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Research Article

TREATMENT OF BIODIESEL WASTEWATER USING YELLOW MUSTARD SEEDS

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ABSTRACT
In this study, removal of original biodiesel wastewater (BOD, COD, oil&greas) by yellow mustard seeds was examined by a batch system. The effect of the adsorption time 300 minutes, adsorbent dose (1.0 g/L) and mixing rate (120 rpm) on the adsorption capacity of pollutants. The applicability of the Langmuir and Freundlich isotherms were examined. According to the data obtained from experiments, biodiesel wastewater can be treated by adsorption using yellow mustard seeds.

Keywords: *Biodiesel wastewater, Agricultural waste, Adsorption, Isotherm*

1. INTRODUCTION

Fossil fuels are non-renewable and limited sources in the World. For this reason, people search for new, sustainable, alternative, environmentally and renewable power sources. Today, biodiesel has an attracted much more attention for biodegradable, nontoxic, renewable, burns with a low sulfur, carbon monoxide and lower harmful emissions. Biodiesel is produced from the transesterification reaction in the presence of alcohols and catalyst (Ngamlerdpokin *et al.*, 2011; Jaruvat *et al.*, 2010; Rattanapan *et al*., 2011; Ceclan *et al.*, 2012). Washing process is produced biodiesel wastewater. The washing process is remove soap, suspanded solids and residual alcohol (Daut *et al*., 2015; Srirangsan *et al*., 2009). It is depending on the impurity level of methyl ester, with about 20–120 L of wastewater being generated per 100 L biodiesel produced.

There are many physico-chemical proses for removal of polluted from wastewater. However, these methods are too expensive also they are doing secondary pollution. For this reason, both environmental friendly and low-cost effective methods should be investigated. Adsorption is the one of the most promising method for treatment wastewater. The adsorption which is a simple, effective and low-cost process compared to other processes (Elkady *et al*., 2011). Although activated carbon is the best adsorbent in removal of chemical substances from wastewater, there are many negative aspects such as they are expensive and washing needs (McKay, 1981; McKay, 1982; Blum *et al*., 1993; Meshko *et al*., 2001). After that scientist are working adsorbents that they are inexpensive. Peat (Xiong and Mahmood, 2010; Calderón *et al*., 2008); agricultural waste (Mittal *et al*., 2006; Moussavi *et al*., 2010), chitin (Gupta *et al*., 2012; Sokker *et al*., 2011) are low cost adsorbent for using adsorption. Liu et al., (2009) used adsorption processed biodiesel washwaters for the glycerol in conical flasks with continuous shaking. They used activated carbon, clay minerals, natural and synthetic zeolites as an adsorbent. According to the results, activated carbon has the highest adsorption capability of glycerol from aqueous solution. Another study reported by Pitakpoolsil and Hunsom (2014), for biodiesel wastewater and commercial chitosan flakes (Pitakpoolsil *et al*., 2014). According to the study, the biological oxygen demand (BOD), chemical oxygen demand (COD) and oil & grease were removed by batch system. Assawasaengrat et al., (2015) used magnesium silicate as an adsorbent for removal of free fatty acid (FFA), soap and glycerine from biodiesel (Assawasaengrat *et al*., 2015).

When Rudolph Diesel invented diesel engines that they are using agricultural sector, vegetable oils were used for producing biodiesel. The first biofuel patents around the world, Professor Expedito José de Sá Parente, is considered by many to be the inventor of biodiesel. The first small pilot biodiesel plant was built in 1985 in Austria. After that the biodiesel plant that it is working with microalge was built in New Mexico in 1987. Figure 1 shows The world's biggest biodiesel producers in 2015, by country (in billion liters).

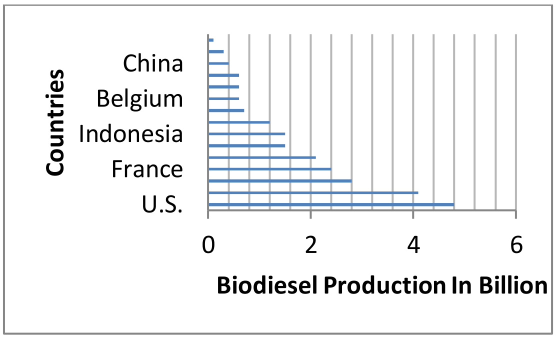

Fig. 1. The world's biggest biodiesel producers in 2015, by country (in billion liters) (The Statistic Portal, 2017).

