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# TREATMENT OF BIODIESEL WASTEWATER BY SOLVENT EXTRACTION: EVALUATION OF KINETIC AND THERMODYNAMIC DATA

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## Abstract

Transesterification is one of the main biodiesel production method that produces huge amount of wastewater due to the high organic substance content (COD =300000-400000 mg/L, oil and grease = 17000-25000 mg/L). Although there are several treatment methods, flotation is the current conventional treatment method for oil and grease (O&G) before the biological treatment. In this study solvent extraction method was developed for pre-refining of biodiesel wastewaters. For the solvent extraction method, hexane and methyl-tertiary-butyl ether (MTBE) were determined as the most efficient solvents for the extraction of O&G. In this work, extraction kinetics and extraction thermodynamics were investigated for COD and O&G. The effect of solution pH and solvent ratio were investigated onto the solvent extraction process to optimize the developed method. The experimental results show that extraction method effectively removes the COD and O&G by 99.0% at pH 2 for both solvents. Experimental results also showed that depending on free energy change COD removal efficiency of hexane is higher than MTBE. COD extraction kinetics perfectly fits to the pseudo-second order kinetics. The necessary solvent/water ratio was found as 1/1 volume ratio for both solvents. The experimental results show that hexane extraction could effectively remove the COD, O&G and TOC by 96.0%, 99.8% and 91.0%, respectively, at the optimized conditions of pH 2.0, 1/1 solvent-water ratio and 30 min extraction time.

Key words: biodiesel wastewater, treatment, extraction, kinetic, thermodynamic

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## 1. Introduction

The world energy demand increases every year and this brings use of high petroleum-based fuels. The petroleum resources of the world will be enough around 50 years from now and this reality force the human being to find other energy sources. Although it is limited, one of those alternate sources is bio-based fuels especially biodiesel (Dunn and Knothe, 2001; Jaafar et al., 2016; Karmee and Chadha, 2005). Production of biodiesel might be straightforward process but remaining waste becomes a real problem for environment. Biodiesel is a nontoxic, biodegradable and produces low sulphur, carbon

monoxide and aromatic-free emission profile after it burns. Biodiesel is manufactured through transesterification of lipids including vegetable oil or animal fat by an alcohol. The main raw materials of biodiesel are vegetable seed oil, soybean oil, some recovered animal fats and microalgae (Chavalparit and Ongwandee, 2009; Elsheikh et al., 2014; Xue et al., 2006). The production of biodiesel requires transesterification reaction using an alkali catalyst. The reaction converts triglycerides (oil) to fatty acid methyl esters (biodiesel) by a simple chemical reaction. After esterification biodiesel will not be pure and needs to be separated from free glycerol, residual catalyst, water, free alcohol, and soaps that were

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generated during the reaction (Ahmad et al., 2006; Çanakçı and Sanlı, 2008; Mata et al., 2010; Singh and Gu, 2010). After synthesis of biodiesel, all the impurities need to be removed from the mixture. There are several methods for purification including wet washing, dry washing and membrane extraction (Berrios and Skelton, 2008). Dry washing contains some ion exchange process or a magnesium silicate powder to remove impurities but this method does not provide high purity biodiesels. Wet washing is a widely used method for purification and provides 99% biodiesel purity if hot water is used for washing. Although wet washing is a better choice for purification, it produces a certain amount of biodiesel wastewater and this can be dangerous if it is discharged into the sewage systems (Berrios and Skelton, 2008). In wet washing system, water is a best choice to remove those polar components like alcohol, glycerol and also any sodium salt residuals and soaps (Berrios and Skelton, 2008; Leung et al., 2010; Sharma et al., 2008). This washing step has to be repeated several times depending on the impurities in the mixture. If one would like to produce 100 L of biodiesel by using 100 L waste oil, 20 L methyl alcohol and 1000 g of KOH, at least 20 L of biodiesel wastewater has to be discharged after the cleaning step. Biodiesel amount determines the amount of waste and also amount of wastewater. Because of high content of KOH and waste oil, discharged waste is basic (alkaline) and mostly contains oil. In case of discharging huge amount of waste into the public drainage, it will cause plugging of the drainage and decreases biological activity in sewage treatment. Biodiesel polluted wastewater does not contain too much nitrogen and phosphorus and also inhibits the growth of the most microorganisms, thus biological treatment becomes very hard in this kind of wastewaters (Suehara et al., 2005).

