Electrocoagulation-H₂O₂-dimethicone combined system for COD reduction and phosphate removal of sewage wastewater

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Abstract. Sewage wastewater contains large volume of pollutants and its discharge pose a serious environmental problem due to possible ground water contamination. This could be treated by electrocoagulation (EC) because of its proven effectiveness in treating different pollutants from various industries, however, this technology is not yet fully optimized. Process enhancements through chemical dosing were investigated in this study wherein electrocoagulation - H_2O_2 - dimethicone combined treatment was considered for the reduction of COD and removal of phosphate from an actual sewage wastewater source. Varying concentration of H_2O_2 and dimethicone was considered and it was found that at 1% H_2O_2 and 1% dimethicone, the phosphate removal of an EC system was improved from 83.06% to 100%. Likewise, the COD reduction increased from 68.25% to 82.89% after an hour of electrolysis time. Furthermore, using this blend, it reduced the settling time, minimized the electrode consumption and reduced froth height. Thus, the efficiency of the EC process improved using these additives.

1 Introduction

Improper wastewater discharge, particularly in urban areas, has fuelled concerns in the recent years about the sustainability of water resources. In the Philippines, where only 10% of the wastewater is properly treated before discharge, almost 58% of the groundwater is contaminated mostly because of the domestic or municipal wastewater [1]. The percentage of the Philippines population which has a proper sewage system connected to sewers is only less than 5% [2]. The vast majority uses flush toilets connected to septic tanks which are not regularly serviced, allowing effluent to directly pollute bodies of water [3]. Improper disposal of municipal wastewater due to lack of sewage treatment facilities is the main reason for the degradation of water quality allowing more than 90% of the untreated domestic wastewater to be discharged into surface water [4]. Domestic sewage is mainly polluted by feces and urine from establishment and or residential house toilet [5]. In consequence, untreated sewage water usually contains diverse kinds of biological and chemical constituents which are hazardous to both environment and human health [6].

Phosphorus together with nitrogen and carbon are important to living organisms and are the main nutrients present in natural water [7]. Large amounts of these nutrients are also present in municipal wastewater stream as well as in non-point agricultural run-off and point sources from industrial plants [8]. Nutrient pollutants primarily phosphorus from untreated sewage water pose a serious problem because they are responsible for the eutrophication of receiving water [9]. Recently, many countries realized the catastrophic implications of treated wastewater containing residual phosphorus and have amended more stringent phosphate effluent limit, for instance, 0.5-1.0 mg/L in USA, [10], 1-2 mg/L in France, less than 0.2 mg/L in South Korea [11] and effluent limit of 1 mg/L in the Philippines [12]. Phosphorus has proven to be expensive to mitigate and the conventional secondary biological treatment processes do not remove phosphorus to any substantial In a typical biological treatment plant, extent [11]. phosphorus is passed through to the sludge phase, and then removed depending on the amount of excess sludge. Thus, its removal is limited and variable, resulting in low removal efficiency even less than 30% [13, 14].

Electrocoagulation (EC) is a promising technology for its proven effectiveness in treating different pollutants from various industries including wastewater of food industry [15,16,17] tannery and textile industry [18,19] and removal of nutrient pollutants from municipal wastewater [20,11]. Compared to other conventional method, EC is more economically sustainable [21]. Electrochemical-based systems like EC allow controlled and fast reactions, higher efficiency, smaller systems get to be feasible, and instead of using chemicals and microorganisms, the systems employ only electrons to facilitate water treatment [22, 23, 24]. EC combines the effectiveness of electrochemistry, flotation and coagulation for water and wastewater treatment [25]. In EC, the coagulants are generated in situ by the electrolytic oxidation of an appropriate anode material

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typically fabricated from either aluminum or iron, which eleases polyvalent metal cations causing destabilization of pollutants [21]. It offers several advantages over the conventional chemical coagulation and other waste treatment technology, but this technology is not yet fully tuned and optimized [25]. Several process enhancements through chemical dosing could improve the chances of EC as a practical industrial wastewater treatment method. Some studies investigated the effect of combining electrocoagulation with coagulant aids like poly aluminum chloride (PAC) to treat textile water [26], polyelectrolytes to treat real sugar mill [27]. Another process enhancement of electrocoagulation is the addition of hydrogen peroxide called peroxielectrocoagulation [28, 29] or combine it to PAC [30]. The results showed that the hybrid-treatment process of electrocoagulation-chemical coagulation-oxidizing agent enhance pollutant removal.

