Coagulation-Flocculation Treatment of White Pepper (*Piper nigrum L.*) Processing Wastewater

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ABSTRACT. *Wastewater generated in white pepper (Piper nigrum L.) processing contains high Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and hydrolyzable tannins that results dark tan/brown colour effluent which cannot be discharged to the environment without proper treatment. Therefore, these experiments were conducted to investigate the effectiveness of electro-coagulation using aluminum (Al) electrodes and coagulation-flocculation with Alum [$Al_2(SO_4)_3.18H_2O$] in reducing the strength of pepper soaked effluent. A laboratory scale electro-coagulation unit was made using two aluminium plates (9 cm × 5 cm × 0.3 cm) as electrodes leaving a 0.5 cm gap between plates and powered with a 12 V DC power supply through a resistance box which is used to regulate the current density. The current density could be controlled between 0-1 A. Coagulation flocculation with Alum was tested at five doses; 1 to 5 g/L with 1 g increments at laboratory scale. The effluent colour was measured using a spectrophotometer at a wave length of 600 nm. According to the results, removal efficiencies of colour, Turbidity and COD were 94%, 91% and 89%, respectively for 20 minutes of electro-coagulation and 92%, 90% and 92%, respectively with 3 g/L Alum treatment. The pH of the effluent during electro-coagulation for 20 minutes increased to 9.0 while Alum treatment with 3g/L reduced to 5. When treated effluent filtered through a fine sand filter, Total Dissolved Solids (TDS), Electrical Conductivity (EC) and COD could be reduced further and reached the standard values to discharge in to the environment as irrigation water.*

Keywords*: Alum treatment, aluminium electrodes, coagulation-flocculation, tannins, white pepper wastewater*

INTRODUCTION

White pepper is the de-husked berry produced by removing the outer skin, pericarp and outer portion of the mesocarp of the well matured berries or in some cases dried black pepper. Black pepper gets the colour due to the enzymatic browning by fermentation and oxidization of phenolic compounds present in the outer skin of fruits (Amala Dhas and Korikanthimath, 2003). White pepper has demand in high the European markets due to its colour and lower

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pungency. Traditional retting includes washing, soaking, pulping, washing and drying, and soaking is done for 3 to 5 days (Bunchol, 2011). When black pepper is used as the raw material, soaking requires about 2 m^3 of water per tonne. The wastewater discharged from soaking is rich in organic matter including tannins adding a dark tan colour. Gallotannin, or common tannic acid, is the best known hydrolyzable tannin and it leach into the effluent during soaking and produce undesirable dark brown color (Hansen, 1992).

Treatment of pepper wastewater at industrial level has become a great challenge due to its peculiar colour and high BOD_5 value above 3500 mg/L. Electro-coagulation has been successfully used in removing pollutants of various industrial wastewaters (Babuna et al., 1999; Gurses et al., 2002; Lin et al., 1994Vlysside et al., 2001). Electro-coagulation has many advantages such as simple equipment, easy operation and possibility of automation, a short retention time, low sludge production.

Coagulation flocculation with Alum is another simple traditional method to alter the colloids so that they will be able to approach and adhere to each other to form larger flock particles. In this process, small particles of color/pigments, turbidity and bacteria into larger flocks, either as precipitates or remain as suspended particles. However, the performance is highly dependent on pH and dosage (Song et al., 2004).

Therefore the objective of this study was to investigate the effectiveness of electro-coagulation and coagulation flocculation with Alum on reducing the strength of pepper soaked wastewater separately. It was also attempted to optimize the retention time for electro-coagulation and dosage of Alum for the best treatment.

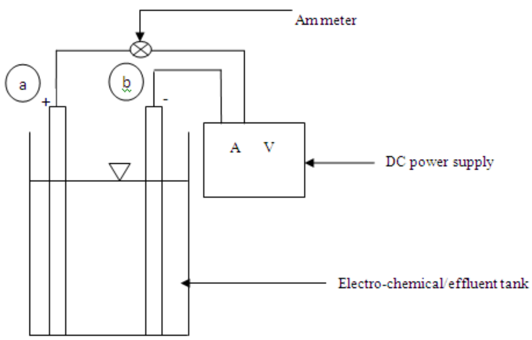
MATERIALS AND METHODS

Sample collection and preparation

Black pepper soaked wastewater was collected from a commercial white pepper processing plant located in the Matale district and they were stored in an incubator at 4 ^{0}C. The test sample was allowed to reach the room temperature (25-26 ^{0}C) before using it for the experiments.