Although there are number of works about technical process of the biodiesel production, environmental aspect of this production is neglected most of the time (Jaruvat et al., 2010). Currently there are several techniques for the treatment of biodiesel wastewaters including microbiological process (Suehara et al., 2005), electrocogulation (Ahmadi et al., 2013; Chavalparit and Ongwandee, 2009; Ngamlerdpokin et al., 2011; Srirangsan et al., 2009), acidification and coagulation processes (Rattanapan et al., 2011), the combined processes of chemical recovery and electrochemical treatment (Jaruvat et al., 2010), physical-chemical and biomethanization (Siles et al., 2011), biocatalyst microbial fuel cell (MFC) (Sukkasem et al., 2011), adsorption (Pitakpoolsil and Hunsom, 2014), Combined Electroflotation and Electrooxidation Processes (Romero et al., 2013). When these techniques are individually evaluated, these reported techniques might have particular advantages and disadvantages like cost effect and efficiency.

The main objective of this paper is to show the treatment of raw biodiesel wastewater by a solvent

extraction process at a laboratory scale and to investigate the removal efficiency of extraction process by evaluating extraction kinetics and extraction thermodynamics for COD and O&G removal. To develop a useful and simple extraction system for biodiesel wastewater, experiments were carried out in accordance. This work is showing the first time the best kinetics and thermodynamic parameters for biodiesel wastewater treatment using extraction process. The effects of key operating parameters, including the extraction time, initial wastewater pH, solvent ratio, temperature upon the removal efficiency were investigated in this work.

## 2. Material and methods

## 2.1. Production of wastewater

Biodiesel were prepared in a 50 L laboratoryscale reactor equipped with thermostat, mechanical stirrer, sampling outlet. The canola oil (35 L) was preheated to the set temperatures (40°C) on a heating plate before starting the reaction. Alcohol solution was prepared with 5 L methanol and 20 g KOH. A fixed amount of alcohol solution of catalyst was added into preheated oil and stirred during the reaction. The mixture was transesterified at 55°C for 50 min with mechanical stirring. The reaction was ended after 50 min and cooled in a separation funnel to separate the biodiesel from aqueous waste that contains glycerol, unreacted oil, methanol, catalyst residue and a small amount of soap produced during transesterification. In separation funnel, white colored biodiesel wastewater was collected bottom of funnel. After washing several times, the biodiesel and water phases was separated (Demirbas and Kara, 2006, Predojevic, 2008; Rashid and Anvar, 2008; Tomasevic and Siler-Marinkovic, 2013).

Characteristics of the biodiesel wastewater and analytical methods are shown in Table 1. The biodiesel wastewater carries high content of COD and O&G due to the contamination by oil feed stock, soap, methanol and glycerol. Since the alkali catalysts were used in the transesterification process, pH of the wastewater was expectedly high (10.5).

Table 1. Characteristics of the biodiesel wastewater

Parameter	Value	Analytic method/Instrument	
pН	10.5	pH meter (Hanna)	
COD (mg/L)	403540	Closed reflux <sup>(APHA,1995)</sup>	
O&G (mg/L)	25252	Gravimetric (hexane extraction) method <sup>(APHA,1995)</sup>	
TOC (mg/L)	110000	TOC/TN instrument (HACH-LANGE)	
TN (mg/L)	0	TOC/TN instrument (HACH-LANGE)	
SS (mg/L)	12800	Gravimetric method <sup>(APHA,1995)</sup>	

## 2.2. Method

A solvent extraction method for separation and recovery of O&G from biodiesel wastewater produced in the lab. All the experimental process was designed to represent the industrial production of biodiesel wastewater.

The process for the recovery of O&G carried out in three stages: pH adjustment; solvent extraction and separation of phases. In the solvent extraction experiments a water bath with a contact thermometer and a magnetic stirrer were used. The leaching was done in 1000 cc glass balloons using Teflon coated magnets. A condenser attached to the balloon prevented the vaporization losses. During the experiment, the whole system was controlled precisely by a contact thermometer. At the end of each leaching experiment, the solvent phase was separated from the wastewater by a separating funnel. n-hexane and tertiary methyl butyl ether were used as a solvent for extraction of O&G and methyl esters from biodiesel wastewater.

