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Original Article

Separation of oily sludge and glycerol from biodiesel processing waste by coagulation

Qiao-guang Xie[1], Wirach Taweepreda[2], Charongpun Musikavong[1]* and Chaisri Suksaroj[1]*

[1] *Department of Civil Engineering, Faculty of Engineering,*

[2] *Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand.*

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Abstract

Raw waste glycerol is a by-product of biodiesel production from transesterification, which is high in salt, and has a high pH value (more than 9.6). The purpose of this research is to reduce the water pollution from waste glycerol by using a coagulation process and discussing the possibility of waste glycerol reuse. The commercial coagulant (2% by weight), which was composed by cationic polyamine (PA) 6% and poly-aluminium chloride (PACl) 94% (w/w), was used as coagulant to treat waste glycerol. The results showed that after acidification and coagulation process, most of the chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total suspended solids (TSS), and oily sludge (such as fatty acid, methyl ester, methanol and soap) in raw waste glycerol were removed, except glycerol. The removal efficiencies of COD, BOD_5, TSS, soap and methanol were 96.2%, 93.3%, 98.1%, 100%, and 85.8%, respectively, but the removal efficiency of glycerol was only 65.4%. There was still a certain amount of glycerol (about 147.5g/L) in the solution, which is separated from oily sludge.

Keywords: coagulation, glycerol recovering, oily sludge, water pollution, waste glycerol

1. Introduction

With global warming and the price of fossil fuel rising, biodiesel is becoming favored as a kind of carbon neutral fuel (Topaiboul and Chollacoop, 2010). During the biodiesel production process by transesterification, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acid, with glycerol as a primary by-product. In general, production of 100 kg of biodiesel yields approximately 10 kg of raw waste glycerol, which is impure and of low economic value (Dasari *et al.*, 2005; Chi *et al.*, 2007).

* Corresponding author.
Email address: mcharongpun@eng.psu.ac.th, schaisri@eng.psu.ac.th

Raw waste glycerol contains a variety of harmful compounds, such as 12-16% alkalis especially in the form of alkali soap and hydroxides, and 8-12% methanol, which may cause water pollution and environmental problems. Moreover, the cost for disposal of raw waste glycerol is quite expensive (Yazdani and Gonzalez, 2007; Gervásio Paulo da Silva *et al.*, 2008). In order to reduce the cost for disposal of raw waste glycerol, it has been suggested to use some methods to convert waste glycerol into some valuable products. One application that has been evaluated is the conversion of crude glycerol into propylene glycol and acetone (Chiu *et al.*, 2006). Another application being investigated is the fermentation of glycerol to 1,3-propanediol, which is an intermediate compound for the synthesis of polymers used in cosmetics, foods, lubricants, and medicines (Zheng *et al.*, 2008).

Coagulation is a process by which small particles are separated from a solution in a reasonable amount of time using simple or pre-hydrolyzed metal salt, such as alum and

PACl, polyelectrolyte, or long chain polymers like PA as the primary coagulation. This process is not only simple and economic, but can also effectively reduce levels of COD, BOD_5, TSS color and organic compounds (Yue *et al.*, 2008). In addition, the coagulation process can remove organic compounds effectively but not good for glycerol removal (Wang *et al.*, 1996).

In this study, the raw waste glycerol was pretreated by acidification with hydrochloric acid (HCl). After pretreatment, the waste glycerol was taken to be treated by PA blend with PACl in the coagulation process. The effect of acidification process and the optimum conditions of coagulation process were examined.

2. Material and Methods

2.1 Material

Raw waste glycerol samples were collected from the waste glycerol tank in the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crop, Thailand, in October 2009. This facility uses alkali-catalyzed transesterification to produce biodiesel from waste cooking oil and palm oil. The characteristics of raw waste glycerol samples were analyzed to measure pH, COD, BOD_5, TSS, fatty acids, and methyl ester in accordance with the standard method (Eaton and Franson, 2005). The other parameters were analyzed with different methods; glycerol (ASTM D7637, 2010), soap (AOCS, 1996), and methanol (ASTM D7059, 2009).

2.2 Acidification pretreatment

The pH of raw waste glycerol was adjusted from 9 to 3 with 0.8 M of HCl. The effect of acidification on raw waste glycerol in this pH range was studied to indentify the appropriate pH value for acidification process in order to separate soap and oil. An appropriate pH range for acidification was selected, which provided the concentration of COD, BOD_5, TSS, and soap. Mass fraction of fatty acid and methyl ester were analyzed with gas chromatography. The treated waste glycerol with appropriate pH from acidification pretreatment was taken to the coagulation process.

