ADSORPTION OF METALS FROM RECOVERED BASE OIL USING ZEOLITE

S U S I W I

UNIVERSITI TEKNOLOGI MALAYSIA

ADSORPTION OF METALS FROM RECOVERED BASE OIL USING ZEOLITE

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

JULY 2010

To

My beloved husband, son, mother, father, brother and sisters….

ACKNOWLEDGEMENT

In the name of Allah, Most Gracious, and Most Merciful

Praise to Almighty Allah (Subhanahu Wa Ta'ala) who gave me the courage and patience to carry out this work. Blessing of Allah be upon his last prophet Mohammed SAW and all his companions who devoted their lives towards the prosperity and spread of Islam.

My deep appreciation and heartfelt gratitude goes to my supervisor, Assoc. Prof. Dr. M. Wijayanuddin Ali for his kindness, constant endeavor, guiding and the numerous moments of attention he devoted through out this work. I would like to extend my deepest gratitude to my co-supervisor, Assoc. Prof. Adnan Bin Ripin and Prof. Dr. Arshad Ahmad for providing their workstations to complete my work.

Furthermore, this study would have been impossible without technical support from Unit Operation Laboratory, Faculty of Chemical and Natural Resources Engineering UTM, special thanks for En. Arsad, En. Mior, En. Rafy, and En. Shairray for their assistance.

Many thanks also go to my research colleagues, staff of the department and my friend for their help, suggestion and discussion in this work. The financial support of Ministry of Science, Technology and Innovation (MOSTI) is gratefully acknowledged.

Finally, I would like to thank my parents, my husband Mohd. Khairudin Samsudin, and my son Fattah Ghiyas Khairi for their continuous support and understanding over the years.

ABSTRACT

Extraction process of used lubricating oil produces organic sludge and recovered base oil. However, the base oil contains metal components as impurities. The metal components need to be removed in order to obtain a base oil that is suitable for the formulation of new lubricants. In this study, metals such as calcium, zinc, and lead from the recovered base oil were removed by using adsorption process. The parameters of adsorption such as zeolite/oil ratio, temperature, and time were investigated. The experiments were carried out using the Full Factorial Design (FFD) and Non-Factorial Response Surface Design (NFRSD) methods. The experimental results were analyzed and developed by Response Surface Methodology (RSM) to obtain empirical models. The models were the FFD no interactions, the FFD two way interactions, the linear main effects only NFRSD, the linear main effects+2ways NFRSD, the linear and quadratic main effects NFRSD, the linear and quadratic main effects+2ways NFRSD. The goodness for fit of the models were evaluated by the coefficient determination and the analysis of variances (ANOVA). The comparison study of those models shows that the linear and quadratic main effects+2ways NFRSD was the best model. Furthermore, this model was used to obtain the optimum condition of the calcium, zinc and lead removal. The results showed that the highest value of calcium removal was found to be 35.18 % at 39.9 °C, 6.2 minutes, and 0.06 g/ml of zeolite/oil ratio. The zinc removal was 35.86 % at 34.1 °C, 6.6 minutes, and 0.063 g/ml of zeolite/oil ratio. The lead removal was 86.17 % at 52.1 °C, 5.8 minutes and 0.05 g/ml of zeolite/oil ratio. The average errors of metal removal of the linear and quadratic main effects+2ways NFRSD model were 6.4 %, 15.2 %, and 4.0 %, for calcium, zinc, and lead, respectively.

