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Effects of Ferrous Sulfates and Poly-aluminum Chloride in Beverage Wastewater Treatment

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Abstract: *Effects of ferrous sulfate (FeSO4) and poly-aluminum chloride (PAC) during wastewater treatment process at a local beverage company were investigated. Optimum concentrations of FeSO4 and PAC together with the effluent quality in wastewater treatment plant were studied. The application of FeSO4 was examined at different concentration of 6.0 ppm, 6.5 ppm, 7.0 ppm, 7.5 ppm, and 8.0 ppm whereas that of PAC was investigated at the concentrations of 9.0 ppm, 9.5 ppm, 10.0 ppm, 10.5 ppm, and 11.0 ppm, respectively. Physicochemical characteristics of wastewater viz pH, color, dissolved oxygen (DO), total dissolved solid (TDS), total phosphorus, iron, ammonia and chemical oxygen demand (COD) before and after treatment were determined. Ferrous sulfate at the concentration of 7.5 ppm was most effective in removing total phosphorous taken into account the cost effectiveness. At this concentration, the effluent compliance in terms of pH, color, DO, TDS, total phosphorous, iron, ammonia and COD was obtained based on the standard value of Ministry of Environment in Cambodia. Similar compliance of effluent quality was achieved at poly-aluminum chloride optimum concentration of 10.0 ppm during which phosphorous flocculation in wastewater treatment plant was accelerated.*

Keywords: Poly-aluminum chloride; Ferrous sulfate; Beverage Company; Wastewater treatment;

1. **INTRODUCTION**

Industrial wastewater is one of the major concern for its adverse environmental and human health impacts if it is not treated properly. In such a case, proper industrial wastewater treatment is necessary to remove pollutants from industrial wastewater before discharging into the receiving waterbody. In Cambodia, the effluent water quality has to be complied with the standard values of Ministry of Environment (MoE) before being released into the municipal sewage systems or any waterbody. In order to achieve the effluent standard, the combination of physical, chemical and biological methods is commonly used in industrial wastewater treatment plants, including food and beverage industries (Davis & Cornwell, 2008).

 To remove the suspended solids, chemical coagulation process is one of the popular and conventional methods for wastewater treatment; moreover, selecting a suitable coagulant for the maximum contaminant removal and at reasonable cost was quite challenging for wastewater treatment plant (Farajnezhad & Gharbani, 2012). So far, aluminum sulfate, poly aluminum chloride, ferrous sulfate, ferric chloride are commonly used as coagulants to flocculate the solids in the wastewater (Amokrane et al.,

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1997). In the present study, ferrous sulfate $(FeSO₄)$ and poly-aluminum chloride (PAC) were used as the coagulant during the beverage wastewater treatment. The objective of this study was to investigate the effects of ferrous sulfate and poly-aluminum chloride during wastewater treatment process at a local beverage company and to determine their optimum concentrations taken into account of Cambodian effluent water quality compliance.

2. METHODOLOGY

2.1 Experimental operation

To replicate the actual condition of wastewater treatment, wastewater was collected from aeration tank at a local beverage company and subjected to further treatment with FeSO₄ and PAC. The application of FeSO₄ was studied at different concentrations of 6.0 ppm, 6.5 ppm, 7.0 ppm, 7.5 ppm, and 8.0 ppm while that of PAC was investigated at different concentrations of 9.0 ppm, 9.5 ppm, 10.0 ppm, 10.5 ppm, and 11.0 ppm, respectively. To determine the effects of FeSO4 and PAC on the treatment efficiency, well-mixed wastewater sample taken from aeration tank was placed in different 6L-plastic tanks before subjecting to the addition of different concentrations of FeSO₄ and PAC. Tanks were then aerated for 35 min and left settled for 5 h to simulate the actual operation of wastewater treatment. The supernatant of

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wastewater sample were then subjected the physicochemical analysis.

2.2 Physico-chemical analysis

2.2.1 pH and color

pH values of wastewater before and after the application of coagulants were measured in triplicate by using pH meter (827-pH-lab, Metrohm, Switzerland). Samples were also subjected to color analysis with the use of Photometer Multi-Direct (Lovibond, Tintometer GmbH Ltd., Dortmund, Germany). Prior to color measurement, samples were filtered by using cellulose nitrate filter paper and 10 mL of filtrate was then placed into the clean vial and measured in triplicate. Color values were expressed in Pt-Co.

2.2.2 Dissolved oxygen

Concentrations of dissolved oxygen in wastewater samples were measured in triplicate by using DO meter (SensoDirect 150, Lovibond, Tintometer GmbH Ltd., Germany) and expressed in mg/L.

2.2.3 Total dissolved solids (TDS)

Concentrations of TDS presented in wastewater samples were analyzed in triplicate by using a TDS meter (HI 9034, HANNA instruments) and expressed in mg/L.

