LIQUID-LIQUID EXTRACTION AND ADSORPTION ON SOLID SURFACES APPLIED TO USED LUBRICANT OILS RECOVERY

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Abstract - In this work, the recovery of base oils from waste lubricants following the steps of solvent extraction, adsorption on solids and solvent removal by evaporation was evaluated. In the step of solvent extraction, the most efficient was 1-butanol, followed by tert-butanol, 2-propanol and ethanol; for the step of adsorption, activated carbon was the most effective solid for PAH removal, confirming the similarity of these compounds with petroleum aromatic fractions. Thus, the optimum solvent-adsorbent pair for the recovery of used lubricant oils through the proposed methodology was 1-butanol/activated carbon. At the end of the process, it was possible to establish a set of steps that permit the recovery of lubricant base oils with lower content of contaminants.
Keywords: Lubricant oils; PAHs; Recovery; Adsorption; Solvent extraction.

INTRODUCTION

Lubricant oil degradation under working conditions occurs mainly due to oxidation and thermal decomposition at high temperatures, changing its original composition and generating suspended particles (lees), a fact that endangers its lubricant capacity (Raadnui and Kleesuwan, 2005; Rincón et al., 2007; Santos et al., 2004).

Waste automotive lubricant oils present in their composition non-oxidized base oil, which can be extracted; not yet consumed additives; organic acids; polycyclic aromatic hydrocarbons (PAHs); residual metals from machines and stressed motors such as lead, chromium, barium and cadmium; water from the combustion chamber or from the accidental contamination of the lubricant oil or, worst yet, from chemicals that sometimes are unscrupulously added

(Fuentes et al., 2007; Hamad et al., 2005; Pécora, 2004; Rauckyte et al., 2006).

The presence of heavy metals and PAHs in the oils' composition turns them highly noxious and carcinogenic (ABNT, 1987; Brandenberger et al., 2005; Lima et al., 2003; Rauckyte et al., 2006) and, when released into the environment, they contaminate live organisms, the soil and surface and underground waters. As usually happens in many countries, the Brazilian legislation recommends the collecting of all used oils and considers direct discharge into nature to be an environmental crime (CONAMA, 1993). Nonetheless, about 28% of those wastes are drained into the environment (Assunção Filho, 2004) and, with respect to the international context, it is estimated that mineral oil consumption in 1995 exceeded 36 million tons (Lee et al., 2007); even so, less than 45% of the total oil used in the world

was collected that year (El-Fadel and Khoury, 2001). However, recent studies indicate that the world demand of such products is about 40 million tons, while residual used oils reach 24 million tons per year (Fuentes et al., 2007). In Brazil, nowadays, the alternative widely used to minimize the impact generated by the draining of those residues into nature has been used oil recycling, recovery and refinement.

The recovery, or re-refining, consists of subjecting used lubricant oils to a series of processes that are able to eliminate all contaminants, including water, solid particles, soluble compounds, oxidation products, additives previously added to the base oil, allowing the reestablishment of the original characteristics of the pure base oils, which can be returned to the production chain (Carreteiro and Belmiro, 2006).

Several techniques can be used to recover used lubricant oils (Bhaskar et al., 2004; Fuentes et al., 2007; Pécora, 2004; Yokozeki, 2007); however, not all of them are economically feasible, mainly due to the high energy consumption along the recovery process, together with the residue production which, in its turn, also needs treatment (Ramasamy and T-Raissi, 2007; Yokozeki, 2007).

The classical clay-acid treatment process uses concentrated sulfuric acid to remove asphaltenic compounds, yielding highly toxic acid materials. In the recovery process using acid-free clays, waste oils are initially treated with natural polymers to remove carbonic materials and, soon after, are subjected to vacuum distillation and clay treatment in the appropriate amount to obtain the right end product coloration. Besides the high costs due to the required quantity of clay, recovered oils obtained by this process still have relatively high metal percentages. Thus, both processes are out of use, mainly in developed countries (Hamad et al., 2005).

