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Optimization of acidic activated conditions for natural clay and its application in waste oil bleaching

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Abstract

The used oil regeneration using extraction technique has been widely known as one of the cheapest and most competent processes. This research study the effect of activated clay treatment by nitric acid .The effects of some important factors such as acid concentration and contact time were studied on natural clay. The used oil treated by using solvent mixtures, (xylene+butanol+methanol) at solvent: oil ratio 3:1 followed by bleaching on activated alumina and activated clay adsorbent material to generate base oil. The characterization and physico-chemical properties show that the refined oil adsorbed by activated clay has good properties by comparing to activate alumina.

Keywords: waste engine oil, Recycling process, solvent extraction and adsorption technique

Introduction

Lubricating oil that has good characteristics shows a very major role in the industry. Lubricants used in internal combustion engines could be offended by various strains, depending on operating conditions, fuel quality, ambient conditions and operating parameters (Ko,Y.G.,2006),(Kamal,A.,2009).Without the suitable treatment, the used lubricating oil will be subject to be discarded that degrades the environment (Ogbeide,S.O.,2010),(Hamad ,A.,2005). So, recycling and rerefining of waste oil into fresh lubricating oil may be auditable choice for protecting the environment from hazardous waste. Another benefit associated with waste lubricating oil recycling could be the economic gain due to the high cost (Sadeek A. Sadeek, 2014).Different techniques have been accomplished for refining waste oil such as chemical (acid/clay) treatment, physical treatment by distillation and thin film evaporation, and solventextraction(Manasomboonphan,W.,2012),(Bal adincz,,J.,2008),(Bridjianian,H., 2006),(ElsayedA.E.,2016).

The mainly types of process that's used in Italy are under vacuum distillation and hydrogenation process, where 93% of collecting oil is recycled by these system technologies. This represents 175,700 t of oil per year60% of the resultant products are base oils and 8% are light oils (Eman A. Emam ,2013),(Kaewsaiyoy.A,2003).

Between the alternative processes proposed during recent years, a solvent extraction process has gotten significant consideration. It is a simple process which

used oil and solvent are blended in appropriate proportions to assure complete miscibility of the base oil in the solvent. The extracting solvent should also remove the additives and carbonaceous impurities normally found in waste oils (El Din.O.I.S,1987).The performance of 1-butanol and methyl-ethyl-ketone (MEK), 2-propanol in recycling waste oil was investigated experimentally (Elbashir,N.O.,2002),(Al-Zahrani S.M.,2013),(Katiyar,V.,2010) .The results showed that the solvent extraction technique is an efficient process in recovery of waste oil. The lowest percent oil loss as well as the best performance was achieved by the use of MEK. Extraction with MEK and n-hexane followed by adsorption on magnetite gives the lowest color index oil. This method, however uses two solvents and thus requires two solvent recovery steps (Kamal,A.,2009),(Abro,R.,2013). The acid clay recycling process uses sulfuric acid of high concentration to remove the asphaltic materials. It generates acid sludge and adverse material that is very difficult to dispose off (Muller Association,1989).

The propane extraction process uses liquefied propane to recycle the lubricating oil from used oil (Saunders. J.,1996).Natural clay is used as adsorbent in the bleaching of used oil. Clay has been activated and dried up. There are mainly two clay treatment methods. These are achieve by combination treatment and percolation or filtration through a bed of adsorbent (Josiah.P.N,2011).

One of the aggressive processes for refining of waste lubricating oil is solvent extraction followed by adsorption . Solvent selected should have highest

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solubility for base oil and lowest of additives and carbonaceous matter. The solvent could be recovered by distillation (Durrani H.A., 2012).The chemical treatment applied to certain types of clay to develop their capacity to absorb coloring matters and other contamination in the oils (Euphrosine Ujeneza ,2014).

In the present work, the solvent extraction treatment followed by adsorption is carried out on used oil. The application of an adsorption process using adsorbent material such activated alumina and activated clay were investigated.

Experimental

1.Sample collection and Material used in the study :

Used engine oil (Total Quartz 9000) was collected from oil service station in Egyptian petroleum research institute (EPRI). All the chemical reagents (purchased from Merck Co., Aldrich and Fluka chemical Co.) were of analytical grade and used without further purification (Xylene, 1-butanol,methanol, ethanol, iso propanol and cyclohexane),nitric acid ,methylene blue ,alumina, and natural clay.

2.Refining process of used oil sample:

2.1.Solvent extraction process:

One extracting solvent mixture = (xylene+1-Butanol + Methanol), is treated individually with used engine oil sample at oil: solvent ratio (1:3)(ElsayedA.E.,2016).

3.Activation of alumina :

The raffinated oil obtained by solvent extraction was treated by neutral alumina which activated at 300 °C for 24 hours.

4.Acid activation of clay:

Natural clay is purified by thermal activation process by heating at temperature 110 °C for 24 hours to remove water and impurities.

Prepare different concentration of nitric acid (1,3and 4mol per L). Dry clay was mixed with first concentration of acid (1mole) at clay: acid ratio 1:3 with constant stirring at 200 rpm for 20 min. at 40° C. The mixture was filtered under vacuum and washed by distilled water several times until the filtrate was free of nitrate ions. The sample was dried at 105°C for 48 hrs and ground to a particle size that passed through 200 mesh sieve. This procedure was repeated with (3 and 4 mole per L) acid concentrations and at different times (60 to 100min) and at different temperature (60° to 80°C). Methylene Blue (MB) test is a measurement of the adsorption of methylene blue dye on clay.