2.2.4 Total phoporous

Total phosphorous test kits (Tintometer GmbH Ltd., Dortmund, Germany) were used to determine the total phosphorous concentration. 10 mL of sample with the phosphate tablets 1 and 2 were well-mixed and stood for 10 min prior to its measurement with Photometer Multi-Direct (Lovibond, Tintometer GmbH Ltd., Dortmund, Germany). Triplicate samples were then subjected to total phosphorous analysis and expressed in mg/L.

2.2.5 Iron

Iron concentrations in wastewater samples were measured with the use of Iron test kit (Tintometer GmbH Ltd., Dormund, Germany). 10 mL of wastewater sample was mixed with Iron LR tablet and stood for 5 min. The mixture was then subjected to iron analysis by Photometer Multi-Direct (Lovibond, Tintometer GmbH Ltd., Dormund, Germany). Triplicate samples were measured and expressed in mg/L.

2.2.6 Ammonia

Ammonia concentrations in wastewater samples were analyzed by Ammonia test kit (Tintometer GmbH Ltd., Dortmund, Germany). 10 mL of wastewater samples was well-mixed silmutanoeusly with ammonia tablets 1 and 2 and the mixture stood for 10 min. Triplicate samples were then measured by using Photometer Multi-Direct (Lovibond, Tintometer GmbH Ltd., Dormund, Germany) and the concentration was expressed in mg/L.

2.2.7 Chemical oxygen demand

Chemical oxygen demand of the samples was determined by Chemical oxygen demand test kit (Tintometer GmbH Ltd., Dortmund, Germany). 2 mL of sample was added into the ready-made test tube with COD reagents, well-mixed and heated at 150 °C in a pre-heated COD for 120 min. Tube was then cooled down to room temperature pior to COD measurement by using Photometer Multi-Direct (Lovibond, Tintometer GmbH Ltd., Dortmund, Germany). Triplicate samples were subjected to COD analysis and expressed in mg/L.

3. RESULTS AND DISCUSSION

3.1 Effects of FeSO4 and PAC on pH, color, DO and TDS

Effects of FeSO4 at different concentrations on pH, color, DO and TDS value are presented in Fig. 1. During the investigation, pH value remained almost constant at approximately 8.6 despite the change in FeSO4 concentration. This could be attributed to the nature of wastewater and the use of pre-hydrolyzed FeSO₄ which had no effect on pH variation (Ukiwe, 2014). On the other hand, significant difference of color level was observed with the lowest value of 15 Pt-co, i.e., approximately 42% of color reduction, at FeSO4 concentration of 6.5 ppm. In fact, the optimum pH value for color removal with the application of $FeSO₄$ was in the range of $7-9$ while the optimum dosage of FeSO4 significantly depended on the characteristics of wastewater (Verma et al., 2012). Similarly, result of the present study showed that addition of FeSO₄ at concentration of 6.5 ppm was most effective to remove color from wastewater. A slight decrease in DO concentration was observed once FeSO4 was added.

Fig. 1. Effects of FeSO₄ on pH, color, DO and TDS.

However, DO concentration did not change significantly during the course of experiment although different FeSO₄ concentrations were applied. It is well known that FeSO4 formed gel like hydroxides and some positively charged mononuclear and poly-nuclear species during which positively charged compounds combined with negatively charged colloidal particles in water by charge neutralization mechanism as settling process proceeded (Parmar et al., 2011). In the present investigation, no significant effect of FeSO4 application on the TDS removal; this could be explained by the nature of $FeSO_4$ —i.e., a coagulant which was more effective for suspended solids coagulation rather than TDS (Sahu & Chaudari, 2013). The application of FeSO4 at concentration of 6.5 ppm was most effective to remove color, following by those at 7.0 ppm and 7.5 ppm, respectively.

 Fig. 2 shows the effects of PAC on pH, color, DO, and TDS. pH value remained almost constant at approximate 8.5 eventhough increasing PAC concentration was applied. Similar observation with different PAC dosages was also reported in previous domestic wastewater study (Nansubuga et al., 2013). This could be attributed to the fact that PAC is a salt coagulant which in turn has no-significant effect on pH variation. Color value of wastewater after PAC application was slightly fluctuated between 45-48 Pt-Co and the lowest value was observed when 10 ppm of PAC was applied suggesting that PAC did not have a significant effect on color removal. The higher the PAC concentration applied, the lower DO concentration became. In fact, it is well known that PAC had a high hydrolysis characteristic leading to the enhancement of adsorption of hydroxide group whereas simple hydroxide ions might bind strongly to many solid surfaces; this therefore enhanced the formation of covalent bonds between the metal atom and specific sites on the surface of the colloidal particle by reducing the energy necessary to displace water molecules from the coordination sheath (Dawery & Joubori, 2012). At the same time, this reaction released hydrogen ion which could in turn be removed by dissolved oxygen (RMC, 1990). Similar result was also obtained in the case of TDS after the application of PAC compared to that of FeSO₄ (See Fig. 1).

