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Metals Removal from Recovered base Oil using Chitosan Biopolymers

S.M. Jamil, M.W. Ali, A. Ripin and A. Ahmad
Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Abstract: It was common to use solvent extraction to recover base oil from used lubricants. Although, significant amount of contaminants removal was achieved by using solvent extraction, some problems arised which need to be resolved. The recovered base oil from solvent extraction was still in the darkish color with stink odor and only minimum heavy metals were removed. As an alternative, an adsorption method which used chitosan to remove metals and contaminants was being investigated. This paper presents the application of experimental design on the study of metals removal from the recovered base oil using adsorption process. Four parameters namely temperature, contact time, chitosan grain size and chitosan dosage on the performance of chitosan to adsorb metals were studied. It was found that the most influential parameter effecting the metals removal was the chitosan grain size. The metals removals also greatly depended on the temperature of the process and chitosan dosage. The performance of these parameters will be further investigated.

Key words: Experimental design, base oil, used lubricant, adsorption, chitosan

INTRODUCTION

Thirteen billion gallons of used motor and other oils are generated annually (Ciora and Paul, 2000). These waste oils are considered a hazardous waste (Rincon *et al*., 2007) because of their high content of pollutants (contaminated with oxidation and degradation products, water, fine particulates, metals and carbon oil additive products). The used oil generally contains ~0.5 wt. % of ash residue after combustion and for reuse as fuel, this ash creates air pollution concerns. Nevertheless, the used oil still contains a large proportion of valuable base oil that may be used to formulate as a new lubricant, such as crank case fluid if the contaminants are properly removed, odor is eliminated and the color is improved. Thus, the recovery and purification of this base oil not solely give the economic contributions but also an attempt to meet the environmental objections.

In recent years, there are several processes available for the recycling of used lubricant oil. The traditional method used was chemical cracking using acid treatment of the used oil to flocculate carbonaceous particles and other impurities from the used oil. However, this process generates acid sludge, creating environmental concerns and disposal problems. Other popular conventional method used was acid clay treatment, where the base oil was separated from the used lubricant using sulfuric acid as a separate medium. At the end of the process, the acidic sludge was disposed of while the base oil was treated with clay for color and odor removal. Other alternative, evaporation/distillation of the used lubricant oil has been suggested to separate ash and other contaminants from the oil. The high boiling point of the used oil at atmospheric pressure with the assistance of vacuum and high operating temperature was reported to effectively evaporate oil and leave the contaminants and impurities as residue. Although, this process to be technically feasible, it is energy intense due to the phase change involve in evaporation. In addition, to deliver an acceptable quality of color and smell, a polishing step is required.

Solvent extraction has been used for the recycling of used lubricant oil. Studies such as by Lim (2001) and Gary (1999) concluded that solvent extraction technique can be an alternative to be commercialized for re-refining of base oil. This method involves the extraction of base oil from used lubricants via addition of composite solvent. At the end of this process, organic sludge with huge potential as burning fuels was produced. Unfortunately, the recovered base oil is still in darkish color with stink odor. Thus, a need has arisen for an effective method of purifying the recovered base oil in order to achieve the desired product quality.

Adsorption process was found to be an effective method of metals removal in recovered base oil for purification purpose (Ahmad *et al*., 2005). This technique was highly efficient for the removal of color in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Juang *et al*., 1997). Many substances can be used as an adsorbent, but chitinand chitosan were widely used. Chitin is the second most abundant biopolymer in nature next to

Corresponding Author: S.M. Jamil, Department of Chemical Engineering, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

cellulose (Majeti, 2000). Chitosan is a partially acetylated glucosamine polymer encountered in the cell wall of some fungi such as the Mucorales strains. It also results from deacetylation of chitin (Feng *et al.*, 2000). Chitosan has excellent features such as its hydrophilicity, biocompatibility, biodegradability and anti-bacterial properties and remarkable affinity for proteins. This adsorbent is effective in the uptake of metals since the amine groups on the chitosan chain can serve as chelation sites for metals (Giubal *et al.*, 1994).