5. Determination of properties of clay:

5.1. Fourier Transform Infrared Spectroscopy (FTIR):

Infrared spectra was carried out for natural and activated clay perkin Elmer spectrum one (56027).

5.2. X-Ray Diffraction(XRD):

Characterization of natural and activated clay samples were performed by X-ray diffraction(X

pert pro P Analytical) with Cu Kα radiation (λ=0.1542nm) operated at 40kV and 20mA. X-ray diffraction mineral identification was carried out by comparison with the JCPDS files (1985).
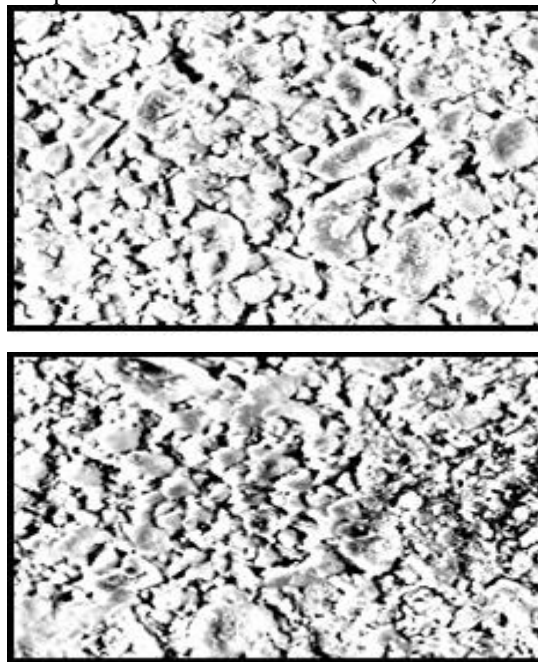

Fig. (1):(a)SEM of natural clay, (b) SEM of activated clay

5.3. Scanning Electron Microscope(SEM):

Investigations of crystal morphology and chemical composition of the clay samples (SEM/EDAX analyses). Samples were carried out using a JEOL JSM-5300 scanning electron microscope. The accelerating potential was 15 kV, the beam current 20 mA.

5.4. Surface analysis using N_2 adsorption technique:

The textural properties were determined from the N_2 adsorption-desorption isotherms at liquid nitrogen temperature (-196ºC) using NOVA 3200 S Unite, automates gas sorption analyzer (Quantachrome Corporation) system. The pore size distributions were determined from Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the isotherm.

5.5. pH and surface acidity and basicity of clay :

The solution pH of the adsorbent was carried out in 60 cm3 glass bottle where 2.5 g of the adsorbent and 25 cm3 of deionised water were added. The mixture was then agitated shaking water bath, for 24 hrs. The pH of the mixture was recorded using a (HANNA pH 213 instruments microprocessor pH meter) and was determined using ASTM D-3838

6.Bleaching of refined oil sample :

6.1. Bleaching of refined oil sample by alumina and activated clay:

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Neutral alumina and activated clay 200 mesh sieve are activated. The refined oil sample after solvent Extraction process are treated with alumina and activated clay at oil : alumina or clay ratio 1:15 in open glass column 150cm in length and 5cm in diameter.

7.Determination of physico-chemical properties of used and refined oil samples:

Physico-chemical properties of used oil sample , refind oils obtained from solvent extraction at ratio3:1 and base oil obtained after bleaching with alumina and active clay are carried out according to ASTM, IP methods (ASTM,2000),(IP,1999).

Result and discussion

1. Physico-chemical Properties of used and re-refined oils after
   solvent extraction and alumina treatment:

The physico-chemical properties of the used oil and its refined oil were determined according to the standard method of analysis in ASTM and IP. The physical properties of the used oil investigated in this work are represented in Table (1). It is clear that the flash point and pour point are low (102°; -15°C) respectively the decrease of them is a reliable indicator that the oil has become contaminated with volatile product such as gasoline and water. Oxidation of used oil would result in the formation of volatile component which leads to decrease the flash points and pour points. The viscosity of the used oil is high (192.82 CST at 40°C) this indicates that the presence of contamination in used oil. The oxidized and polymerized products and suspended substances in the oil may cause an increase of the oil viscosity. As the base oils are subjected to elevated temperature, the process of oxidation occurs. Oxidation leads to the formation of organic acids in the engine lube oil. Total acid number is high (2.46 mgKOH/g) as shown in table (1). Metallic particulates enter the used oil as a consequence of the breakdown of oil-wetted surfaces due to ineffective lubrication, mechanical working, abrasion erosion and/or corrosion. Zinc concentration in the used oil 842.37 ppm as shown in Table (1). The added to the base oils as part of multifunctional additives for improving the oil's performance. The amounts of metals are in the range of 2.55g for Ni, 3.431 for Pd, 7.525 for Cu, 15.973 ppm for Cr and 35.004 ppm for Fe) while Mg and Zn are present in a few hundred ppm (263.18 ppm and 842.37 ppm) respectively. The physico-chemical properties of the base oil obtained by recycling of the used oil with a

solvent mixture improved. The results are represented in Table (1). The refined base oil possesses good pour point. It can be seen an increase in flash points and viscosity index (VI) (256°C) for a solvent mixture as given in Tables (1). The optimum improvement in physical properties reaches at solvent/oil ratio 3:1 .The base oil obtained by solvent mixture was treated with activated alumina at 300°C for 3 hours. The results are represented in Table (1). It is clear that there is improvement in physical properties and The kinematic viscosity , total acid number, sulfur content, water content, ash content and carbon content decreases. Also the result shows that the metallic content of the base oil disappeared. this is due to that the solvent produce a larger dilution of the additives that stabilize waste oil impurities.