2.3 Coagulation process

2.3.1 Jar-tests

The jar test apparatus was a Phipps & Bird Inc., Richmond, Virginia, USA apparatus with six stirrers. In the coagulation experiment process, 400 mL of pretreated solution were prepared and adjusted their pH values by HCl and NaOH. The pH values of samples were adjusted to different values, the optimum concentration of commercial coagulant was mixed with samples to measure the optimum pH value of samples.

2.3.2 Concentration on coagulation

PACl is normally used at pH values between 7 and 9 due to the pH optimize value (Tzoupanos *et al.*, 2008). Thus, the pH value of the pretreated solution was adjusted to 7 after acidification pretreatment. The concentration of the commercial coagulant was varied from 2 g/L to 6 g/L. The commercial coagulant and waste glycerol was mixed by a jar test apparatus at 100 rpm for a period of 2 min and then at 35 rpm for 15 min (Meyssami and Kasaeian, 2005). The removal efficiencies of COD, BOD_5, and TSS in coagulated water after coagulation were measured. The optimum concentration of the commercial coagulant in total solution was identified by comparing the removal efficiency.

2.3.3 pH value on coagulation

After pretreatment, the pH value of the pretreated solution was adjusted to pH values from 9 to 3. The optimum concentration of the commercial coagulant measured in the last step was put into different pH values of waste glycerol. After mixing the commercial coagulant and solution by jar test apparatus at 100 rpm for a period of 2 min and then at 35 rpm for 15 min (Meyssami and Kasaeian, 2005), the COD, BOD_5, TSS, and organic matters of the samples from wastewater were measured. The optimum pH value was identified by comparing the removal efficiencies of COD, BOD_5, TSS, and organic matters.

3. Results and Discussion

3.1 General characteristics of raw waste glycerol

As it is evident from Table 1, waste glycerol has a high pH value and consists of high concentrations of COD, BOD_5, TSS, and organic matters. The ratio of BOD_5:COD had a value of 0.53, which was difficult for biological treatment processes. From other values of organic compounds, the raw waste glycerol can be used as a carbon source or compost. However, the impurities include methanol and soap and the

Table 1. Selected characterizations of raw waste glycerol.

Characterizations	Unit	Concentration
pH		9.7-10.4
COD	$\times 10^6$mg/L	1.7-1.9
BOD_5	$\times 10^6$mg/L	0.9-1.2
TSS	$\times 10^5$mg/L	21.3-38.7
Total glycerol	g/L	413-477
Soap	$\times 10^5$ppm	2.1-2.7
Methanol	g/L	112-203
Water	% by weight	9.3-11.9

high pH value would affect the anaerobic or coagulation process and utilization of raw waste glycerol. In addition, as waste glycerol contains 9.3-11.9% water it cannot be used as a fuel (Peereboom *et al.*, 2007). It could be concluded that the pH value of raw waste glycerol needs to be reduced, and soap also need to be removed from the raw waste glycerol before the coagulation process.

3.2 Effect of acidification process on waste glycerol

3.2.1 Effect of pH on COD, BOD_5, and TSS removal

When pH values were in a range of 3 to 7, the soap were converted into free fatty acids and salt, the waste glycerol separated into two layers. The oil layer was mainly free fatty acid and methyl ester; the liquid layer was mainly glycerol, water and methanol. Samples were taken from the liquid layer solution to measure COD, BOD_5 and TSS. When pH values were 8 and 9, the samples were taken from waste glycerol solution.

The concentrations of residual COD, BOD_5, and TSS are shown in Figure 1. The COD and BOD_5 of waste glycerol decreased with the reduction of pH from 9 to 5. The TSS rapidly increased from pH 9 to pH 8, because when pH value was 8 a water-in-oil emulsion with a positive charge absorbed on the interface of the soap and solid particles (Kemmer, 1979). As the pH value was reduced, the neutralization charge and emulsion were broken, the TSS rapidly reduced from pH 8 to 7. And then TSS slowly reduced from pH 7 to 5. In addition, when the pH values were between 3 and 5, the values of COD, BOD_5, and TSS were stable.

3.2.2 Effect of pH on soap removal

Samples were taken from both layers of solution to measure the concentration of soap. When the pH values were between 5 and 3, the oil layer solutions were used to measure the concentration of free fatty acid, methyl ester, and impurities. The concentrations of soap in two layers and total solution, and the mass fraction of fatty acid in the oil layer solution are shown in Figure 2 and 3. When the pH value was reduced, the concentration of soap in the two layers and total solution also decreased, but the mass fractions of free fatty acid and methyl ester increased. This indicates that the soluble soap was converted into salt and insoluble free fatty acid, the chemical equation as follow:

$$KC_{17}H_{35}COO + HCl \rightarrow C_{17}H_{35}COOH + KCl \quad (1)$$

The soap in waste glycerol is potassium soap, since the potassium hydroxide is usually used as an alkali catalyst during the biodiesel production process (Gerpen, 2005). In addition, most of the soap was in the oil layer as shown in Figure 2. This shows that most of the soap with negative charge was absorbed by water-in-oil emulsion. Figure 3 shows that when the pH values were 5 to 3, the total mass fractions of fatty acid and methyl ester were 78.8%, 85.9%, and 89.8%, respectively. The oil layer solution can be re-covered and reused as a raw material in biodiesel production