The fatty acid methyl ester quantitation in the wastewater was carried out in a Shimadzu GC-QP 2010 gas chromatograph with a MS detector were used. FAMEs were separated by a highly polar Rt-2560 capillary column (100 m length, 0.25mm diameter, 0.20 um film thickness,) coated with biscyanopropyl polysiloxane using a GC-2010 coupled to a GCMS-QP2010 detector from Shimadzu. The injection volume was 1 ul and a programmed temperature vaporizer (PTV) was used and injection mode was used a split mode and a split ratio of 1:50 until end of the run.

Injection temperature was  $225^{\circ}$ C. The temperature program was as follows: the initial oven temperature 100°C was hold for 4 min, then programmed to increase with 3 °C/min to 220°C and hold for 36 min. Helium was used as carrier gas with a constant linear velocity of 18 cm/s. The detector temperature was kept at 175°C.

### 3. Results and discussion

## 3.1. Effect of initial pH on the extraction

The pH is a very important parameter for the extraction studies. To determine the effect of initial pH on the removal efficiencies of COD, O&G, and TOC initial pH of biodiesel wastewater was adjusted with either HCl or NaOH. As shown in Fig. 1, the pollutant removal efficiencies increased as the initial pH decreased to the acidic level. Around pH 2, the mixture separated into two phases. The lower phase was the aqueous phase having a low turbidity and transparent color, whereas the upper phase was oil-rich and yellow in color similar to biodiesel. Fatty acid anions are converted into acid molecules at the lower pH values and they can be extracted to the solvent phase from aqueous phase.

In Fig. 1, COD extraction yield of both solvents were the highest at pH=4. At this pH value, COD extraction yields were found as %96.0 and %94.2 respectively for hexane and MTBE. Hexane extraction shows more dependence to the pH changes. Increase in pH value decreases the COD extraction by hexane (% 81.3 at pH= 12).

pH change does not affect the MTBE extraction at same ratio (%90.6 at pH=12). In a similar manner, at pH=2, the removal efficiency of both solvents show highest level for O&G (% 99) and increase in pH value decreases the oil removal efficiency of hexane (%10.7 at pH=12). The pH change does not affect the extraction efficiency of MTBE at same amount (%80.4, at pH=10.7). Evaluation of pH for extraction process reveals that hexane is the best solvent for O&G extraction at pH=2.

The GC chromatogram presented in Fig. 2 and Fig. 3 shows peaks related to the fatty acid methyl esters (FAMEs) with different retention times for the biodiesel wastewater extracted by hexane and MTBE.



Fig. 1. Effect of initial pH on the removal efficiency of COD, O&G and TOC (agitation rate: 385 rpm; temperature: 25°C; duration of extraction: 30 min.; V<sub>hex</sub>/ V<sub>wat</sub>: 1/1)



**Fig. 2.** GC chromatogram of biodiesel wastewater after first extraction with hexane (agitation rate: 385 rpm; temperature: 25 ° C; duration of extraction: 30 min; V<sub>hex</sub> / V<sub>wat</sub>: 1/1)



Fig. 3. GC chromatogram of biodiesel wastewater after first extraction with MTBE (agitation rate: 385 rpm; temperature: 25°C; duration of extraction: 30 min;V<sub>MTBE</sub> / V<sub>wat</sub>: 1/1 )

FAMEs	Hexane extraction		MTBE extraction		
(mg/L)	First extraction	Second extraction	First extraction	Second extraction	
C16:0	851.23	40.58	795.50	19.59	
C18:0	100.77	-	96.64	-	
C18:1 C	990.31	46.85	938.12	25.76	
C20:0	351.63	13.72	166.92	41.98	

Table 2. The concentrations of FAMEs after extraction

Intensity of two peaks in GC chromatogram, number 1 and 3 have higher intensity. By comparison with the GC chromatograms of the standard mixture, 1 and 3 peaks were identified as C16:0 and C18:1 respectively. Other two peaks (C18:0 and C20:0) have lower intensity. Table 2 shows gas chromatographic results of FAMEs extraction from biodiesel wastewater by hexane and MTBE. Tabulated results show that hexane is a better extraction solvent than MTBE. The amount of extracted FAMEs was calculated from peak area of each component in GC chromatogram. The amount of extracted material is higher for hexane than for TMBA. High extraction capacity of hexane for nonpolar compounds comes most probably form its nonpolar property.