2.Chemical analysis of clay:

The physical properties of natural and activated clay samples were determined by using chemical analysis, XRD and N_2 adsorption-desorption data, SEM and IR.

2.1.The surface properties:

The adsorption of pollutants in various matrices depends on the basicity and acidity values of adsorbent surface. The results are represented in Table (2). It is clear that the rise of surface area from 49.577 m^2/g for natural clay to 67.789 m^2/g for activating clay. Also, the total pore volume is 0.1183 cm^3/g for natural clay increased to 0.1307 cm^3/g for activating clay. This is a result of the chemical changes which occurred in the mineral structure of clay. The acid treatment decomposes the impurities and the basic cations between the layers of clay forming empty spaces.After acid activation for clay, its acidity increased to 32 ml of NaOH/gm clay and its pH is 2.61 it is strongly acidic .

2.2.SEM

SEM investigates of crystal morphology and chemical composition of the clay samples and improves activation of the clay surface.

2.3.XRD analysis:

The results in Figs (2b), indicate that the activated clay with nitric acid causes the change in the chemical compositions of natural clay. There is a removal of calcium, sodium (Montmorillonite), aluminium silicate hydroxide. This may be due to the expected exchangeable cation such as Ca^{+2}, Mg^{+2} and Al^{+3} are removed during the acid treatment. However, some part of these elements remain in the activated clay as shown in Fig .(2a)

Table (1): Physico-chemical properties for refined oil obtained by extraction method using solvent mixture xylene, butanol and methanol at ratio (1:1,1:3 and1:5)) vol. at 70 °C

Test	ASTM	Used oil	Ratio 3:1	After alumina
Denisty@ 15.56°C	IP190	0.9077	0.8610	0.852
Kinamatic viscosity, cSt,				

@40°C	D-445	192.82	100.97	90.6
@100°C		18.82	13.21	12.4
Viscosity index	D-2270	109.48	128.547	131. 733
Flash point, °C	D-93	102	256	315
Pour point, °C	D-97	-15	-3	-3
TAN,mg KOH/g	D-664	2.461	0.364	0.1651
Sulfur content, wt %	D-4294	1.24	0.51	Nil
Water content, ppm	D-6304	2405.115	50.485	Nil
Ash content, wt %	D-482	1.17	0.11	Nil
Carbon residue, wt %	D-189	1.65	0.21	Nil
Sludge content, wt %	D-4310	5.8	2.01	Nil
Metal analysis ,ppm				
Fe	Atomic	35.004	Nil	Nil
Cu	absorption	7.525	Nil	Nil
Cr	Analysis	15.973	Nil	Nil
Ni		2.559	Nil	Nil
Pd		3.431	Nil	Nil
Mg		263.18	9.414	Nil
Zn		842.37	5.34	Nil

2.4. IR spectra:

To study the effect of acids on the natural clay IR spectra were carried out in the range of 400-4000 cm^{-1} as represented in Figs.(3) .The natural clay is shown in Figs. (a) two peaks in the OH–stretching region. The band at 3635 cm^{-1} corresponding Al–OH and Mg–OH vibration. A wide band observed at 3417cm^{-1} assigned to the high amount of water absorbed by the clay. The band appeared at 1638 cm^{-1} corresponding to the bending vibration of physical absorbed water. The weak band at 1384 cm^{-1} is corresponding to (Si-) CH$_3$. The broad band at 1051 cm^{-1} is corresponding to the hydrous Si-O stretching vibrations. The band at 795cm^{-1} is related to cristobalite. The IR spectra shows band at 623cm^{-1} is attributed to the vibration in the octahedral layers such as Al–O–Si and Mg–O–Si. The band at 522 cm^{-1} was related to Si–O–Al and band at 467 cm^{-1} was assigned to Si–O–Si bending vibrations.