One of the problems encountered during EC treatment is the persistent formation of froth above the surface of the wastewater causing foam build up. A lot of foam may be formed due to bubbles of the gases like hydrogen or oxygen, generated on the electrodes which hinder the smooth operation of EC [31]. Entrapped air prohibits the settling of sludge. Usage of foam control agents which also acts as deaerator are recommended in order to achieve an optimized wastewater treatment Dimethicone process [32]. also known as polydimethylsiloxane is one of several types of silicone oil which is commonly used as component of defoamers, and are used to suppress the formation of foams

With the increasing problem in water quality degradation due to improper domestic wastewater discharge, this study aimed to investigate the efficiency of peroxi electrocoagulation tandem with dimethicone as defoamer for the simultaneous removal of phosphate and COD in real sewage wastewater. The effect of operating parameters, such as electrolysis time, amount of hydrogen peroxide and dimethicone were investigated. Only the concentrations of additives were optimized and all other operating parameters such as current density, electrode configuration and initial pH were made constant. Thus study is also designed to compare EC with the hybrid treatment in terms of electrode consumption, settling time, froth height, and effluent quality.

2 Methodology

2.1. Electrocoagulation cell

The reactor was made of clear glass with a length of 100 mm, width of 100 mm, depth of 600 mm and an interelectrode distance of 16mm. The EC reactor has a total capacity of 3.86 L and a reaction zone of 2.56 L. The electrocoagulation cell, which operated under batch mode was equipped with four iron plate electrodes operated in a bipolar configuration. Dimensions of iron plate electrodes in all electrochemical processes were 80 \times 500 \times 2 mm and 200 mm of the length of the electrodes were immersed in the solution. The metal plate electrodes were obtained from Supply and Uni-Good Steel Industrial Corporation in Sta. Cruz, Manila.

2.2 Electrocoagulation experiment

Grab samples of sewage water were collected from Pasay water reclamation plant in Barangay Malibay, Pasay City Philippines. The initial sewage water characteristics are: $175.33 \pm 11.93 \text{ mg/L}$ total COD, $51.00 \pm 4.58 \text{ mg/L}$ soluble COD, $2.17 \pm 0.36 \text{ mg/L}$ phosphorus as phosphate, $929.33 \pm 8.33 \mu$ S/cm conductivity, initial pH of 8.04 ± 0.06 and adjusted pH of 2.10 ± 0.03 . Samples were preserved by adding concentrated H₂SO₄ and were refrigerated at 6^oC.

Experiments were carried out at room temperature and 2.5L of samples were run from the adjusted pH in triplicates. Before the EC run, iron electrodes were scrubbed and washed thoroughly with water to remove any solid residues on the surfaces and then dried. Dried electrodes were placed in the EC cell and were connected in a bipolar configuration. The distance between each electrode is 16mm. Magnetic stirring was set at 220 rpm and a constant current of 3.3 A was supplied using a digital DC power supply (Korrad, KD3005, 0-5A, 0-31V).

EC was run by first varying the amount of H_2O_2 (1%, 2% and 3%) and then the amount of dimethicone (0.5% - 1.5% of the wastewater volume). The optimized condition of the electrocoagulation – H_2O_2 – dimethicone combined treatment were evaluated based on electrode consumption, settling time and effluent quality in terms of COD and phosphate removal at varying electrolysis time. The results were compared from EC run without any additive.

2.3 Wastewater analysis

COD determination was done using COD digestion solution (Hach, 0 -1500 ppm), COD reactor (Lovibond, RD125) and COD photometer (Lovibond, MD200). The residual hydrogen peroxide was first removed by heating the sample at 40 °C for 10 minutes. The pH of the sample was then adjusted to about 9 by addition of 1 M sodium hydroxide and decanted to remove the ferrous Total COD was run on undiluted and hvdroxide. unfiltered samples. For soluble COD, the samples are filtered through a 0.45 mm filter before analysis to remove biological interference. 2 mL of the sample was pipetted into a COD digestion reagent vial. The vial was then inverted several times to mix. The vial was placed in the COD reactor at 150 °C for two hours, cooled and was tested using the COD photometer. The chemical oxygen demand was read in mg/L for both total and soluble COD. Accuracy check of the method was done using 500 mg/L COD standard. The standard solution was prepared by dissolving 425 mg of dried (120 °C, overnight) KHP and diluted to 1 liter with deionized water.

The phosphate content was determined by standard calibration method. Samples were filtered first using Whatman filter paper (No.1, 11µm size). 1 mL of 11 N

sulfuric acid and 4 mL of ammonium molybdateantimony potassium tartrate were added to 50 mL of sample and/or standard and mixed, followed by 2 mL of ascorbic acid. After 5 minutes, the absorbance was measured at 650 nm using a microplate reader (ClARIOstar®).