Experimental set up of the electro-coagulation cell

A laboratory-scale reactor cell was used to conduct the electro-coagulation experiments. The testing unit had an AC to DC converter and a resistant box to regulate the current density to the electrodes. Two groups of alternating electrodes being cathode and anode, made from plates of aluminum with the dimensions of 9 cm × 5 cm × 0.3 cm and a working area of approximately 65 cm^2per plate was used. The aluminium plate electrodes were arranged vertically and parallel with a spacing of 0.5 cm were connected to the DC 12 V power supply. The power supply converted AC in to DC using a transformer and provided a current from 0 to 1 A using a resistance as a current density regulator. An ammeter was connected in series to the system to determine the electric current supplied to the treatment cell. The effective volume of the treatment cell was about 250 mL. The five treatments; T1- 0.0 min (raw sample as control), T2- 5 min, T3-10 min, T4-15 min, T5- 20 and T6- 25 min were performed at 25-26 °C. The optimum working pH was in the range 5–7, allowing pepper soaking wastewater to be treated directly without pH adjustment. Before conducting each experiment, the electrodes were washed with water, dipped in dilute hydrochloric acid (HCl, 5 % v/v) for 5 min, thoroughly washed again with water and finally rinsed twice with distilled water. After electrolytic treatment, the effluent was allowed to stand for 30 minutes for settling and then sampled for analysis. The schematic diagram of the electro-chemical cell and electrode assembly is shown in figure.1



(a) Aluminium anode, (b) Aluminium cathode

Fig. 1. Schematic diagram of the electro-coagulation cell

Application of Alum

Analytical grade hydrated Alum ($Al_2(SO_4)_3.18H_2O$) was used for the experiment. Beakers (250mL) were filled with 100 mL effluent and pre-determined five doses of Alum; T1- 0.0 g/L (raw sample as control), T2-1.0 g/L, T3-2.0 g/L, T4-3.0 g/L, T5-4.0 g/L and T6-5.0 g/L were added. Then the mixtures were shaken in a magnetic stirrer at 600 rpm for one minute and at 200 rpm for 10 minutes, allowed to settle for another two hours. Rapid mixing is the most important physical factor affecting the coagulant efficiency (Hosseinian, 1991). After the settling period, the supernatant was withdrawn from the beaker and then sampled for analysis. The results of both treatments were compared with environmental accepted values and no need to go for statistical analysis.

Analysis of wastewater quality parameters

Electro-coagulation was performed for the predetermined time periods and Alum treatment with predetermined dosages separately. Effluent samples from each experiment were collected after allowing 30 minutes settling time. After the settling period, the supernatant was withdrawn from the beaker, and was used for chemical analysis.

The parameters pH and Turbidity were determined using a glass electrode pH meter and a turbidity meter (HACH 2100Q). The EC, TDS and salinity were measured using a multi meter (Thermo orion model 145A$^+$, USA). COD of the treated effluent was measured according to IS: 3025 (Part 58) Using Hach DRB 200. The DO content of soaking water was measured by Winkler's titration method. DO concentration was measured only at the beginning and after five days. The difference was recorded and it's correlated to environmental standard BOD_5 value. Color of the effluent was measured using a UV–Vis spectrophotometer (Hitachi U 2800, Tokyo, Japan) at 600 nm. Finally, the treated sample was filtered through a fine sand column to assess the effectiveness of sand filtration on TDS, EC and salinity. Turbidity, COD and colour removal efficiencies after each treatment were calculated using the following formula (Eq. 1):

$$Removal\ Efficiency = \frac{C_0 - C}{C_0} \times 100\% \qquad \text{(Eq. 1)}$$

Where, c_0 and c are turbidity, COD or colour of wastewater before and after treatment.

Tukey's mean separation test was performed using SAS statistical package in order to test the significance of mean values and the difference was considered significant at $p<0.05$.