In the propane extraction process, based upon used oil deasphaltation, liquid propane is used to eliminate asphalt particles and other insoluble impurities. Before the solvent addition, the used oil is distilled under atmospheric pressure to remove light hydrocarbons and water. At the end of the process, the remaining solvent is vacuum distilled and can be reused, while the oil is clarified by means of thermal treatment with clay, yielding a product (Clonfero and Schieppati, 1999; Hamad et al., 2005) that can still be submitted to additional purification treatment by adsorption, increasing the recovery efficiency (Clonfero and Schieppati, 1999). In spite of good results, the requirement of propane in the liquid phase makes the process quite expensive.

The distillation-hydrogenation process involves steps such as: atmospheric distillation; vacuum distillation under controlled temperature; hydrogenation, executed to eliminate residual sulfur, nitrogen, and compounds of oxygen; and fractioning (Carreteiro and Belmiro, 2006). The main difficulty in this process is in the hydrogenation step, due to the nature of the heteroatoms (S, O, N), that can form gaseous compounds as well as stable compounds that remain in solution, both potentially pollutant, depending on several factors such as the oil's deterioration state, temperature and catalyst; in addition, metals that are usually present as contaminants can be deposited in the catalysts, deactivating them permanently (Almutairi et al., 2007; Ancheyta et al., 2002).

Besides, some studies still indicate the possibility that aromatic compounds present in the used solvents and in the contaminants adsorb concurrently on the catalysts surface, thus inhibiting its action (Rayo et al., 2004).

Other processes were developed in several studies, mainly in private companies, basically involving the same previous processes with little variation as, for example, the use of solvents with different catalysts (Carreteiro and Belmiro, 2006). However, some of these processes, such as vacuum distillation and pyrolysis (cracking) (Fuentes et al., 2007; Ramasamy and T-Raissi, 2007), which involve temperature and pressure control, include steps with several disadvantages because they require installation of expensive equipment that can end up raising the final cost of the recovered product (Pécora, 2004; van Grieken et al., 2008). Alternative studies involving recovery via radiation revealed that this method can be developed fewer steps than the already cited ones (Zaykina and Zaykin, 2002); however, in this case high temperatures are used and the industrial scale presents the same restrictions, not yet compensated in such processes by more promising results.

In Brazil, the process commonly used for the recovery of used lubricant oil is distillation, generically called re-refining. Currently, however, there are not enough re-refining units to support the large demand of the country. A high operational cost of processing and implantation of the units is also verified. Moreover, classic methods such as propane addition can become impracticable due to unavailability of solvents in some regions.

Thus, studies aiming at the development of alternative processes for the recovery of lubricant oils involving better operational conditions, lesser cost and greater accessibility are of great importance for optimum exploitation of regional products. For example, taking into account that the country is self-sufficient in the production of cane sugar alcohol, the use of ethanol as solvent in some stage of the treatment in place of the solvents traditionally used could be more viable.

On the other hand, among the various alternative processes recently proposed, extraction with solvents (Coto et al., 2006; Elbashir et al., 2002; Espada et al., 2007; Martins, 1997; van Grieken et al., 2008) gained a good deal of attention because it is simple, economical and ecologically correct since their waste products (organic sludge) can be used in the asphalt industry. The foundations of this process have been used to recover polluted areas because the handling of oil solubilizing solvents, not miscible in water, allows their removal with no harm to the environment (Wei et al., 2005).

Extraction processes using solvents typically include the separation of paraffin and naphthenic compounds, by solubility difference, from undesirable compounds such as lees, resins and asphaltenes ones (Vogel, 1988). In this process, the waste oil is mixed with a solvent at ratios able to guarantee the highest possible solubilization of the base oil in the solvent. Additives and carbon impurities, normally present in waste oils, are not miscible in the solvent; thus, they flocculate and eventually sediment by gravity, forming lees. The solvent used in this operation can be recovered by distillation and recycled (Elbashir et al., 2002). One of the main steps in this process is the extraction system planning, which includes the selection of the solvent and the appropriate oil:solvent ratio (Hamad et al., 2005; Elbashir et al., 2002).