ABSTRAK

Proses pengekstrakan daripada minyak pelincir terpakai menghasilkan enapcemar organik dan minyak dasar yang dipulih semula, tetapi minyak dasar ini mengandungi bahagian-bahagian logam. Bahagian-bahagian logam tersebut perlu disingkirkan untuk memperoleh minyak dasar yang sesuai untuk perumusan minyak pelincir yang baru. Dalam kajian ini, logam-logam seperti kalsium, zink, dan plumbum daripada minyak dasar yang dipulih semula telah disingkirkan dengan proses penjerapan. Parameter-parameter daripada penjerapan seperti nisbah zeolit/minyak, suhu, dan masa telah diselidiki. Ujikaji telah dibuat dengan menggunakan reka bentuk faktorial penuh (FFD) dan reka bentuk permukaan gerak balas bukan faktorial (NFRSD). Hasil ujikaji telah dianalisis dan dikembangkan dengan kaedah permukaan gerak balas (RSM) untuk memperoleh model-model empirik. Model-model tersebut adalah FFD tiada interaksi, FFD dua hala interaksi, NFRSD linear kesan utama sahaja, NFRSD linear kesan utama + dua hala, NFRSD linear dan kuadratik kesan utama, NFRSD linear dan kuadratik kesan utama + dua hala. Model yang sesuai telah dinilai dengan pekali penentuan dan analisis varians (ANOVA). Perbandingan kajian diantara model-model tersebut menunjukkan NFRSD linear dan kuadratik kesan utama + dua hala merupakan model yang terbaik. Model terbaik tersebut telah digunakan untuk memperoleh keadaan optimum daripada penyingkiran kalsium, zink, dan plumbum. Hasil ujikaji menunjukkan nilai tertinggi penyingkiran kalsium adalah 35.18 % pada 39.9 °C, 6.2 minit, dan 0.06 g/ml nisbah zeolit/minyak. Penyingkiran zink adalah 35.86 % pada 34.1 °C, 6.6 minit, dan 0.063 g/ml nisbah zeolit/minyak. Penyingkiran plumbum adalah 86.17 % pada 52.1 °C, 5.8 minit, dan 0.05 g/ml nisbah zeolit/minyak. Purata ralat penyingkiran logam daripada model NFRSD linear dan kuadratik kesan utama + dua hala adalah 6.4 % 15.2 %, dan 4.0 %, untuk kalsium, zink, dan plumbum.

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LIST OF SYMBOLS

a	-	number of levels
α		level of significance
Å	-	Angstrom
A_0	-	intercept
A_1	-	coefficient of linear effect for parameter *Z/O*
A_2	-	coefficient of linear effect for parameter *T*
A_3	-	coefficient of linear effect for parameter *t*
A_4	-	coefficient of interaction effect for parameter (*Z/O*) and *T*
A_5	-	coefficient of interaction effect for parameter (*Z/O*) and *t*
A_6	-	coefficient of interaction effect for parameter *T* and *t*
A_7	-	coefficient of square effect for parameter (*Z/O*)
A_8	-	coefficient of square effect for parameter *T*
A_9	-	coefficient of square effect for parameter *t*
β_0	-	independent term of regression equation
β_i (i=1, 2, . . ., k)	-	linear term of regression equation
β_{ii} (i=1, 2,. . ., k)	-	second-order term of regression equation
β_{ij} (i=1,2, . .., k ; j=1, 2, . . ., k)	-	interactive term of regression equation
C	-	concentration of metal after adsorption process
C_0	-	initial metal concentration
c	-	concentration
ε	-	error
ΔG^o_{ads}	-	standard free energy of adsorption
H_0	-	null hypothesis

H_A	-	alternative hypothesis
k	-	number of factors
MR	-	metal removal
µm	-	micrometer
N	-	total of observation
nm	-	nanometer
p	-	total of term in model
p	-	probability
q	-	amount adsorbed
r	-	effective radius of the adsorbed ions
R	-	gas constant
R^2	-	coefficient determination
$\overline{R}_{+,i}$	-	average values of Y for high (+) levels
$\overline{R}_{-,i}$	-	average values of Y for low (−) levels
SSE	-	sum squares of the residuals
SSR	-	sum of squares due to regression of the fitted model
SST	-	total variation in the data values
T	-	Temperature
t	-	time
U_{el}	-	electrostatic interaction
$X_1, X_2, \ldots X_k$	-	independent variables (factors), input variables
Y	-	dependent variable (response)
$Y_u s$	-	squares of the observed
$(\hat{Y}_u)$	-	value predicted by the fitted model
$\overline{Y}$	-	average value of Y
Z/O	-	Zeolite/Oil ratio
Γ_i	-	adsorption density