RESULTS AND DISCUSSIONS

Removal mechanism in electro-coagulation process includes oxidation, reduction and decomposition (Vlyssides et al., 1999), whereas the mechanisms in both electro-coagulation and coagulation-flocculation process include coagulation, adsorption, precipitation and flotation. The Aluminium plates and Alum have been used in both treatments for wastewater treatment due to the high coagulation efficiency of Aluminium ion. Chen. (2004) and Mollah et al., (2001) reported that the electrolytic dissolution of the Aluminium (in electro-coagulation anode) produces the cationic monomeric species such as Al^{3+} $Al(OH)_2^+$ under acidic conditions. However, depending on the pH of the aqueous medium, other ionic species, such as $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. In addition, various forms of charged multimeric hydroxo Al^{3+} species may also be formed under appropriate conditions. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption (Yetilmezsoy et al., 2009).

Characterization of white pepper process effluent

The main characteristics of the effluent and standard limits for discharge are shown in Table1. As the effluent carries high concentration of pollutants, it cannot be discharged to environment without proper treatment.

Table 1. Comparison of pepper wastewater characteristics with standard values

Parameters	Black pepper effluent	National Standards for effluent discharge (CEA,1997)	
		Inland surface water	Irrigation
pH	5.0 - 6.3	6.0 - 8.5	5.5 - 9.0
BOD_5 (mg/L)	4260	30	250
COD (mg/L)	7100	250	-
TSS (mg/L)	733	50	-
Colour	Dark brown	-	-
TDS (mg/L)	5190	-	-

Electro-Coagulation treatment

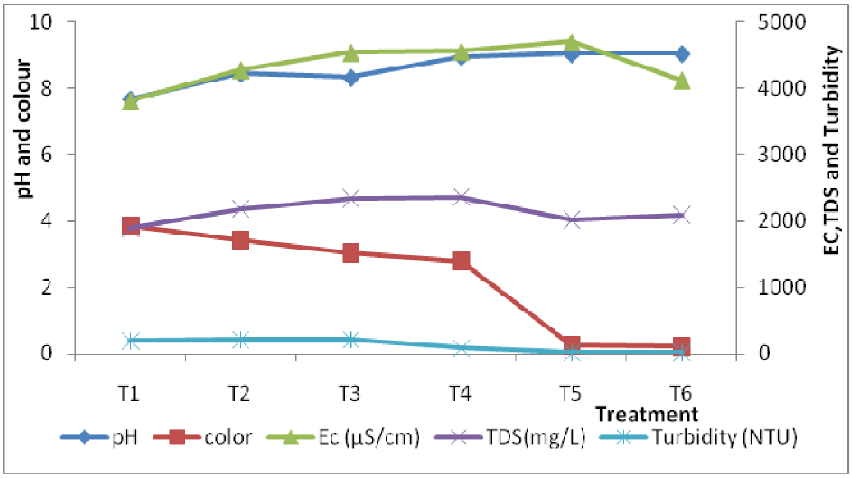
An effluent sample was treated using 12V electro-coagulation system with a 1 A currant density. The quality parameters of raw sample was compared with periods of treatment time as shown in Fig 2.a and b. Colour change was observed in pepper effluent with the increase of retention time.

During the treatment process, pH and total dissolved solids (TDS) content of the effluent increased with increased retention time as shown in Fig 3. Alinsafia et al, (2005) has also reported the same behavior. The change of pH and TDS was not uniform and it depends on released OH^- ions and hydrogen gas concentrations. Initial pH of the raw sample was close to neutral and with the treatment it increased up to 9. Anode released three electrons which attach H_2O molecule and produce H_2 gas. At the same time OH^- and Al^{3+} ions combine with water (H_2O) and produce $Al(OH)_3$ and H^+ ions. OH^- ion production was higher than H^+ ion production. Hydroxide ions combined with waste and coagulate. Due to that phenomenon, after 15 minutes of treatment, a significant effect was not observed in the increase of pH with the treatment. Due to coagulation TDS, treated effluent reduced after 15 minutes and therefore, there is no significant effect after 20 minutes of treatment. The change on turbidity is uneven, during the first 10 minutes, it was increased due to the breakdown of the organic substances and producing the initial level flocks as suspended molecules as shown in Fig 3. After 10 minutes of treatment the turbidity is started to reduce and after 20 minutes of retention time, it was reduced from 192.7 NTU to 17.8 NTU. Finally, with fine sand filtration the value reached 9.8 NTU with 91% of removal efficiency. Production of OH^- ions and hydrogen gas concentration increased and forced to float the light weight flocks towards the surface and the large and heavy flocks settled under the gravitational force. After the 20 minutes of treatment, there was no significant difference observed in turbidity with treatment time. Continuous colour reduction of 94%could be observed with electro-coagulation treatment time up to 20 minutes and there was no significant change after 20 minutes shown in Fig 3. The conductivity and salinity increased when the treatment progress due to high