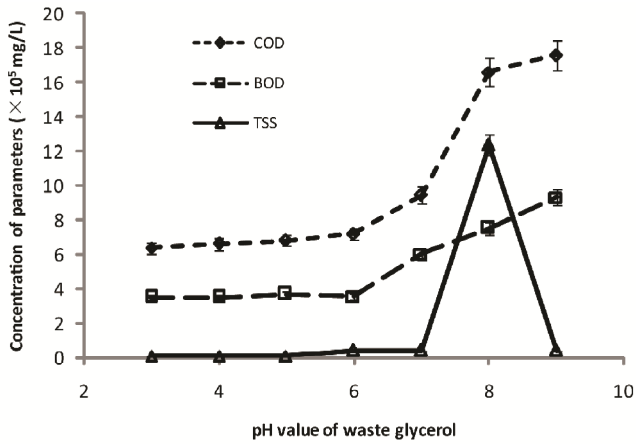

Figure 1. COD, BOD_5 and TSS in different pH values.

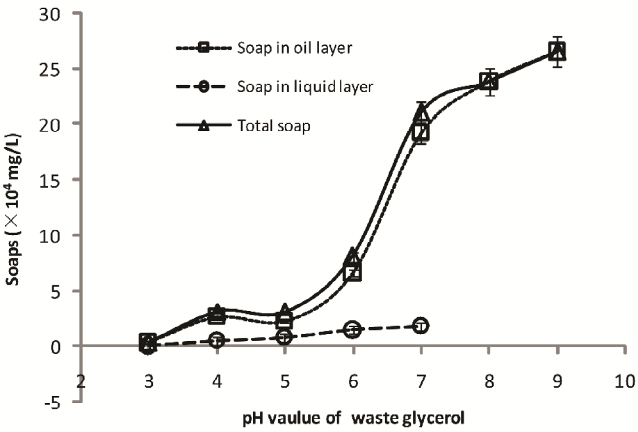

Figure 2. Variation of soap concentrations in different layers of waste glycerol.

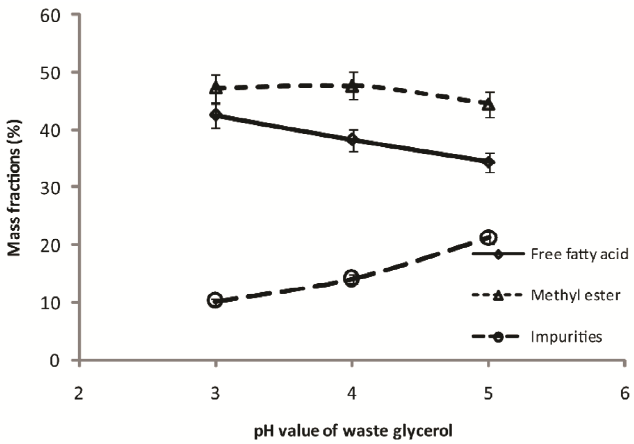

Figure 3. Variation of compositions for mass fractions in different pH values (in oil layer solution).

processes (Prateepchaikul *et al.*, 2007). It could be concluded that as a pretreatment the pH values should be adjusted to 5 and the oil layer solution should be removed from waste glycerol. The acidification process can reduce the COD, BOD_5, TSS, and soap in raw waste glycerol effectively.

3.3 Determination of optimum coagulation conditions

3.3.1 Effect of the commercial coagulant concentration on parameters removal

The removal efficiencies of TSS, COD, and BOD_5 in different concentrations of commercial coagulant are shown in Figure 4. When the concentration of the commercial coagulant was 5 g/L, the removal efficiencies of TSS, COD and BOD_5 were maximum value, 92.3% ± 2.2%, 75.5% ± 4.4%, and 87.9% ± 3.0% respectively. After this concentration, the removal efficiency of COD decreased, and the removal efficiencies of BOD_5, and TSS changed slightly. This can be explained by the influence of excessive PACl on the coagulation (Bogoeva-gaceva, 2010). The optimum concentration of a commercial coagulant was 5 g/L, which was selected to carry out the following experiment.