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variances
ASTM	-	American Society for Testing and Materials
FFD	-	Full Factorial Design
ICP	-	Inductively Coupled Plasma
IUPAC	-	International Union of Pure and Applied Chemistry
MEK	-	Methyl Ethyl Ketone
MPK	-	Methyl n-Propyl Ketone
NFRSD	-	Non-Factorial Response Surface Design
ppm	-	parts per million
RSM	-	Response Surface Methodology

CHAPTER 1

INTRODUCTION

1.1 Background of the Problem

Large quantity of used lubricating oil that is not being disposed of properly can degrade the environment. The re-refining of used oil is a better approach than dumping on the ground, in landfills and waterways. Normally, used oil contains about 75% recoverable base oil, higher than the base oil content of virgin crude oil, so the re-refining used oil requires less energy and has less of an impact on the environment (Voogd *et al.*, 2008). This re-refining process is carried out to remove contaminants. A large number of contaminants such as dirt, water, metals, incomplete products of combustion, or other materials, complicate the selection of appropriate treatment methods. Among the treatment methods proposed during recent years, solvent extraction process has received considerable attention from many researchers (van Grieken *et al.*, 2008) (Espada *et al.*, 2007) (Rincón *et al.*, 2007) (Coto *et al.*, 2006) (Rincón *et al.*, 2005a) (Hamad *et al.*, 2005) (Rincón *et al.*, 2003) (Elbashir *et al.*, 2002) (Wong and Wang, 2001).

Solvent extraction technology has the potential to produce oil products because this technology separates a large fraction of the impurities from the used oil. The bottoms from the solvent technology, which resemble a light asphalt product, may also be a marketable product such as asphalt. The solvent extraction process have many advantages, nevertheless, the recovered base oil still contains metals (Rincon *et al.*, 2005b). The list of metallic content of solvent extraction product is presented in Table 1.1.

Table 1.1: Metallic content of solvent extraction product

Solvent	Metallic Content (ppm)			References
	Zn	Fe	Pb	
2-propanol	333	11	246	- Lide, 1994 - Smallwood, 1996
2-butanol	666	19	282	- Lide, 1994 - Smallwood, 1996
2-pentanol	700	20	487	- Lide, 1994 - Smallwood, 1996
Methyl Ethyl Keton (MEK)	688	13	350	- Lide, 1994 - Smallwood, 1996
Methyl n-Propyl Ketone (MPK)	936	18	443	- Lide, 1994 - Smallwood, 1996
Mixture of 2-propanol /MEK with KOH	155	23	163	Rincon *et al.*, 2005b
Propane	390	13	290	Rincon *et al.*, 2003
Mixture of 2-propanol/ n-hexane with KOH	312.56	69.13	0.10	Lim, 2001

The metallic compounds are important used oil components that should be removed to obtain base oil suitable for the formulation of new lubricants. A few familiar methods in practice for removal of metals are chemical precipitation, ion exchange, solvent extraction, reverse osmosis, and adsorption. The process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and simple (Tran *et al.,* 1999). Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost (Mohanty *et al.,* 2006).

Adsorption is a popular method for the removal of heavy metals from the waste water (Omer *et al.,* 2003; Heping *et al.,* 2006), particularly when natural materials that are available in large quantities or certain waste products from industrial or agricultural activities may have potential as inexpensive sorbents (Bailey *et al.,* 1999). Examples include dead biomass, blast furnace slag, fly ash, clay, tree bark, tea leaves and natural zeolite (Krishna and Susmita Sen, 2006; Ahmet *et al.,* 2007; Bailey *et al.,*1999).