Ionization of fatty acids can be expressed as Eqs. (1-2) (Cheung et al., 1994):

$$HA + OH^- = A^- + H_2O \tag{1}$$

$$M + OH^{-} = [M-H]^{-} + H_2O$$
(2)

The partition coefficient is the ratio of a solute's concentration fraction in the two phases (Eq. 3).

$$K_{p} = \frac{[HA]_{I}}{[HA]_{2}} \tag{3}$$

where:  $[HA]_1$  is concentration of weak acid in the solvent phase and  $[HA]_2$  is concentration of weak acid in the aqueous phase.

Distribution ratio  $(D_c)$  can be expressed as Eq. (4):

$$D_{c} = \frac{K_{p} \left[ H^{+} \right]_{2}}{\left[ H^{+} \right]_{2} + K_{a}}$$

$$\tag{4}$$

where the  $K_a$  indicates acid dissociation constant.  $[H^+]_2$  is molar concentration of  $H^+$  ion in the aqueous phase.

In the case of a weak acid,  $D_c$  is highly dependent on solution pH. Log  $D_c$  as a function of the pH is presented in the Fig. 4 for hexane extraction. As shown in Fig. 4, fatty acids and FAMEs cannot be ionized at lower pH values (<2) in the biodiesel wastewater.

### 3.2. Thermodynamic parameters

Organic matters represent the soluble types between the phases and it is shown as COD. Therefore, the following equilibrium can be written: as Eqs. (5-7):

$$COD_{(aq)} \leftrightarrow COD_{org}$$
 (5)

$$K_{p} = \frac{[COD]_{org}}{[COD]_{aq}}$$
<sup>(7)</sup>

$$\Delta G^{o} = -RT \ln K_{p} \tag{7}$$

where:  $[COD]_{aq}$  = Chemical oxygen demand in water phase (mg/L);  $[COD]_{org}$ = Chemical oxygen demand transferred into the organic solvent phase (mg/L);  $\Delta G^o$ = Standard free energy of extraction (J/mol);  $K_p$  = Distribution coefficient; R = General gas constant (J/mol.K); T = Temperature (K).



Fig. 4. Distribution ratio variation as a function of pH

The hexane partition coefficients are shown in Table 3 depending on the pH change. As seen in Table 3, as the pH increases  $K_p$  values become smaller due to the lower extraction efficiency.  $K_p$  value changes are shown in Table 4 depending on temperature. As seen in the table, increase in temperature does not change the  $K_p$  values significantly.

Fig. 5 and Fig. 6 shows the effect of pH and temperature on the extraction free energy change, respectively. In Fig. 5, as the pH increases,  $\Delta G$  value increases for hexane extraction. For MTBE case, as the pH becomes higher than 4,  $\Delta G$  values does not change significantly. For both solvents,  $\Delta G$  reaches the lowest value around pH=2. In the comparison of  $\Delta G$  values at pH=2, hexane extraction shows lower  $\Delta G$  value than TMBA extraction. These results indicate that hexane is a more effective solvent for extraction.

As seen in Fig. 6, although temperature has higher effect on extraction free energy in hexane, it does not affect that much in MTBE. This is because as shown in Table 5, extraction enthalpy of MTBE is more positive than hexane. This shows that MTBE extraction is endothermic process, so increase in temperature will make the extraction free energy value more negative and this bring higher extraction possibility. However, the extraction free energy of hexane is more negative than that of MTBE at 298 K and this will increase the extraction efficiency of hexane. Another important consideration for extraction process is standard enthalpy and entropy change. Dependence of these two thermodynamic values is given as in Eq. (8):

$$\ln K_{p} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{R} \frac{1}{T}$$
(8)

where:  $\Delta S^o$  = Standard extraction entropy (J/mol.K);  $\Delta H^o$  = Standard extraction enthalpy (J/mol).

pН	2	4	6	8	10	12
Hexane K <sub>p</sub>	24.50	11.40	9.89	6.82	4.52	4.37
$MTBE K_p$	16.37	10.44	10.19	9.89	9.77	9.71

 Table 3. Partition coefficients at different pH values (temperature: 298K; stirring speed: 385 rpm, stirring time: 30 min; Vorgan / Vwat: 1/1 )

 Table 4. Partition coefficients at different temperatures (pH: 2; stirring speed: 385 rpm, stirring time: 30 min; V<sub>organ</sub> / V<sub>wat</sub> : 1/1 )

Temperature(K)	298	303	313	323	333
Hexane Kp	24.538	24.603	24.652	24.685	24.701
МТВЕ Кр	16.37	16.91	17.07	17.48	17.65