In this study, metals removal from recovered base oil using chitosan was investigated. Two level factorial design was applied to investigate the effects of the parameters and their interactions on metals removal by batch adsorption. In the end, the regression equation was obtained.

MATERIALS AND METHODS

Sample preparation: The base oil from used lubricants was extracted using solvent extraction method. In order to increase the capability to remove sludge from the waste oils, several proportion of potassium hydroxide (KOH) was added and dissolved in 500 mL of solvent (Ping *et al.*, 2000). The used oil was then mixed with the solvent (n-hexane and 2-propanol mixture) and KOH in a beaker. Then, the mixture was subjected to intense agitation for 15 min at 300 rpm to allow good mixing between the oil and the solvent. After strong agitation, it was then left at room temperature for 24 h to allow extraction-flocculation. Consequently, the oil was introduced into simple filtration process to allow separation of base oil from the oil sludge. The recycled base oil with darkish color was later collected and kept in a close drum of 20 L where the content have to be homogenized prior to any testing.

Adsorption process: The recovered base oil was mixed with chitosan in a beaker. The samples were analyzed at various conditions according to the design matrix in factorial design analysis. The upper and lower levels for each parameter were shown in Table 1. The recovered base oil was then analyzed for their metals content before and after the adsorption process.

Table 1: Actual and coded values of parameters in 2^4 full factorial design for metals removal by adsorption

	Level of variables	
Variables	Low	High
Temperature (^{0}C)		
Actual (x_1)	30	70
Coded (X_1)	-	+
Time (min)		
Actual (x_2)	10	60
Coded (X_2)	-	+
Grain size (mic)		
Actual (x_3)	250	1000
Coded (X_3)	-	+
Chitosan dosage (g)		
Actual (x_4)	0.5	2.5
Coded (X_4)	-	+

Factorial design: The 2^k factorial designs were found to meet the majority of the experimental needs of those engaged in the improvement of quality. This type of factorial design was easy to use in sequential experimentation, so that even complex systems with many variables can be studied in depth using these relatively simple designs (Box *et al.*, 1978). In this study, there were four quantitative variables involved, namely temperature, contact time, chitosan grain sizes and chitosan dosage. Table 1 shows the parameters involved in the studies. The responses variables used in this study were the percentage of Zinc (Zn), Magnesium (Mg) and Ferum (Fe) removal. For a two-level factorial design with four variables, sixteen runs (2^4 = 16) of experiment were conducted.

The main effects were the difference between two averages:

$$\text{Main effect} = \hat{y}_+ - \hat{y}_- \quad (1)$$

Where:
$\hat{y}_+$ = Average response for (+) stage variables
$\hat{y}_-$ = Average response for (-) stage variables

Using Eq. 1, the most influential parameter that effects the metals removal in the recovered base oil was obtained and shown by the variable with the highest response value. The same method was also used in the analysis on the interacting effects between the selected parameters.

RESULTS AND DISCUSSION

Full factorial design: A design matrix with the responses Y_1 (percentage of Zn Removal), Y_2 (percentage of Mg Removal) and Y_3 (percentage of Fe removal) are illustrated in Table 2.

Table 2: Factorial design result

Run	X_1	X_2	X_3	X_4	Y_1	Y_2	Y_3
1	-	-	-	-	59.09	50	45.5
2	+	-	-	-	57.85	33.33	45.5
3	-	+	-	-	55.37	33.33	45.5
4	+	+	-	-	52.89	33.33	45.5
5	-	-	+	-	69	66.67	72.75
6	+	-	+	-	57.85	50	45.5
7	-	+	+	-	56.61	33.33	45.5
8	+	+	+	-	70.25	50	72.75
9	-	-	-	+	64.05	33.33	45.5
10	+	-	-	+	61.57	33.33	45.5
11	-	+	-	+	49.18	33.33	18.26
12	+	+	-	+	51.65	16.67	18.26
13	-	-	+	+	64.05	50	45.5
14	+	-	+	+	51.65	33.33	45.5
15	-	+	+	+	61.57	33.33	45.5
16	+	+	+	+	47.93	33.33	45.5