Zeolites are naturally occurring alumino-silicates with a 3 dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra. These are linked to each other by sharing all of the oxygen to form interconnected cages and channels (Englert and Rubio, 2005). Zeolites with their chemical, physical and structural characteristics are suitable for a number of applications in various fields such as adsorption, separation, ion exchange and catalysis (Aiello *et al.,* 1980; Dwyer and Parish, 1983; Blanchard *et al.,* 1984; Mulligan *et al.,* 2001). The use of natural zeolite as an adsorbent has gained interest among researchers; mainly because its sorption properties provide a combination of ion exchange and molecular sieve properties which can also be easily modified (Cincotti et al., 2006).

In this study, adsorption of metals using zeolite with conventional method (one of the parameters is varied while maintaining other parameters fixed) was investigated. This method usually involves many experimental runs, ignoring interaction effects between the factors and low efficiency in process optimization. The limitations of this method can be avoided by applying the response surface methodology (RSM) (Cojocaru and Trznadel, 2007).

1.2 Statement of the Problem

The solvent extraction technique is a method for refining of used lubricating oil. In the end, extraction process produces organic sludge and the recovered base oil, but this oil is darkish in colour and has metallic content. The metals are important components that should be removed to obtain base oil suitable for the formulation of new lubricants. The adsorption process has become one of the preferred methods for metal removal from water as it has been found to be very effective, economical, versatile and simple.

1.3 Objectives of the Study

The aim of this study was to remove metal from recovered base oil using zeolite. This can be achieved by the following specific objectives:

i. To investigate the effects of parameters on the adsorption of metals from recovered base oil using zeolite.
ii. To obtain the empirical models of the metal removal.
iii. To predict the optimum condition of the metal removal.

1.4 Scopes of the Study

This study focused on the adsorption of metals (calcium, zinc and lead) from recovered base oil using zeolite as an adsorbent. The recovered base oil was prepared from the refining used lubricating oil by solvent extraction. The 2-propanol and methyl ethyl ketone (MEK) were used as composite solvent and the potassium hydroxide (KOH) was used as flocculating agent. The effects of parameters investigated were zeolite/oil ratio, temperature, and time. The significances of effects were also analyzed. The experiment was carried out using the Full Factorial Design (FFD) and Non-Factorial Response Surface Design (NFRSD). The results of experimental were analyzed and developed by Response Surface Methodology (RSM) to obtain the empirical models. They were the FFD no interactions model, the FFD 2 way interactions model, the linear main effects only-NFRSD model, the linear main effects+2ways-NFRSD model, the linear/quadratic main effects-NFRSD model, and the linear/quadratic main effects+2ways-NFRSD model. The goodness of fit of the model was evaluated by the coefficient determination (R^2) and the analysis of variances (ANOVA), so the best model was obtained. The best model was used to predict the optimum condition of the calcium, zinc and lead removal.

1.5 Research Contributions

The research contributions are as follows:

i. The new finding about effects of parameters on the adsorption of calcium, zinc, and lead from recovered base oil using zeolite.
ii. The new empirical models of calcium, zinc, and lead removal from recovered base oil.
iii. The optimum condition for calcium, zinc, and lead removal from recovered base oil predicted from the best model.

1.6 The Organization of Thesis

This thesis is organized into five chapters. Chapter 1 consists of background of the problem, statement of the problem, objectives of the study, scopes of the study and research contributions. The background of the problem presents an overview of the re-refining used oil, the metal content from solvent extraction product, and the methods of metal removal.

The fundamental theory and literature review about adsorption, adsorbent, zeolite, equilibrium, slurry adsorption, waste oil recycling, metal removal, metal removal by zeolite, factorial design, Response Surface Methodology (RSM) and statistical analysis are presented in Chapter 2.

Chapter 3 presents the research methodology used in this study, consist of material and equipment, experimental procedure, data analysis, Full Factorial Design

(FFD), Non-Factorial Response Surface Design (NFRSD), prediction of the optimum condition of metal removal, and overall flow diagram.

Chapter 4 presents the results of the experimental studies that have been described in Chapter 3. Findings are combined and discussed holistically in this chapter. The last chapter, Chapter 5, stated the conclusions of this study. Recommendations for future studies are also outlined in this chapter.