Actually, main source of biodiesel is plants oil. Plant oil types are depending on climatic factors and soil properties in their countries. Biodiesel producers use palm oil for producing biodiesel in Thailand. In the U.S. they use soybean. In Malaysia, they use palm oil. The palm oil is the most common feed stocks for biodiesel production. Because biodiesel producers get palm oil very easily and palm oil have all-purpose applications. Table 1 depicts the oil sources suitable for biodiesel production.

Table 1. Raw materials for biodiesel production (Olkiewicz *et al*., 2016; Verma and Sharma 2016; Tubino *et al*., 2014; Verma *et al*., 2015).

Edible	Non-edible	Other
Soubean oil	Karanja (Pongamia oil)	Waste cooking oil
Palm oil	Mahua oil	Microalgae
Canola oil	Neem	Fish oil
Sunflower oil	*Jatropha curcas*	Beef tallow
Cottonseed oil	*Pongamia pinnata (Karanja Yağı)*	Poultry fat
Maize oil	Sea mango	Chicken fat
Penut oil	Jatropha oil	Chlorella protothecoides microalgae
Coconut oil	Linseed	Spirulina platensis algae
Mustard oil	Rubber seed	Sewage sludge

The using of waste cooking oil is one of the basic idea for the produce of biodiesel. The using of waste cooking oil in biodiesel producing is very useful for environment and ecology. Because these oils are prevented from being discharged to the drainage system (Kumar and Sharma 2015; Kwon *et al*., 2012; Zhan *et al*., 2013). Microalgae are the one of the important raw material for biodiesel production due to their fast growth and easy cultivation (Tsigie *et al*., 2012).

In this work was focused on investigating the treatment of biodiesel wastewater by batch system using yellow mustard seeds.

2. MATERIAL AND METHODS

2.1. Material

2.1.1. Yellow Mustard Seeds

The seeds of yellow mustard were supplied from Biofuel Laboratory in Yozgat. The crude oil was obtained by screw press. Figure 2 shows that seeds before grinding and after grinding.

Fig. 2. a) seeds before grinding b) after grinding

2.1.2. Wastewater

Original biodiesel wastewater used in this study. It was collected from Biofuel Laboratory of Department of Biosystems Engineering in Bozok University in Yozgat in Turkey. This Plant uses mustard seeds as a raw material. Biodiesel is washed in transesterification method. Wastewater are obtained by transesterification method. The characteristic of wastewater were analyzed according to the standard methods (Standard Methods, 1998). Biodiesel wastewater before treatment is as presented Fig 3.

Fig. 3. Biodiesel wastewater before treatment

2.2. Methods

Biodiesel wastewater was selected as an adsorbate for carrying out the adsorption studies on oil cake was obtained from Bozok University Biosystems Engineering Department Laboratory. Original biodiesel wastewater was obtained from Energy Systems Laboratory in Turkey. Figure 4 presented adsorption of biodiesel wastewater.

Fig. 4. Adsorption of biodiesel wastewater

To estimated that batch experiment was performed using biodiesel wastewater as the adsorbate onto oil cake. Equilibrium tests were done by contacting 1.0 g of waste ash with 1000 mL of biodiesel wastewater at different initials concentrations at room temperature (25 ^{0}C). The incubation times ranged from 60 to 300 minutes. The wastewater was separated from the supernatant and adsorbate by vacuum filtration through filter paper No:1 (Whatman 70 mm). All experiments were conducted twice.

2.2.1. Calculation

The amount of original biodiesel wastewater adsorbed by agriculture waste was calculated using the mass balance equation:

$$qt = \frac{(C_0 - Ct)V}{m} \quad (1)$$

and the amount of original biodiesel wastewater removed (%) was calculated above:

$$\text{Removal (\%)} = \frac{C_0 - Ct}{C_0} \times 100\% \quad (2)$$

where qt (mg/g) is the amount of biodiesel wastewater adsorbed by agriculture waste C_0 and Ct (mg/L) are the initial original biodiesel wastewater concentration at any time t, V is the volume of the original biodiesel wastewater solution (L); and m is the amount of agriculture waste (g) (Baek *et al.*, 2010).