electrode solubility. Organic matter in terms of BOD_5 of the treated effluent could be reduced from 2800 mg/L to 340 mg/L. in 20 minutes and there was no significant reduction after 20 minute of the treatment as shown in Fig 4. Finally, the treated samples were filtered through a fine sand column. There was a significant reduction in pH, EC, TDS, Turbidity, colour and COD. However, there was no significant difference in BOD_5 after sand filtration. According to the results, the electro-coagulation treatment is an efficient COD removal technique and COD reduced from 5757 mg/L to 145 mg/L (89%). This was achieved with 20 minutes retention time followed by sand filtration as shown in figure 5. In addition, it is also reported by Li et al, (2008) that COD of effluent decreases with the decrease in distance (0.5 cm) between electrodes of the electro-coagulation treatment cell. This is because the shorter distance speeds up the anion discharge on the anode and improves the oxidation. It also reduces resistance, the electrical power consumption and the cost of the wastewater treatment. Ghosh et al. (2008) have also reported that with the increase of inter-electrode distance, the percentage removal of dye products from waste water decreases.
Small amount of sludge is produced in this treatment and it should be used for another application after appropriate post-treatment.

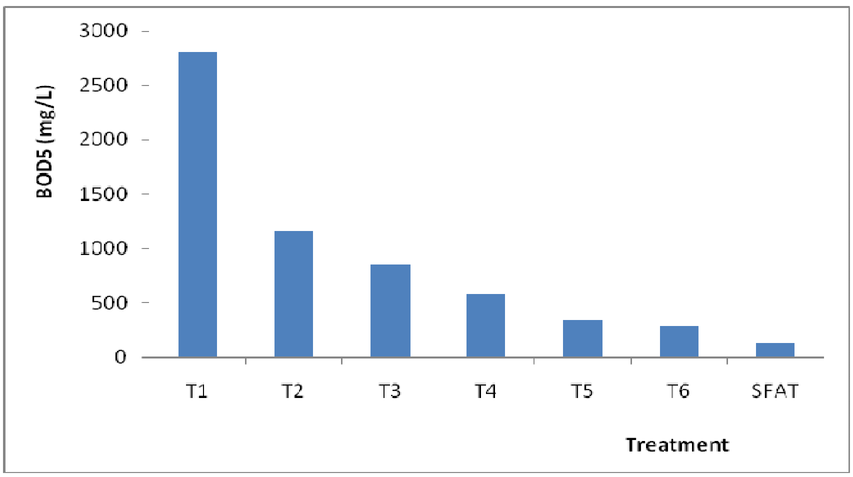
(a) (b)

Fig.2. Raw sample (a) Change of colour after 10, 15 and 20 minutes of electro-coagulation treatment (b)