The IR spectra of activated clay as given in Fig. (b) shows little change in the intensity of OH$^-$ stretching region decreased. The band at 1384 cm^{-1} disappeared. The band at 1384cm^{-1} disappeared.
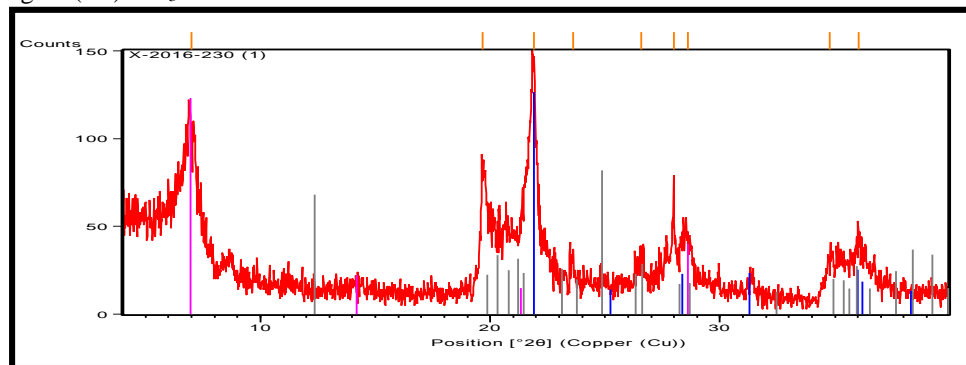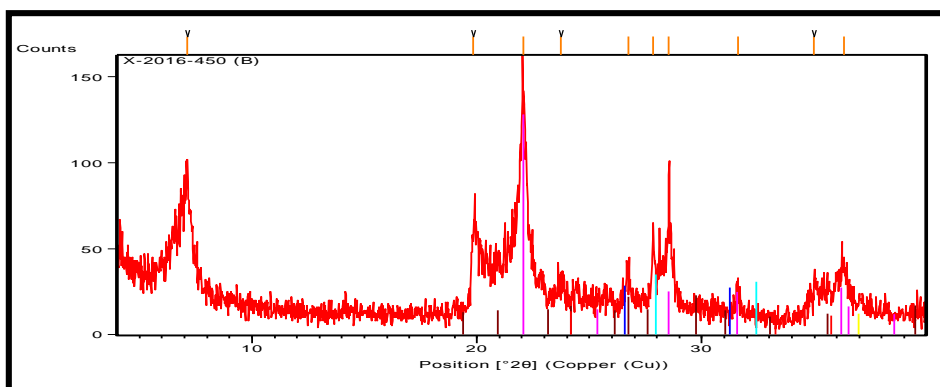

Fig (2):(a) XRD of natural clay

Fig (2) :(b) XRD of activated clay
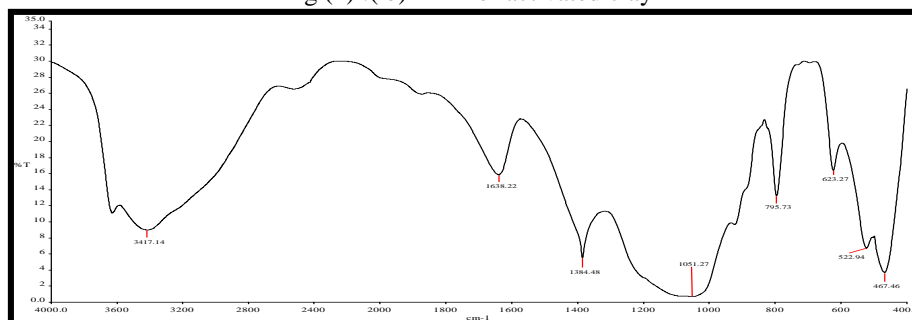

Fig (3) :(a) IR of natural clay
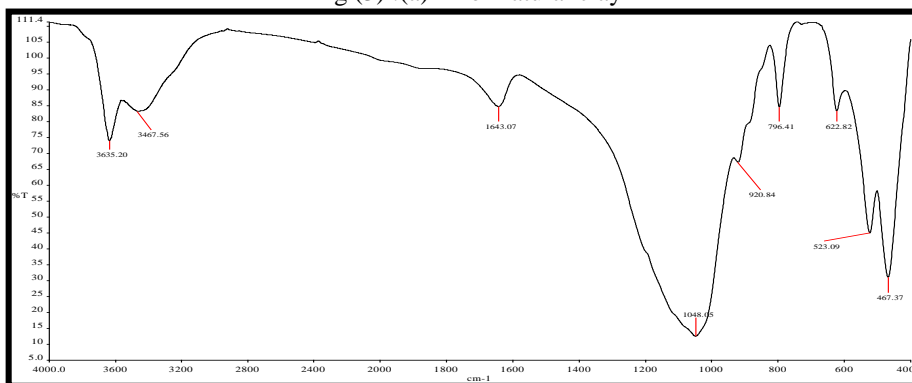

Fig (3):(b) IR of activated clay

3.Factors affecting on acid activation of clay:
3.1. Effect of Acid concentration on absorbance of MB :

The ultraviolet-visible spectra were obtained between 200-1200 nm for methylene blue and oil samples. The initial and final concentrations of (MB) absorbance were determined as shown in Tables (3-5).The results in Table (3) indicate that the final concentration of MB absorbed on natural clay is 31.54 ppm. The reduction in absorbance of MB is observed from 3.154 to 2.30 ppm by increasing concentration of nitric acid from 1 mole/L to 4 mole/L. This is due to that the acid showed a significant effect on chemical composition of clay the higher concentration of acid enhances the removal of some metal content.

It is found that the percent removal of MB of natural clay is 21.15 wt% and increased with increase acid concentrations reach maximum 94.25 wt% at acid concentration 4 mole/L as shown in Table (3) and Fig. (4).

3.2.Effect of time on absorbance of MB dye:

The effect of time on the absorbance of MB on the activated clay was investigated in the range of 20-100 min and the acid concentration kept constant at 4 mol/L and at temperature 80°C as shown in Table (3).It is clear that as the time increase from 20-100 min. the concentration of MB on the clay surface decrease. From 10.32 to 2.3 ppm respectively . The maximum absorbance of MB was achieved during 20 min as shown in Table (4). The percent of MB removal was calculated. It is found that the amount of MB removal increased from 74.2 to 94.25 wt% with increasing time from 20 to 100 min. as given in Table (4) and Fig. (5). This means that the time of activation of clay play an important role in this system in general, an increase in time of activation the percent of MB removal increase.