In spite of the advantages presented by this process, a residual fraction (oxidation product) remains solubilized in the recovered oils, making its partial or total removal imperative for the final product to be commercially desirable (Clonfero and Schieppati, 1999).

Ramos et al. (2001) evaluated the adsorption of polynuclear crude oil fractions, called asphaltenes and resins, on solid surfaces in aromatic solvents, verifying that some solids, like activated carbon and silica, presented good ability to concentrate those substances onto their surfaces. The similarity between crude oil polyaromatic fractions and the products from used lubricant oil oxidation makes the adsorption on solids a possible final step of their recovery process. Other works report the efficiency of adsorbents, such as silica, used to remove nitrogen-polyaromatic compounds present in coal tar (Wu et al., 2000).

Therefore, the present work provides an evaluation of some steps of an alternative process for the recovery of waste lubricant oils based upon extraction by solvents, followed by adsorption on different solids, looking for improvements with respect to the processes currently used and for obtaining a better quality final product (the recovered lubricant base oil).

EXPERIMENTAL

Materials

Waste lubricant oils were gathered at collecting stations in the city of São Luís/MA (Brazil). The samples were homogenized, getting enough oil to conduct the research, and, next, transferred to appropriate flasks kept apart from light and at room temperature for further handling with no additional treatment.

The solvents used were ethanol (Merck, Germany) with purity higher than 99.9%, 2-propanol (Reagen, Brazil) with purity higher than 99.5%, 1-butanol (Grupo Química, Brazil) with purity higher than 99.5%, tert-butanol (Vetec, Brazil) purity higher than 99.0%, toluene (Carlo Erba, Italy), purity higher than 99.5% and n-pentane (Carlo Erba, Italy), purity higher than 99.5%.

The adsorbents employed were chitosan powder (Fluka commercial type), activated carbon (Quimicabrás, Brazil) and silica powder (Vetec, Brazil).

Characterization of the Lubricant Oil by Optical Microscopy

The used lubricant oil was homogenized and evaluated by optical microscopy, as was the recovered base oil at the end of the process. In both cases, the digitalized images were obtained with 400-fold magnification in an Olympus Bx 51/Bx 52 optical microscope linked to a computer with Image-proplus software.

Solvent Extraction of Lubricant Base Oil

In general terms, mixtures were prepared in different ratios, by weight, of solvent and the used oil. Each system was homogenized in a 250 rpm magnetic stirrer for about 20 min and let stand for 24 h, the time necessary for formation and equilibrium of biphasic systems within which the oil concentrated in the extract phase (solvent + recovered lubricant base oil) and the particulate matter in the refined phase (lees).

The percentages of lubricant base oils extracted by the various solvents were calculated by employing Equation (1), according to the procedure described by Elbashir et al. (2002).

$$\% \, E = 100 \left(\frac{W_O - W_P}{W_O} \right) \tag{1}$$

In which %E is the percentage lubricant base oil extracted, W_O is the waste oil mass and W_P is the oil mass obtained by distillation of the solvent in the refined phase.

The recovered oil percentages in the different systems were plotted as a function of solvent:used oil ratio and the Critical Clarifying Ratio (CCR) determined (Elbashir et al. 2002).

It is important to mention that all stages of the considered process (solvent extraction, adsorption on solids and evaporation of the solvent) were evaluated on a laboratorial scale in batch conditions; thus, for industrial implementation, posterior studies aiming at a better definition of the process layout are still necessary.

PAH's Adsorption on Solids

PAHs Separation and Quantification

Lees obtained from the system 1-butanol and waste lubricant oil were separated and used at the ratio 1:2 by weight. Solids were placed on Whatman n.42 paper filters, followed by extraction with toluene, in general a good solvent for aromatic compounds (Mullins et al., 2008); solvent evaporation; and washing with n-pentane to remove any residual saturated compound. This procedure was repeated three times and, at the end, the solid obtained was used to quantify the PAHs of the remaining systems.