Fig. 5. Comparison of pH and free energy change in hexane and MTBE extraction



Fig. 6. Comparison of temperature and free energy change in hexane and MTBE extraction

 Table 5. Thermodynamic parameters of hexane and MTBE extractions

Thermodynamic parameters	Hexane	MTBE
$\Delta G^{o} (J/mol)$	-7924.94	- 6926.03
$\Delta H^{o}$ (J/mol)	+147.64	+1649
$\Delta S^{o} (J/K.mol)$	+27.11	+28.86

Using this equation standard enthalpy and standard entropy variations were calculated by plotting a graph using  $lnK_p$  versus 1/T. The results of calculations from Eq. (8) were summarized in Table 5.

According to the thermodynamic calculations, the extraction process is endothermic and entropy change is positive. This result shows that organic substances are extracted into the more random phase. The entropy increase in hexane extraction is main driving force.

#### 3.3. Investigation of extraction kinetics

Fig. 7 shows the effect of extraction time on biodiesel wastewater treatment efficiency in hexane and MTBE. Although the small variations are seen at the beginning of extraction process, removal efficiency shows similar trends after tenth minute for both solvents. However, extraction time of O&G should be over 30 min for both solvents.

The different kinetic models were investigated for the extraction of biodiesel wastewater by hexane and MTBE. Depending on calculations, the best model that represents the extraction kinetics is pseudo second-order equation.

The linear pseudo second-order equation is given as follows (Özacar and Şengil, 2004):

$$\frac{t}{c} = \frac{1}{\kappa_2 \kappa_c^2} + \frac{1}{\kappa_c} t \tag{8}$$

where:  $k_2$  = Extraction rate constant (L /mg.min); c = the amount of COD concentration in water (mg/L);  $K_c$  = Concentration constant (mg/L).

All the kinetic parameters are given in Table 6. Pseudo-second-order linear correlation coefficients were calculated as ( $R^2 = 0.999$ ) showing that this model is the best kinetic model for the extraction process.

#### 4. Comparison of solvent ratio

Fig. 8 shows the effect of solvent ration on the extraction rate of hexane and TMBA. As the solvent ratio increases, the extraction efficiency increases for both solvents. In terms of O&G removal, 2/8 ratio is a sufficient amount for both solvents. For COD case, the best ratio is 7/3. In case of higher solvent volumes, bigger reactors are required thus, solvent ratio could be accepted as 5/5(1/1).

Table 6. Parameters of pseudo second-order kinetics

	$k_2$ (L/mg.dak)	$K_c (mg/L)$	$R^2$
Hexane	-1.81.10 <sup>-4</sup>	$1.666.10^4$	0.999
MTBE	-2.28.10 <sup>-4</sup>	$2.5.10^4$	0.999



Fig. 7. Effect of extraction time on removal efficiency of hexane and MTBE



Fig. 8. Comparison of solvent ratio in hexane and MTBE extraction

#### 5. Conclusions

This study demonstrates the extraction efficiencies of two selected solvents. The results revealed that hexane is a better solvent for the removal of O&G, COD and TOC. The optimum conditions (pH=2, 25°C, 30 min extraction time and 1/1 solvent ratio) were determined experimentally. At optimum conditions, COD, O&G and TOC extraction efficiencies were determined as 96%, 99.8% and 96%, respectively. However, despite the high extraction efficiency, the ratio of COD and TOC values are still high in the remaining part due to high organic content of biodiesel wastewater. In optimum conditions, the determined COD and TOC values were 15780 mg/L and 4830 mg/L, respectively.

Extraction process is possibly suitable for a primary treatment for biodiesel wastewater. It requires a further treatment like advance oxidation treatment or biological treatments can be performed after the solvent extraction. For hexane and THMB extraction, kinetic and thermodynamic parameters were also investigated. Comparison of  $\Delta G$  values at pH=2, hexane extraction shows lower  $\Delta G$  value than TMBA extraction. These results indicate that hexane is a more effective solvent for extraction. The thermodynamic calculations also showed that the extraction process is endothermic and entropy change is positive. Thus, the entropy increase in hexane extraction is main driving force.

We also calculated that pseudo-second-order equation is the best model for extraction kinetics and calculated correlation coefficient was found as  $R^2 = 0.999$ . Extraction process is possibly suitable for a primary treatment for biodiesel wastewater but it requires a further treatment like advance oxidation treatment or biological treatments after the solvent extraction.

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