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3.3.Effect of temperature on the absorbance of MB dye:

The effect of temperature on the absorbance of MB on the activated clay was studied in the range of 40 to 80°C with acid concentration 4 mol/L at time 100 min. It is found that the concentration of absorbed MB on activated clay decreased from 6.59 to 2.3 ppm with increase temperature from 40°C-80°C respectively.

The calculated MB removed indicate that it increased from 83.52 to 97.25 wt% with increasing temperature from 40°–80°C respectively as represented in Table (5) and Fig. (6). This improve of MB removal was probably due to the increase of kinetic energy of the molecules with increase of temperature which enhanced the contact between clay surface and acid leading to more adsorption of MB.

Table (2): Physical properties of natural and activated clay

Clay type	Pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Acidity (ml of NaOH/gm clay)	Basicity (ml of HCl/gm clay)	PH
Natural	0.77	49.5m	0.1183	-	6.08	8.5
Activated	0.95	67.79	0.1307	32	-	2.61

Table (3): Effect of acid concentration on absorbance of dye

Acid concentration,ppm	Final concentration of MB, ppm	Percent of removal %
zero	31.54	21.15
1	6.36	84.1
3	4.95	87.625
4	2.30	94.25

Table (4): Effect of time of activation on absorbance of MB

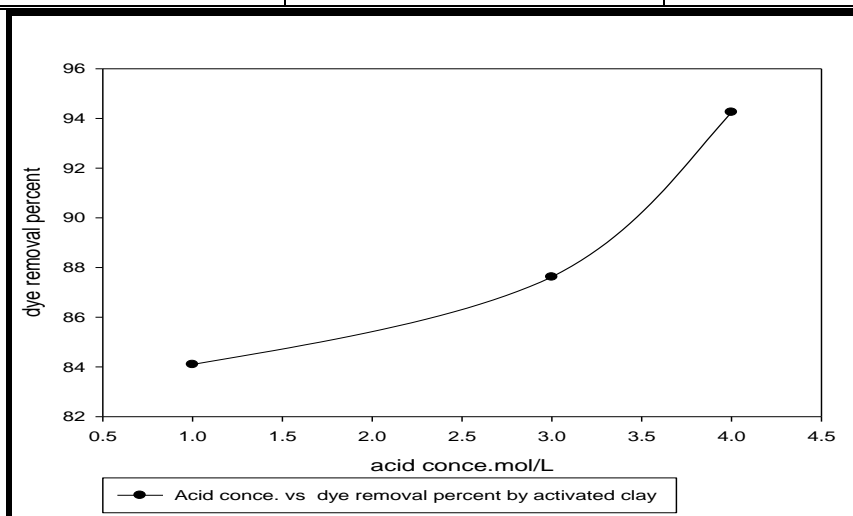| Time, min	Final concentration of MB,ppm	Percent of removal%
20	10.32	74.2
60	6.15	84.62
100	2.30	94.25

Fig (4): Effect of acid concentration on absorbance of MB

3.4.Absorbance of MB on natural clay and activated clay at optimum conditions:

Fig. (7) indicates the effect of acid activation of natural clay on the adsorption of MB at acid concentration 4 mol/L, time 100 min. at temperature 80°C, It is clear that the adsorption of MB increased by 73% as compared with natural clay. This is due to that the broken metal –OH of clay crystal structure produce negative charge in the clay structure and the MB cation can easily adsorbed.