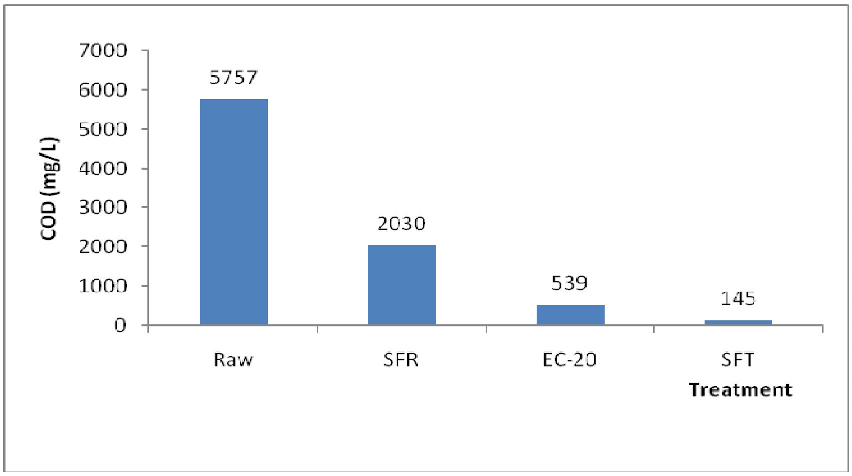
*Retention time; T1- 0.0 min (raw sample as control), T2-5.0 min, T3-10.0 min, T4-15.0 min, T5-20.0 min, T6-25.0 min

Fig. 3. The effect of electro-coagulation time on some effluent quality parameters



*Retention time; T1- 0.0 min (raw sample as control), T2-5.0 min, T3-10.0 min, T4-15.0 min, T5-20.0 min, T6-25.0 min

Fig. 4. The effect of electro-coagulation time and sand filtration on BOD_5

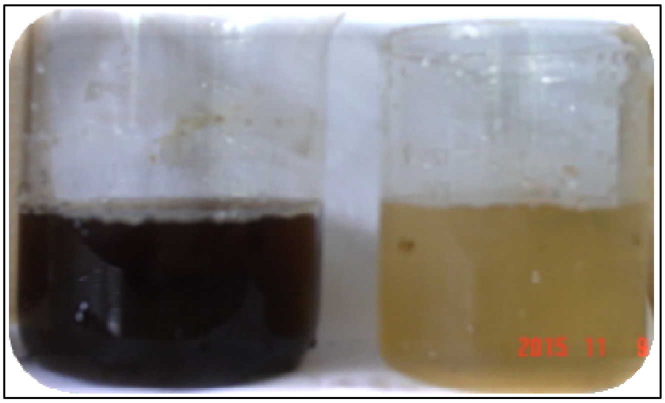


*SFR – Sand filter raw; SFT – Sand filter treated; EC-20-Electro-Coagulation treatment for 20 minutes