Despite the different concentrations of $FeSO₄$ and PAC applied, pH, DO and TDS of wastewater samples after the treatment were complied with the effluent wastewater quality standard of MoE in Cambodia (MoE, 1999). Moreover, slightly higher color removal was observed in the application of FeSO4 comparing to that of PAC in this study. DO concentrations of effluents were significantly affected by PAC than FeSO4. This could probably be attributed to the hydrolysis nature of PAC during which hydrogen ion was produced whereas none was produced during the hydrolysis of FeSO4 (Parmar et al., 2011; Dawery & Joubori, 2012; RMC, 1990); therefore, higher amount of DO was consumed during the application of PAC rather than that of FeSO4.

3.2 Effect of FeSO4 and PAC on total phosphorus, iron, ammonia and COD

Effects of FeSO4 and PAC on total phosphorus, iron, ammonia and COD, are presented in Fig. 3 and Fig. 4, respectively. In the present study, highest total phosphorus removal could be obtained by using $FeSO₄$ at concentration of 7.5 ppm or PAC at concentration of 10 ppm; in fact, the efficiency of PAC to remove total phosphorus was more than twice higher than that of $FeSO₄$ suggesting that PAC was more effective to remove total phosphorous than FeSO₄ in this case. This could be explained by the fact that PAC contained high charged poly-aluminium species and released hydrogen ion to neutralize phosphorus compounds during its hydrolysis (Dawery & Joubori, 2012). On the other hand, phosphorus compounds could probably be removed by the adsorption to amorphous iron oxy-hydroxides in FeSO4 solution; this process was relatively less effective in comparison to that of PAC application (Wang et al., 2014; Sahu & Chaudari, 2013).

 Iron concentration varied in the range of 0.06—0.08 mg/L and of 0.04—0.05 mg/L during the application of FeSO4 and PAC, respectively. According to the maximum allowable discharge iron value of MoE (1999)—i.e., less than 2.0 mg/L, the present effluent after either the use of FeSO4 or PAC could be discharged into any receiving waterbody. In fact, a slight increase of iron concentration was observed once FeSO4 was applied; this could be directly attributed to the iron containing FeSO₄ dissolution. Moreover, iron compounds were generally corrosive and often present difficulties in dissolving, and the use of iron containing substance might result in high soluble iron

Fig. 3. Effects of FeSO₄ on total phosphorus, iron, ammonia and COD.

concentration in effluent (Sahu & Chaudari, 2013). On the other hand, no significant difference of iron concentration was observed when PAC was used; this could be well explained by the nature of PAC which did not contain any iron. With the use of FeSO₄ and PAC, ammonia concentration varied in the range of 0.2—0.4 mg/L and 0.3—0.5 mg/L, respectively which were complied with the maximum allowable standard value of MoE—i.e., less than 7 mg/L (MoE, 1999). The more FeSO4 applied, the higher NH3 concentration was observed. Despite the different PAC concentrations used, a slight fluctuation of ammonia concentration in effluent was detected. Similar fluctuation of total ammonium nitrogen was also observed in a domestic wastewater treatment study (Nansubuga et al, 2013). In fact, this fluctuation could be attributed to number of operational conditions such as mixing speed and time.

 On the other hand, higher COD removal at about 25— 35% could be obtained by adding FeSO4 solution at 7.5 ppm compared to that with the use of PAC at 10 ppm concentration. Similar investigation on the COD reduction with the use of PAC in textile wastewater treatment, it was found that the application of 10 ppm of PAC could reduce 48% of COD in the wastewater (Farajnezhad & Gharbani, 2012); this could be thus inferred that the nature of wastewater characteristics significantly affected the performance of coagulants—i.e., PAC and FeSO4, even though the same type of coagulant and dosage were applied.

4. CONCLUSIONS

The effects of ferrous sulfate and poly-aluminium chloride on physico-chemical characteristics of wastewater during wastewater treatment process at a local beverage company were investigated. The application of ferrous sulfate at concentration of 7.5 ppm was most effective to remove total phosphorous taken into account the cost effectiveness among all five different concentrations. At this concentration, pH,

color, DO, TDS, total phosphorous, iron, ammonia and COD were complied with the maximum allowable standard values of MoE of Cambodia. On the other hand, poly-aluminum chloride at concentration of 10 ppm was the optimum concentration to improve the phosphorous flocculation. At this concentration, all results of physico-chemical parameters except DO were complied with MoE standard values. Further study to replicate the aeration condition in the actual wastewater treatment plant is necessary to improve DO concentration after the application of either PAC or FeSO₄ prior discharging into any water-body.

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