3.5. Effect of clay ratio on absorbance of MB:

The effect of clay/MB ratios on the absorbance of MB was represented in Table (6). The results indicate that the final concentration of MB on natural clay was 31.54 ppm. After treatment of clay with nitric acid at different ratios (1: 3 to 1:10), the concentration of MB decreased to reach minimum value 2.3 ppm at clay /MB ratio 1:10. The calculated percent of MB removal indicate that the adsorption of MB increased quickly to clay/MB ratio 1: 3. After that the adsorption increased slowly till reach maximum value 94.25 wt% at clay/MB value 1:10 as shown in Fig. (8). This may be due to the increase in available adsorption active sites.
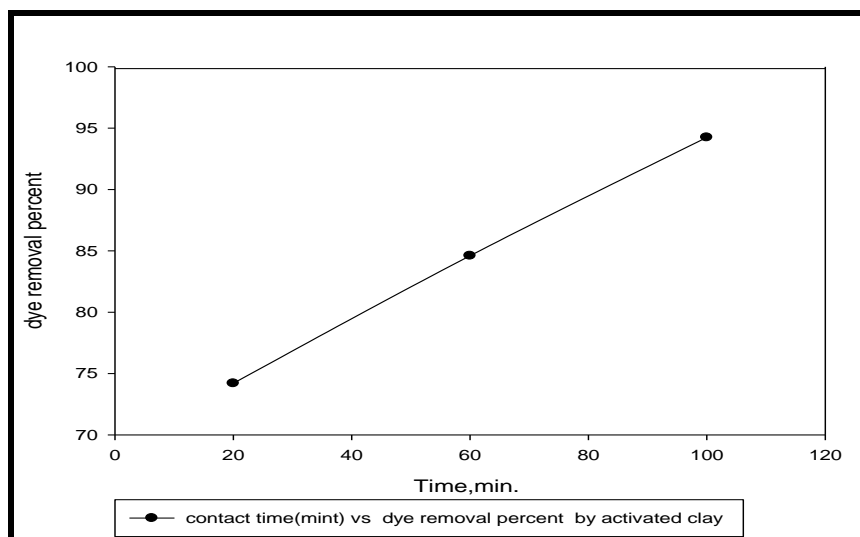
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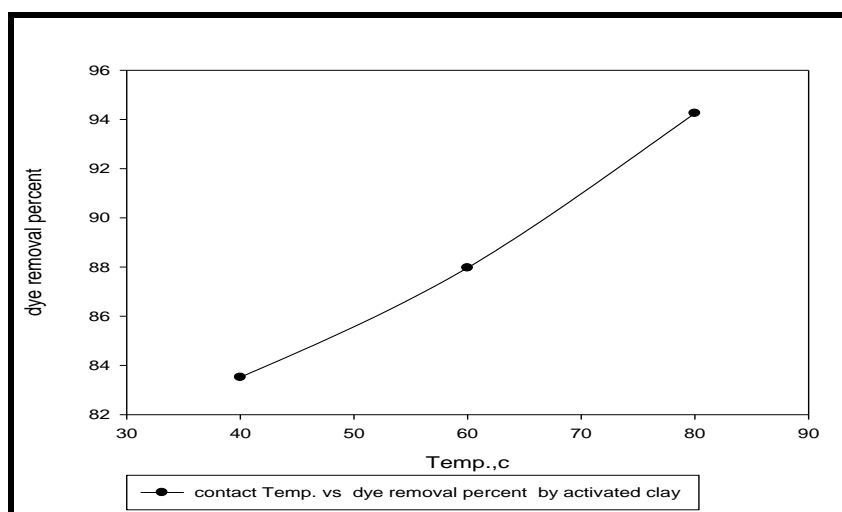Fig. (5) Effect of time of activation on absorbance of MB

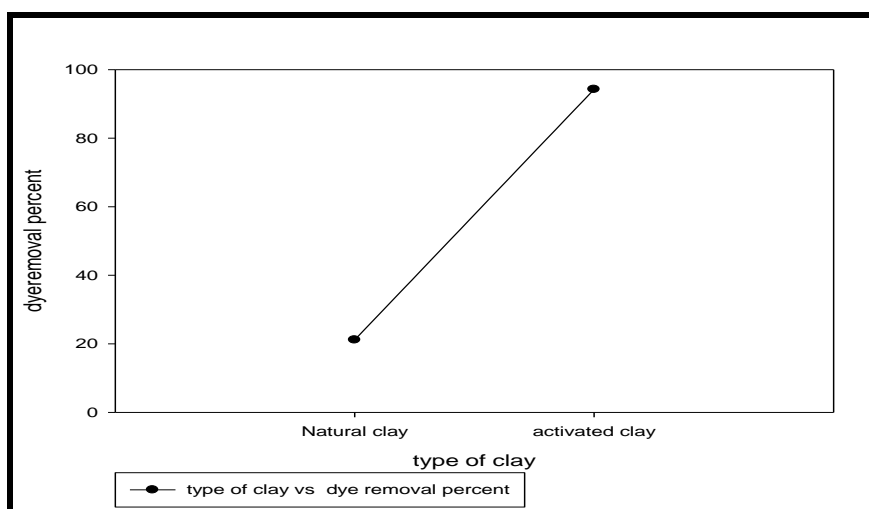Fig. (6) Effect of temp. of activation on absorbance of MB

Fig (7): Comparison between MB removal percent by natural and activated clay

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3.6. Moisture content for clay activated by different acid concentration:

The results in Table (7) indicate that the natural clay contains 4.25 of moisture content. This is due to that the layer of natural clay are kept together by relatively weak forces, polar molecules e.g. (water) can penetrate in the interlayer gap as shown in Fig.(3) of IR. It is found that the moisture content increased first with increasing acid concentration reach maximum value (4.82) at 1 mol/L of acid. This is because the acid increase the capacity of clay to hold water as given in Table (7) and Fig. (9). After that the moisture content decreased as the acid concentration increased reach minimum value (2.31) at acid concentration 4 ml/L as shown in Table (7) and Fig. (9). This is due to the increase of porosity after partial loss of exchangeable metal ions by hydrogen ions which have smaller volumes than the metal ions.

3.7. Effect of clay oil ratio on bleaching efficiency of refined oil:

The refined oil obtained by using solvent extraction process with xylene + butanol and methanol at solvent oil ration 3:1 vol. was treated with natural and activate clay with nitric acid at optimum conditions. The influence of acid concentration of activated clay on UV-absorbance of refined oil was studied by obtaining the peak intensity at maximum wave length λ_{max} (510 nm). The results obtained were represented in Table (8). It is clear that as the oil/clay ratio increased from 1:1 to 1:15 the absorbance decreased linearly from 4.72 to 0.85. as given in Table (8). The UV absorbance of oil refined by activated clay is lower as compared with that of natural clay. This is due to the higher specific surface area and the interlayer spacing. This data indicates that the acid concentration plays an important role in the adsorption capacity.The data are represented in Table (8) and Fig. (10). It is found that the bleaching efficiency increased sharply with increase of oil/clay ratios from 1:1 to 1:10 ratio after which littel increase in the bleaching efficiency reach 87.53 at oil/clay ratio 1:15 as shown in Fig. (10). This is due to the adsorption equilibrium has been reached between the oil/clay mixture, thereby preventing further impurities removal by the excess clay content .Fig. (11) shows the comparison between the bleaching efficiency of natural and activated clay with nitric acid. It is clear that the bleaching efficiency of activated clay is higher than that of natural clay. There is about 69% increase in the bleaching efficiency by activated clay.