The pH of the samples was measured using a pH meter (Mettler Toledo FiveEasyTM) while conductivity was measured using conductivity meter (Eutech, Con 510).

The total electrode consumption was obtained by getting the difference between the initial and final weight of the electrode after EC treatment.

After the given period of electrolysis, the settling time was determined based on the period of time it takes for the flocculated particles in the EC reactor to be fully submerged at the bottom while the height of froth was measured based on the level of foam formed above the surface of sewage water in the reactor.

3 Results and Discussion

The design of the EC reactor is one of the major factors that affect the efficiency of an electrocoagulation process. Recently, we reported our reactor design for treatment of distillery wastes [33] and improved it in this study as shown in Figure 1. Improvements include the use of clear glass for the reactor to make it light weight and clear compared to acrylic glass, installation of water and sludge outlet for easy removal of treated water without disturbing the flocculated particles, and putting a slotted cover where electrodes are fitted and held in place.



Fig. 1. Modified reactor

In this study, peroxi – electrocoagulation with dimethicone was employed. It is necessary to determine first the optimum amount of H_2O_2 to be used because excessive dose of H_2O_2 trigger adverse effects [34] aside from the additional operational cost. Different doses of H_2O_2 was employed and its effect on phosphate and COD removal as well as on the operational parameters such as electrode consumption, froth height, and settling time were evaluated. It is evident in Figure 2 that the optimum dose of H_2O_2 is 1% due to the highest

and COD removal, lower electrode phosphate consumption, lower froth height and shorter settling time. The increase in phosphate and COD removal upon addition of H₂O₂ demonstrate that hydroxyl radicals formed helped in the oxidation and coagulation [35]. The ferrous ions are oxidized to ferric ions and ferric hydroxo complexes that coagulated the suspended solids in the sewage waste. However, at a higher concentration these radical presumably reacted with one another causing a termination reaction, thus cancelling its effect, which leads to lower COD removal. On the other hand, considering the operational parameters, the electrode consumption and froth height increases compared to that of without H₂O₂. The addition of H₂O₂ helps in the formation of more oxygen causing more air bubbles and foam formation and increase reaction rate that leads to more electrode consumption as well. However, the addition of H₂O₂ decrease the settling time which is an economic advantage. Combining all these effects, it can be concluded that the optimum dosage of H_2O_2 is 1%.



Fig. 2. Water quality and EC operational parameters at various amount of H_2O_2

The next additive considered is the dimethicone. Industrial wastewater treatment processes use foam control agents to suppress the formation of foam and to achieve an optimized treatment process. Among the different chemical additives used to enhance the efficiency of electrocoagulation, anti-foaming agents like dimethicone has not yet been studied. The effect of varying the amount of dimethicone added to peroxielectrocoagulation at 1% H₂O₂ was investigated. As shown in Figure 3, 100% phosphate removal was still achieved with the addition of dimethicone. The total COD removal increased up to 83.06% with the addition of 1% dimethicone. Likewise, the weight of electrode consumed decreases, as the amount of dimethicone increases from 0 - 1.5%. EC requires migration and electrophoretic current to vacillate between the anode and cathode. However, the dimethicone might cause passivating effect due to its viscosity which hinders the effective anodic dissolution of the electrode material. Thus, presence of dimethicone, resulted to slightly lower electrode consumption. On the other hand, froth height has significantly decreased (p<0.05) from 6.53 cm down to 2.33 cm. Dimethicone was able to suppress the formation of foam due to its low surface tension. Layer of dimethicone acted as deaerator and made it possible for EC to avoid foam build up. However, the addition of dimethicone resulted to longer settling time compared to EC with H₂O₂ only. This can be attributed with the larger volume of sludge produced with the addition of dimethicone. The settling of sludge was more facilitated than floatation of particles. Dimethicone is an example of a polymer with high molecular weight which in principle can help with the bridging of colloidal particles and in the entrapment of particles in precipitate. In pollutant removal mechanism of EC, when metal coagulants were polymerized, they can form links between colloidal particles and high molecular weight, long chain dimethicone [36]. The bridging of colloidal particles results in the formation of bigger particles. hence, easier separation of sludge and treated water could be done. Large volume of flocs also helps with physical entrapment of pollutants [25]. Post hoc analysis on the effect of varying concentration of dimethicone in phosphate and COD removal shows to be insignificant (p>0.05). Nonetheless, a significant improvement with the operational parameters was obtained. Tukey and Fisher pairwise comparison show that significantly lesser electrode consumption and froth formation and settling of larger volume of sludge were observed. Also. significantly (p<0.05) shorter settling time was needed as compared with treatment using EC only. Agglomeration and enmeshment of fine particles to become larger flocs outweighs the passivating effect due to dimethicone and still higher COD and phosphate removal were attained. Generally, incorporating H₂O₂ and dimethicone with EC increases the pollutant removal efficiency due to enhance adsorption capability and advance oxidation. Addition of 1% H₂O₂ and 1% dimethicone successfully minimized the electrode consumption and froth height without having degressive effect with the COD and phosphate removal efficiency. Given that, 1% H₂O₂ and 1% dimethicone were the optimized additive concentration.