Langmuir and Freundlich models were employed for adsorption isotherm model. The linearized form of the Langmuir model can be written as (Ho, 2006):

$$\frac{C_e}{q_e} = \frac{1}{K_L} + (\frac{a_L}{K_L})C_e \quad (3)$$

where; Ce = the equilibrium concentration of adsorbate in solution after adsorption (mg/L),
qe = the equilibrium solid phase concentration (mg/g), K_L (L/g) and aL (L/mg) = the Langmuir constants.

The linearized form of the Freundlich model can be written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where;
Ce = the equilibrium concentration of adsorbate in solution after adsorption (mg/L),
qe = the equilibrium solid phase concentration (mg/g),
K_F (L/g) and Freundlich constants (n) related with adsorption capacity and intensity.

3. RESULTS AND DISCUSSION

Original biodiesel wastewater used in this study and characteristic of biodiesel wastewater show in Table 1. The effect of the adsorption time 300 minutes, adsorbent dose (1.0 g/L) and mixing rate (120 rpm) on the adsorption capacity of pollutants. The biodiesel wastewater adsorption equilibrium was attained within 180 min.

Pitakpoolsil *et al.* (2013) were also found similar results for biodiesel wastewater and chitosan flakes systems. Initial adsorption tests showed that yellow mustard seeds adsorbed biodiesel wastewater (Fig. 5) (Pitakpoolsil and Hunsom 2013).

Table 2. Biodiesel wastewater characteristic used in the experiment

Parameter (mg/L)	Test Result
Oil&grease	7457
TDS	15165
TSS	1363
COD	85904
BOD	25901

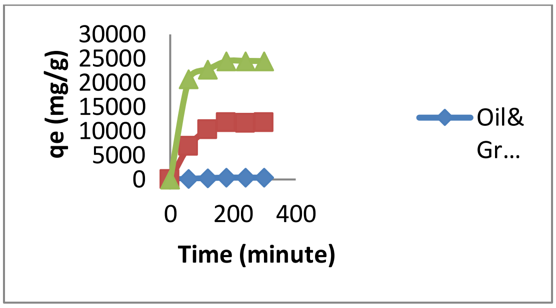

Fig. 5. Effect of the time on the adsorption capacity

Several adsorption isotherms were studied in order to identify the optimization conditions of an adsorption system for removal of BOD, COD, oil&grease from biodiesel wasteater. The adsorption data of the BOD, COD, oil&grease on the yellow mustard seeds were analyzed using Langmuir and Freundlich models.

Figure 6-7-8 show the Langmuir isotherms for oil&grease, BOD, COD whereas the isotherm constants are presented in Table 3-4. As can be seen from Table 2-3, although better correlation coefficient was obtained from Langmuir and Freundlich isotherm model, however values of q_{max} and n were found negative. These negative value was also reported by Robinson *et al*. (2002) and Basibuyuk *et al*., (2007).

Table 3. Langmuir Isotherm Constants

Parameters	q_{max} (mg/g)	a_L (L/mg)	K_L (L/g)	R^2
BOD	-4.043	-15281.9019	6.1785	0.9999
COD	26.287	-0.002758	-0.0725	0.9982
Oil-grease	32.102	-0.000176	-0.00565	0.9937