4.10. Physico-chemical properties of refined oil after treatment with activated clay:

Table (9) show comparison between the results of analysis of refined oil after treatment with alumina and that those with activated clay, The physico-chemical analysis of refined oil after treatment with activated clay at temperature 80°C for time 100 min and acid concentration 4 mol/L. The results indicate the improvement in all properties. Density (0.803 mg/L) viscosity index (139.29), flash point (325°C), pour point (–3°C) and TAN (0.071 mg KOH/g)., and the result show complete removal of metal. It is clear that the refined oil treated with activated clay shows the best properties for performance. Also, the results show that the physical properties of refined oils treated with alumina and activated clay fall with the specification of the fresh oil.

Table (5): Effect of temperature of activation on absorbance of MB

Temperature, °C	Final concentration of MB, ppm	Percent of removal%
40	6.59	83.52
60	4.81	87.97
80	2.30	94.25

Table (6): Effect of clay MB ratio on absorbance of dye

Clay/ MB ratio	Final concentration of MB, ppm	Percent of removal%
zero	31.54	21.15
1:3	11.45	71.35
1:5	7.81	80.47
1:10	2.3	94.25

Table (7): Effect of acid concentration on moisture content

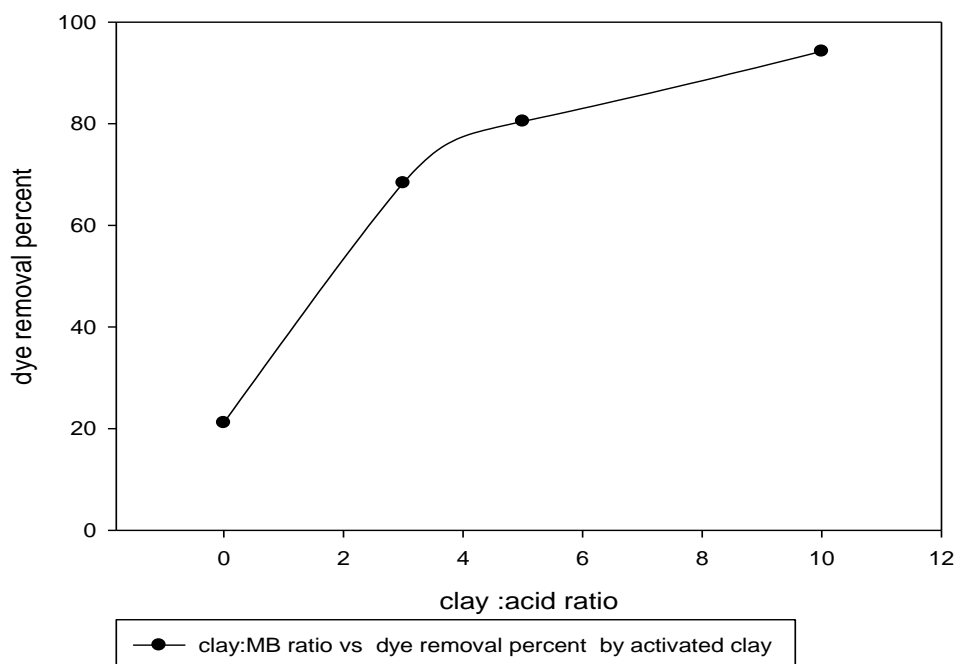| Acid concentration	Weight after drying gm	Moisture content%
Zero	0.0425	4.25
1	0.482	4.82
3	0.0313	3.13
4	0.0231	2.31

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Fig (8). Effect of clay MB ratio on absorbance of dye

Table (8): Effect of clay oil ratio on bleaching efficiency of refined oilAbsorbance of unbleached oil=6.85nm

Oil /clay dose	Absorbance of bleached oil	Bleaching efficiency
Natural clay	5.62	17.95
1:1	4.72	31.09
1:5	3.42	49.75
1:10	1.32	80.64
1:15	0.85	87.53

Table (9): Physico-chemical properties of regenerated oil according to the Egyptian organization for standardization and quality (EOS).

Test	Used Oil	regenerated oil after alumina treatment	regenerated oil after activated clay treatment	Fresh oil according to (EOS)
Denisty@15.56°C	0.9077	0.852	0.803	0.841
Kinamaticviscosity,cSt				
@40°C	192.82	90.6	92.2	92.8
@100°C	18.82	12.4	13.1	12.5
Viscosity index	109.48	131. 733	139.291	125
Flash point, °C	102	315	325	268
Pour point, °C	-15	-3	-6	-9
TAN,mg KOH/g	2.461	0.1651	0.071	0.1
Sulfur content,wt %	1.24	Nil	Nil	Nil