Fig. 3. Water quality and EC operational parameters at various amount of Dimethicone

Having known the optimum amount of additive, the electrolysis time was then considered. The reaction time is directly proportional with efficiency of pollutant removal in EC. As the electrolysis period increases the amount of metal ions that dissociates from the electrodes also increases. This results to a higher concentration of coagulant and higher percentage of pollutant removal. However, it is not economical to have a very long time for electrolysis, thus, an optimum period must be obtained. Shown in Figure 4 are the effects of electrolysis time with phosphate and COD removal and pH. The phosphate and COD removal efficiency increases and reaches plateau at some time. 100% phosphate removal and optimum COD removal of 82.89% were both achieved after 60 minutes. It can be observed from post hoc analysis that at 30 min to 120 min electrolysis, the COD removals do not have significant differences. On the other hand, the pH of the reaction mixture increases with time due to water electrolysis forming hydroxyl ions. The hydroxyl radicals formed during the hybrid treatment is highly dependent with pH. According to Farhadi et al., [34], the initial pH value has to be in acidic range (2.5-3.5) to generate the maximum amount of hydroxyl radicals and oxidize the organic compounds. It can be observed that between 15 to 30 minutes the solution is in the optimum pH range. The high increase in COD removal from 15 to 30 minutes is probably due to the maximum amount of •OH generated. The COD removal performance due to oxidative capacity declines at neutral and basic pH. This occurs due to formation of the ferric hydroxo-complexes, namely the precipitation of Fe³⁺ as Fe(OH)₃, hindering the reaction between Fe³⁺ and H₂O₂ and therefore the regeneration of Fe²⁺. Although the oxidative capacity of the peroxi-electrocoagulation decreases, the formation of hydroxide complex serves as coagulant, thus still high COD removal was attained.



Fig. 4. Water quality (phosphate and COD) and pH at various electrolysis time

Finally, to clearly differentiate the effect of the additives, presented in Figure 5 is the comparison of the different systems namely: electrocoagulation only (EC), EC with hydrogen peroxide (ECP), EC with dimethicone (ECD) and EC with hydrogen peroxide and dimethicone (ECPD) at the optimum conditions $(1\% H_2O_2, 1\% H_2O_2, 1$

dimethicone and 1hr reaction time) obtained. It was evident that ECPD system has the highest phosphate and COD removal. In addition, it has relatively similar electrode consumption, lower froth height and lower settling time making the system economically viable.



Fig. 5. Water quality (phosphate and COD) and pH at various electrolysis time

4 Conclusion

In this research, performance of electrocoagulation with and without H_2O_2 and/or dimethicone were investigated for the removal of COD and phosphate from sewage water. Addition of H_2O_2 significantly improved the EC performance through the formation of hydroxyl radicals. It can be stated that combining the coagulation and oxidation mechanism with free radicals has better performance than coagulation alone using EC. On the other hand, addition of dimethicone served as a defoamer and also as flocculants which aided the bridging of colloidal particles and formation of larger flocs. These leads to higher phosphate and COD removal.

EC with H₂O₂ has greater electrode consumption compared to EC. The presence of H₂O₂ generated more hydrogen and oxygen bubbles causing foam build up which then affects the settling and formation of sludge. In contrast, addition of dimethicone reduces the electrode consumption through passivating effect. Moreover, because of the defoaming capability of dimethicone, the formation of sludge was promoted over the floatation of flocs. This resulted to higher volume of sludge, easier separation and clearer effluent. Incorporating the two additives in EC improved both the efficiency of operation and pollutant removal. A shorter electrolysis time of 1-hour lessened the amount of consumption. Electrocoagulation-H2O2energy dimethicone hybrid treatment allows settling of sludge without consuming too much time. Furthermore, electrode consumption and froth height were minimized without degressive effect with the COD and phosphate removal efficiency. Thus, both the treatment period and operating cost were potentially lessened.

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