0.2 mg/L or more even though COD is not considered to have a significant reduction (Table 4). Negative ions are created from an electrode of the DBD reactor in high voltage [6]. In addition to negative ions, DHF also produces ions, radicals, and excited species that react to the function of decomposing organic compounds [26, 27]. These electrons collide the stable charged ions in the gas and water. It produces high reactive negative ions, which then attack the organic substances in the liquid waste and transform them into other non-polluting substances. The number of ions produced in the DBD ionization process increases along with the increase of dot ionization-time [6]. The increasing number of ions increases more electrons that able to break organic substances in the wastewater. In this study, DBD ionization for 10 min reduced COD of 515.80 mg/L and continues to 460.31 mg/L after 20 min of DBD ionization. This study proved that the reduction of COD occurred as time increased. However, it was also proved in Table 4, using the Kruskal–Wallis test, that the reduction of DBD ionization is not significant.

Meanwhile, TSS reduction at 0 and 0.1 mg/L coagulants reduced gradually after it was processed at DBD ionization for 10 min (Fig. 7). Afterward, a small reduction occurred until it was processed for 50 min. However, DBD ionization in this study was not observed significantly to reduce TSS. The significant reduction of TSS occurred due to the increase of coagulant.

The trends of color reduction in wastewater after DBD ionization process is shown in Fig. 8, but the reduction is
not significant (Table 4). A substantial change occurred in 0 and 0.1 mg/L coagulants. However, very small changes of color occurred in 0.2 mg/L of coagulant or more.

This study applied 15 kV for DBDi, which is higher than the previous study conducted by Sucipta [20]. High voltage that flows into the reactor ionizes the O, and H2O molecules in wastewater [28]. It produces various active radicals such as OH\(^{•}\), O\(^{•}\), and H2O\(_2\). There is an interaction between active radicals with the bond of substances of color in the coating wastewater that breaks the bond, eventually reduces the color of the wastewater.

This study observed that the longer DBD is processed, the more the color concentration decrease in wastewater. Time of ionization produces electrons resulting in high voltage [6]. More electrons produce more free radicals. Electrons generation influence more OH\(^{•}\), O\(^{•}\), and ozone formations. Thus, more bonds of color will be attacked by free radicals, resulted in color reduction.

The number of electrons generated at each time of ionization were calculated and presented in Table 5. COD, TSS, and color predictions from the production of electron can also be seen in Table 5. The calculation of electron follows Eqs. (1) and (2).

\[
Q = \frac{I}{t}
\]  
\[
n = \frac{Q}{e}
\]

where \(Q\) is a charge (coulomb), \(I\) is current (ampere), \(t\) is time (second), and \(n\) is the number of electrons.

Around \(3.3 \times 10^{21}\) electrons were generated at 10 min that reduces COD by 50.39 mg/L. The number of electron increases as the time increases. More electrons generated produce more free radicals. This implies more organic substances to be decomposed.

### 3.4. Effect of TSS parameter decrease on the effectiveness of DBD ionization process

Processing of pretreatment of coagulation–flocculation is expected to assist the processing of doping ionization by initially decreasing the TSS content first. The result of TSS parameter degradation with pretreatment using coagulation–flocculation and DBD ionization is shown in Table 5. TSS removal using DBD ionization has a similar percentage value of TSS removal, when given or not given the pretreatment of flocculation–coagulation. This indicates that the decrease of TSS has no significant effect on the effectiveness of the DBD ionization process. However, pre-treatment of flocculation–coagulation is beneficial in reducing TSS parameters, since the study conducted by Nur et al. [13] observed ineffective TSS parameter elimination by the DBD reactor. Pre-treatment of flocculation–coagulation has a beneficial to decrease the TSS, thus it can meet the quality standard. Table 5 shows a high concentration of TSS in effluent treated only with DBD ionization. On condition when pretreatment is carried out before doping ionization, the TSS concentration value can meet the quality standard.

### 4. Conclusions

- Flocculation–coagulation treatment with the combination of PAC and chitosan coagulant has shown promising results to decrease COD parameter with the optimum amount of 0.4 g/L, TSS with the optimum amount of 0.3 g/L, and color with the optimum amount of e 0.4 g/L at pulp and paper industry wastewater.
- Coagulation processing of flocculation has more roles in color and TSS removal with the maximum allowable percentage of 98.83% and 98.95%, respectively.
- Processing of DBD ionization could decrease COD, TSS, and color parameters in pulp and paper industry waste with 50 min optimum contact time.
- Processing with DBD ionization was more important in COD removal with a provision percentage of 89.81%.
- Pretreatment of flocculation coagulation may assist to decrease TSS in wastewater, as DBD ionization treatment was less effective in TSS removal.

### References