Table 3: Analysis of variance for metals removal (%)

Response (%)	Source	Sum of square	df	Mean square	F-value	R^2
Zn removal	Model	600.50	14	600.500	9.255	0.90
	Error	64.88	1	64.880		
	Total	665.38	15			
Mg removal	Model	2049.01	14	2049.010	118.100	0.99
	Error	17.35	1	17.347		
	Total	2066.36	15			
Fe removal	Model	2783.52	14	2783.520	14.990	0.94
	Error	185.64	1	185.640		
	Total	2969.16	15			

Factorial design analysis: Statistica 6.0, a Statistical Software release (Version 15) was used to analyze the effects, coefficients, standard deviation of coefficients, and other statistical parameters of the fitted models, besides the statistical plots. Table 3 shows the analysis of variance for each of response.

From the analysis of variance, the R^2 value for each response shows a good agreement between experimental data and the model when the values were greater than 0.80.

The regression equation for the matrix is represented by the following expression:

$$\begin{aligned} Y_i &= a + bX_1 + cX_2 + dX_3 + eX_4 + fX_1X_2 + gX_1X_3 + hX_1X_4 + iX_2X_3 \\ &+ jX_1X_4 + kX_3X_4 + lX_1X_2X_3 + mX_1X_2X_4 + nX_1X_3X_4 + oX_2X_3X_4 \end{aligned} \quad (2)$$

The effect of individual variables and interactional effects can be estimated using the above equation. According to Eq. 2, each response can be represented respectively by the following expression:

$$\begin{aligned} Y_{znremoval} &= 66.697 - 0.222X_1 - 0.217X_2 + 0.009X_3 - 4.065X_4 \\ &+ 0.003X_1X_2 + 0.00001X_1X_3 + 0.177X_1X_4 - 0.00001X_1X_2X_3 + \\ &- 0.002X_1X_2X_4 + -0.0027X_1X_3X_4 + 0.00007X_2X_3X_4 \end{aligned} \quad (3)$$

$$\begin{aligned} Y_{Mgremoval} &= 60.351 - 0.47X_1 - 0.358X_2 + 0.040X_3 - 15.179X_4 \\ &+ 0.005X_1X_2 - 0.0002X_1X_3 + 0.254X_1X_4 - 0.001X_2X_3 + \\ &0.285X_2X_4 + 0.0003X_3X_4 + 0.000X_1X_2X_3 - 0.006X_1X_2X_4 - \\ &0.0001X_1X_3X_4 + 0.0004X_2X_3X_4 \end{aligned} \quad (4)$$

$$\begin{aligned} Y_{Feremoval} &= 47.942 - 0.199X_1 - 0.102X_2 + 0.056X_3 - 6.019X_4 \\ &+ 0.005X_1X_2 - 0.0006X_1X_3 + 0..238X_1X_4 - 0.001X_2X_3 \\ &- 0.023X_2X_4 - 0.013X_3X_4 + 0.00002X_1X_2X_3 - 0.007X_1X_2X_4 \\ &+ 0.00000X_1X_3X_4 + 0.00036X_2X_3X_4 \end{aligned} \quad (5)$$

The effects of individual variables and interactional effects were estimated from the above equations. According to these equations, chitosan grain size has a positive effect, while temperature, contact time and chitosan dosage have a negative effect on the metals removal by chitosan adsorption in the range of each variable studied. The greatest effect found was from the chitosan grain size.

The interaction effect between temperature and time, and temperature and chitosan dosage have a positive effect on metals removal. On the other hand, the interaction between temperature and chitosan grain size has a negative effect. The triple effect was found to be almost negligible.

CONCLUSIONS

The major conclusions derived from the present work were:

- From the studies of parameters involved in the process, the most influential parameter effecting the metals removal was the chitosan grain size
- In the interacting effect study, the metals removals greatly depended on the temperature of the process and chitosan dosage

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