Fig. 5. Comparison of the COD values raw sample with other selected treatments

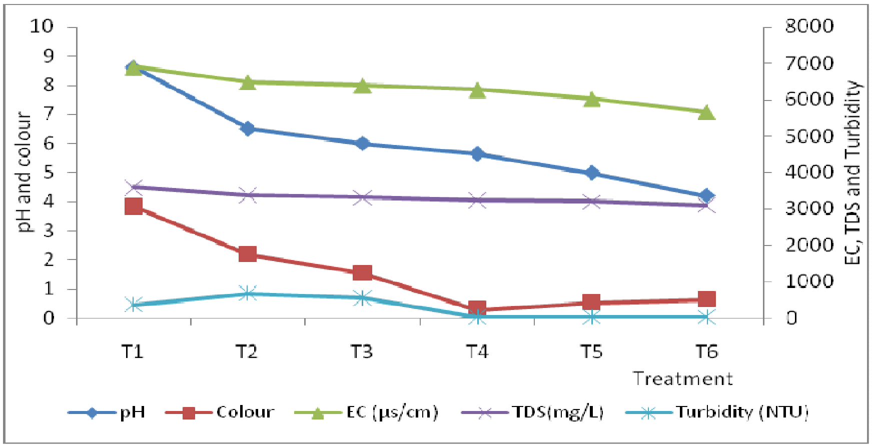
Application of Alum

The optimum coagulant dosage and resulting pH value were determined by comparing the effective dose of Alum [$Al_2(SO_4)_3.18H_2O$] for obtaining maximum color, turbidity, BOD and COD removal. The effectiveness of Alum varied between the application dosage and the resulting pH as shown in Fig. 7. TDS, pH and EC decrease with the increase of Alum dosage as shown in the figure and a significant reduction was observed with sand filtration after Alum treatment ($p = 0.000$). The minimum Alum dosage of 3 g/L was needed to effectively remove the color (Fig.6.a &b) and turbidity by precipitating phenolic compounds. A pH value of 5 and the color removal efficiency of 92.2% could also be achieved at that dosage. The best removal capacity of turbidity from 360.3 NTU to 12.8 NTU (90%) was measured with fine sand filtration after 3 g/L of Alum treatment and no further significant reduction was observed above that dosage. An acceptable reduction of COD from 6197 to 152 mg/L (92%) (Fig.8) and organic matter (71.7%) in terms of BOD_5 from 3333 mg/L to 143 mg/L (Fig.8) could be achieved with an Alum dosage of 3 g/L. Sand column filtration (using fine sand with 2.0 mm particle size) after Alum treatment was effective in further reducing EC,TDS and COD parameters.



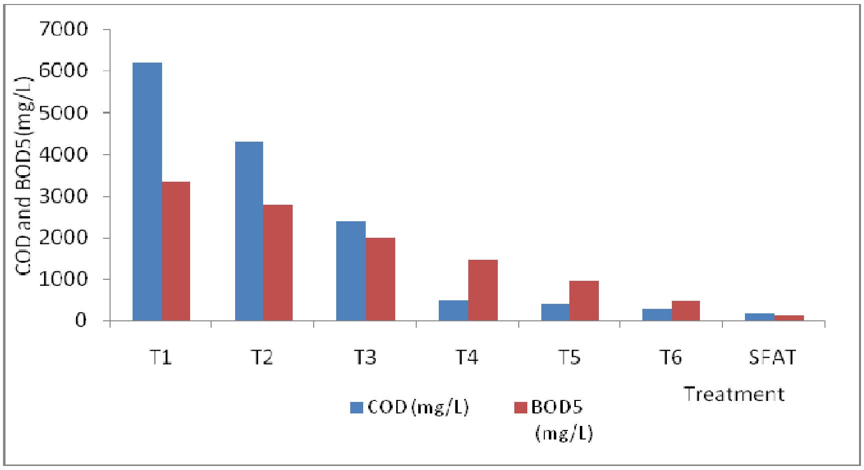
a. Raw sample b. Alum treated (3g/L)

Fig. 6. Change of color after Alum tratment



*Doses of Alum; T1- 0.0 g/L (raw sample as control), T2-1.0 g/L, T3-2.0 g/L, T4-3.0 g/L, T5-4.0 g/L, T6-5.0 g/L

Fig. 7. The effect of Alum dosage in coagulation flocculation time on some effluent quality parameters



*Doses of Alum; T1- 0.0 g/L (raw sample as control), T2-1.0 g/L, T3-2.0 g/L, T4-3.0 g/L, T5-4.0 g/L, T6-5.0 g/L, SFAT-sand filtered after treatment

Fig. 8. Effect of Alum dosage and sand filtration on COD and BOD_5

CONCLUSSION

In the present study, satisfactory diminution of various parameters, mainly of colour, turbidity, COD and BOD_5 were investigated. From the initial characterization of the effluents, electro-coagulation with aluminum plates is a convenient route for the treatment of pepper waste effluent. According to the results, electro-coagulation for 20 minutes reduced the BOD_5 from 2800 mg/L to 120 mg/L, COD from 5757 mg/L to 145 mg/L (89%), turbidity from 192.7 NTU to 9.8 NTU (91%) and colour by 94% which is a remarkable achievement. Alum treatment was also effective in reducing not only the color, but also the turbidity, BOD and COD. An optimum dosage of 3g/L of Alum reduced the BOD_5 from 3333 mg/L to 143 mg/L (71.7%), COD from 6197 to 152 mg/L (92%), turbidity from 360.3 NTU to 12.8 NTU (92.2%) and colour by 90% while maintaining a final pH above five. Alum treatment proved to be better for reducing EC and TDS than electro-coagulation. Effluent from both treatments could be used for irrigation purpose. In addition, there was a considerable reduction of TDS and EC after sand filtration for both treatments and final discharge reached the permissible level for irrigation. In conclusion, the electro-coagulation followed by sand filtration could be considered as the best treatment but one should conduct a cost comparison after testing at the industrial scale to recommend the most economically compatible treatment for white pepper processing effluent.

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