3.3.2 Effect of pH on coagulation

The results of removal efficiencies in different pH values of waste glycerol are shown in Table 2. The PA blended with PACl coagulant cannot coagulate waste glycerol in low pH values. This is because PACl form positive charge aluminum species that adsorb negatively charged natural particles, but when pH values were 3, 4, and 5, the charges of the particles and soap were positive that cannot adsorb on the interface of the coagulant. The PA blended with PACl coagulant cannot charge, neutralize, and bridge with particles between pH 3 and 5 (Avci *et al.*, 2002).

When the pH value of waste glycerol was 7, the removal efficiencies of TSS, COD, BOD_5 reached the maximum value, and the efficiency of TSS, COD, BOD_5, methanol and glycerol were 98.1% ± 1.5%, 96.2% ± 0.7%, 93.3% ± 1.2%, 85.8% ± 2.9, and 65.4% ± 2.0% respectively. Moreover, when the pH value is 7, the soap and other impurities were removed by the coagulation process. The organic and inorganic matters are removed effectively, except glycerol. The residual glycerol can be recovered by distillation (Gerpen, 2005), since the solution separated from coagulation mainly contains water and glycerol, or can be recovered by cyclodextrin (CD) inclusion complexation from the solution (Song *et al.*, 2009).

In addition, when the pH value was 7 and the concentration of the commercial coagulant was 5 g/L, the concentrations of TSS, COD, BOD_5, methanol and glycerol in the wastewater separated from the coagulation were 118mg/L, 23,311mg/L, 22,416mg/L, 16.5g/L, and 147.5g/L, respectively. The ratio of BOD_5:COD had a value of 0.96, which is higher than the ratio in the raw waste glycerol (0.53).The free fatty acid, methyl ester, and soap can reduce the BOD_5:COD ratio, but the coagulation process can remove this oily sludge. Therefore, the coagulation process can improve the biodegradability of waste glycerol.

It can be concluded that the optimum conditions of the PA blend with PACl coagulating waste glycerol were as follows: (1) the optimum concentration is 5 g/L; (2) the optimum pH value of waste glycerol for coagulation process is 7; (3) in the conditions of this research, the TSS, COD, BOD_5 and methanol were removed effectively. In addition, the oil and soap, which were toxic matters for microorganisms, were removed in the coagulation process. Thus, wastewater that was separated from coagulation was easily treated by biodegradation.

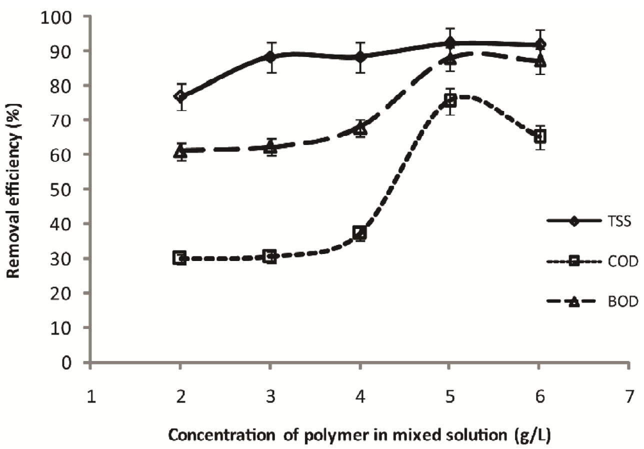

Figure 4. COD, BOD_5 and TSS in different concentrations of polymer (pH values of solution is 7).

Table 2. Removal efficiencies of parameters in different pH values (concentration of polymer is 5 g/L)

pH values	TSS(%)	COD(%)	BOD_5(%)	Glycerol(%)	Methanol(%)
6	97.3±2.0	64.9±3.4	65.7±4.2	78.6±2.9	92.1±3.9
7	98.1±1.5	96.2±0.7	93.3±1.2	65.4±2.0	85.8±2.9
8	98.9±0.6	82.7±1.6	84.0±2.9	66.9±1.2	83.4±2.8
9	96.1±1.1	95.9±0.9	90.2±1.6	76.3±2.1	39.5±4.0

4. Conclusion

On the basis of operation from a laboratory scale model of PA and PACl coagulation treatment of raw waste glycerol, the following conclusions can be stated: (1) raw waste glycerol needs to be pretreated by 0.8M HCl to adjust the pH value and remove parts of the soap, fatty acid, and methyl ester, (2) in optimum conditions, the removal efficiencies of COD, BOD_5, TSS, and organic compounds were considerable. However, there was still a certain amount of residual glycerol (147.5g/L) in the solution separated from coagulation, and (3) the oily sludge produced by the coagulation process of waste glycerol and the commercial coagulant, contains abundant organic matters, which may be used as an energy resource, carbon source or compost. Additionally, these methods can be used as a pretreatment for the free fatty acid, methyl ester, and glycerol recovered from waste glycerol, which can be purified and sold, and by this bring economic benefits for biodiesel facilities in the future.

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