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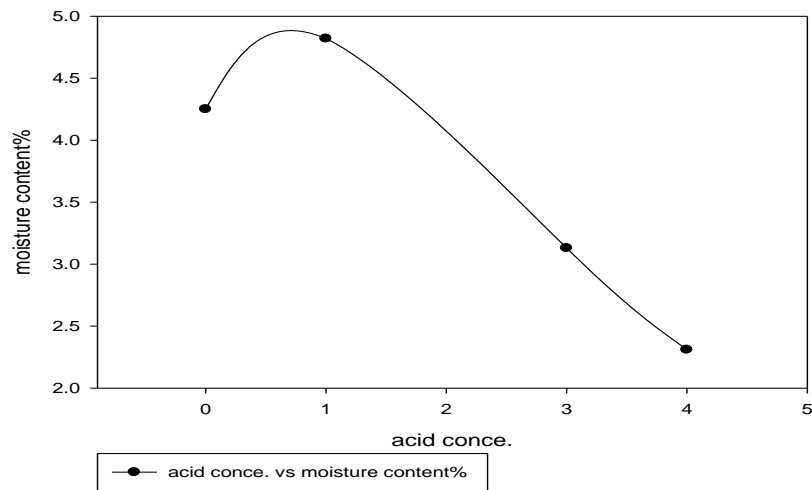| Water content,ppm	2405.115	Nil	Nil	Nil
Ash content,wt %	1.17	Nil	Nil	0.05
Carbon residue,wt %	1.65	Nil	Nil	0.05
Sludge content,wt %	5.8	Nil	Nil	Nil
Metal analysis,ppm				
Fe	35.004	Nil	Nil	Nil
Cu	7.525	Nil	Nil	Nil
Cr	15.973	Nil	Nil	Nil
Ni	2.559	Nil	Nil	Nil
Pd	3.431	Nil	Nil	Nil
Mg	263.18	Nil	Nil	Nil
Zn	842.37	Nil	Nil	Nil

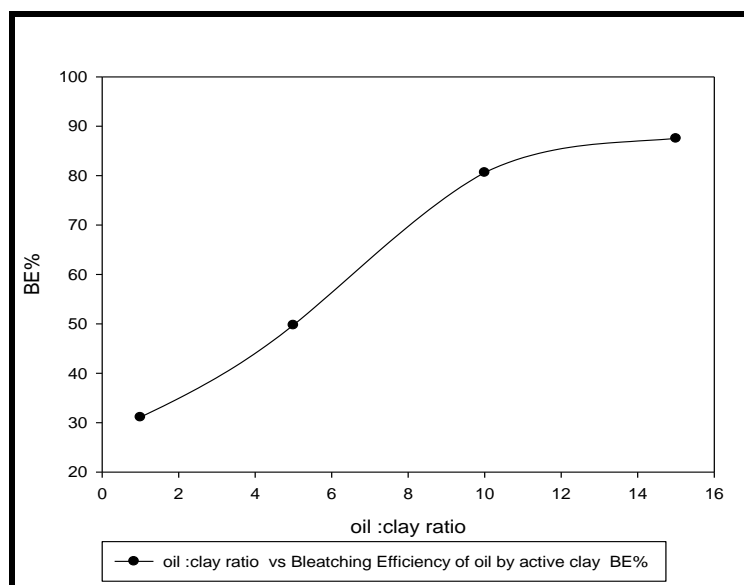Fig. (9): Effect of acid concentration on moisture content of activated clay

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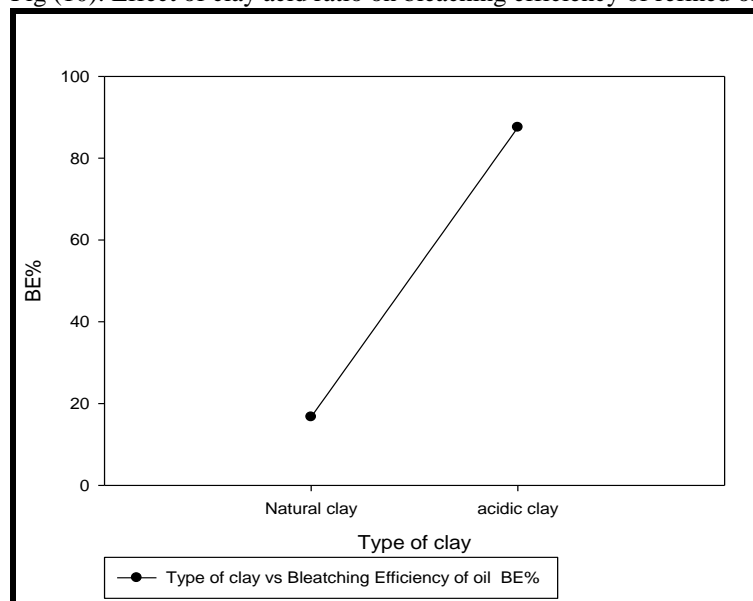Fig (10): Effect of clay acid ratio on bleaching efficiency of refined oil

Fig. (11): Comparison between the bleaching efficiency of natural and activated clay

Conclusion

- This study was carried out on Used engine oil(Total Quartz 9000) was collected from oil service station in EPRI. The re-refining processes were studied, namely: solvent extraction/adsorption processes .
- It is clear that the physico-chemical properties of the re-refined base oil obtained by solvent mixture after treatment with activated clay more performance than the re-refine base oil obtained after treatment with activated alumina.
- The re-refined base oil obtained by solvent mixture after treatment with activated clay and activated alumina are fall with the specification of the base fresh oil .

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