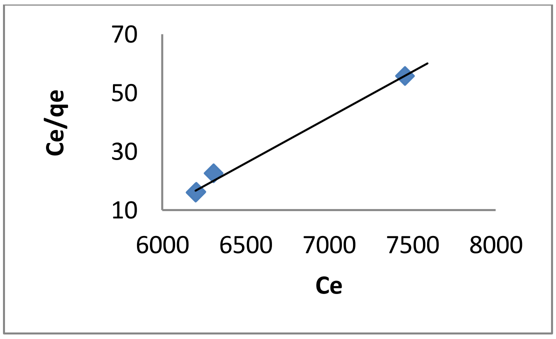

Fig. 6. Langmuir Isotherm for oil&grease

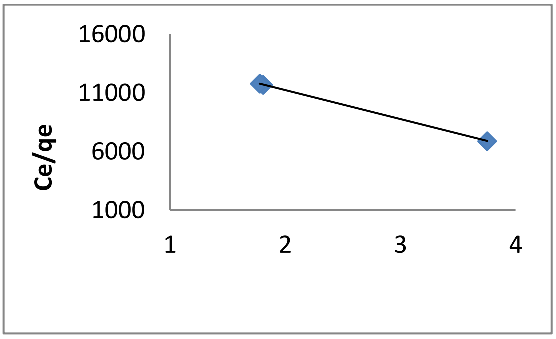

Fig. 7. Langmuir Isotherm For BOD

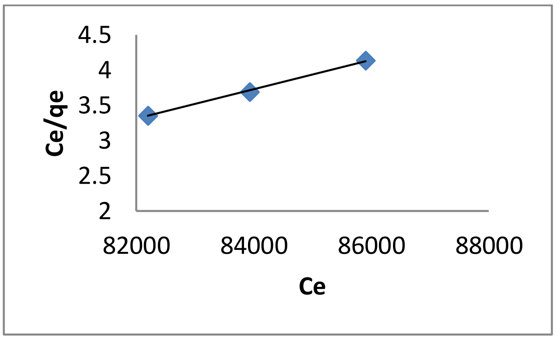

Fig. 8. Langmuir Isotherm For COD

Figure 9-10-11 show the Freundlich isotherms for oil&grease, BOD, COD whereas the isotherm constants are seen in Table 3.

Table 4. Freundlich Isotherm Constants

Parameters	K_f (L/g)	n	R^2
BOD	1.452	-0.389	0.9999
COD	4.064	-0.269	0.9993
Oil&grease	5.584	-0.179	0.9536

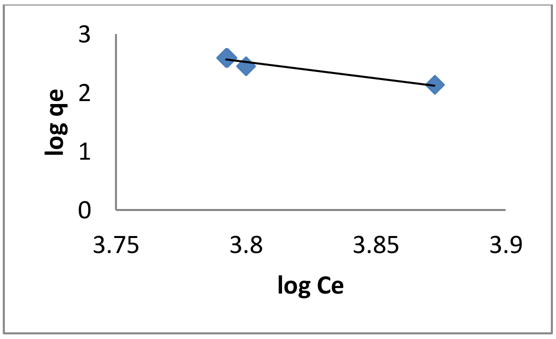

Fig. 9. Freundlich Isotherm For oil&grease

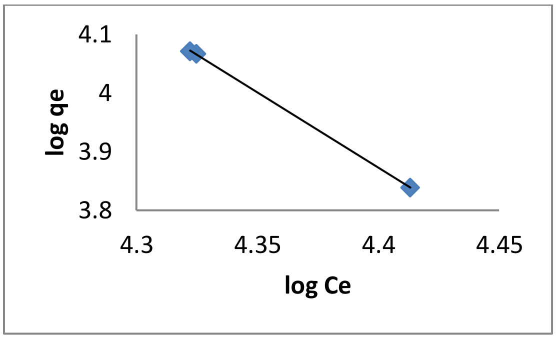

Fig. 10. Freundlich Isotherm For BOD

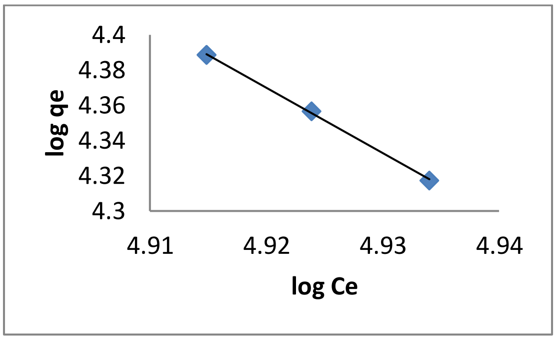

Fig. 11. Freundlich Isotherm For COD

4. CONCLUSIONS

This study has shown that adsorption is a useful method as a treatment of polluted from biodiesel wastewater such as COD, BOD, oil&greas. The treatment of biodiesel wastewater was carried out in laboratory conditions (25 ^{0}C). The effect of the adsorption time 300 minutes, adsorbent dose (1.0 g/L) and mixing rate (120 rpm) on the adsorption capacity of pollutants. Data obtained from equilibrium studies fit both Langmuir and Freundlich models however for the both Langmuir and Freundlich model negative values were obtained and indicating the inadequacy of these models for these particular wastewater-yellow mustard seeds system.

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