To make the calibration curves, the reference solids were solubilized in toluene at various concentrations and absorption spectra registered in the visible UV HP Model 8452A absorption spectrophotometer). Absorbances were evaluated at the wavelength of 350 nm, a value in the interval reported in the literature as being expressive for the absorption of polycyclic aromatic hydrocarbons (PAHs) (Brüggemann and Freitag, 1995).

Adsorption Kinetics

Systems of used oil+solvent (ethanol, 2-propanol 1-butanol and tert-butanol) were prepared with an oil:solvent ratio of 1:3 by weight; each system was homogenized using a magnetic stirrer at 250 rpm for 20 min, followed by settling under gravity for 24 h for the formation of the two phases, extract (supernatant) and refined (lees).

To evaluate the adsorption of the PAHs on the differents solid surfaces, after the phase separation, 20 mL of each extract was put in contact with approximately 0.15 g, 1.0 g, and 1.0 g, respectively, of the solids activated carbon, silica and chitosan. Then the measurements of absorbance (HP Model 8452A absorption spectrophotometer) were made at the wavelength of 350 nm in each system at 24 h intervals, until saturation of the adsorption was reached. The masses of each solid employed were chosen in order to

provide a maximum absorbance smaller than 2 in relation to the concentration of PAHs.

In order to assess the amount of PAHs transferred to the adsorbents, the absorbance obtained from the calibration curve (section 2.4.1) was converted into concentration. After this, the initial and equilibrium concentrations of the PAHs in each extract and the volume of each sample were applied in Equation (2) for the calculation of the mass of PAHs adsorbed on the solid surfaces.

$$\Delta M = V(C_i - C_e) \tag{2}$$

Where V is the volume of the sample of each supernatant; C_i is the initial concentration of PAHs (g L^{-1}); and C_e is the equilibrium concentration of PAHs (g L^{-1}).

Thus, these data were used to made graphs of the mass of PAHs transferred to the solid (adsorbed mass) as a function of time (h).

Solvent Removal

The solvent removal of each system base oil: solvent was carried out after the adsorption of the PAHs onto the solids. The contact between supernatants and solids was maintained for approximately 96 hours, the equilibrium time determined from the graphs of the adsorbed mass of PAHs as a function of time. After that, the supernatants were collected and the solvents were removed by vacuum distillation using a rotoevaporator (Quimis, Q344-B2) connected to a vacuum pump (Quimis, Q355B), taking into account the boiling point of each solvent. The remaining material was characterized as recovered lubricant base oil.

Determination of Some Properties of the Recovered Lubricant Base Oils

The following physical-chemical properties of the recovered lubricant oil samples were determined: kinematic viscosity at 40ºC (procedure ASTM 446/D2515), total acidity index (procedure ASTM D3339-95) and water content (Karl-Fischer Titration) (ABNT, 1987).

RESULTS AND DISCUSSION

Layout of the Proposed Process for Used Lubricant Oils Recovery

Fig. 1 represents a simplified diagram of the global process used in this work aiming at the recovery of waste oils, representing the following

sequence of steps: extraction by solvents, adsorption on solids and solvent evaporation. Initially, the steps include contact between the used lubricant oil and a solvent to form the binary system in which the oil concentrates in the extract phase (the supernatant: solvent + lubricant base oil) and the particulate material in the refined phase (lees); next, the extract phase is separated and put in contact with adsorbents to remove soluble compounds. The recovered oil is obtained after solvent evaporation. For each step, several parameters were evaluated such as lubricant base oil extraction percentages; equilibrium time and concentration for the PAHs removal by solids; lubricant base oil recovery and some physical-chemical properties of the recovered oils.

According to the solvent nature and the kind of

adsorbent, it is expected that, at the end of the process, the lubricant base oils are produced with distinct characteristics.

Used Oil Digitalized Images

Samples of used lubricant oils were employed with no additional treatment. The presence of particulate matter was detected by means of optical microscopy (Motic BA300). As shown in Fig. 2, a massive amount of suspended particles with average diameter of $1.0 \pm 0.1\mu$ was observed, characterizing the residual state of the oil, which is consequently improper for consumption. Nevertheless, the presence of other phases in the form of emulsions or foams was not observed.
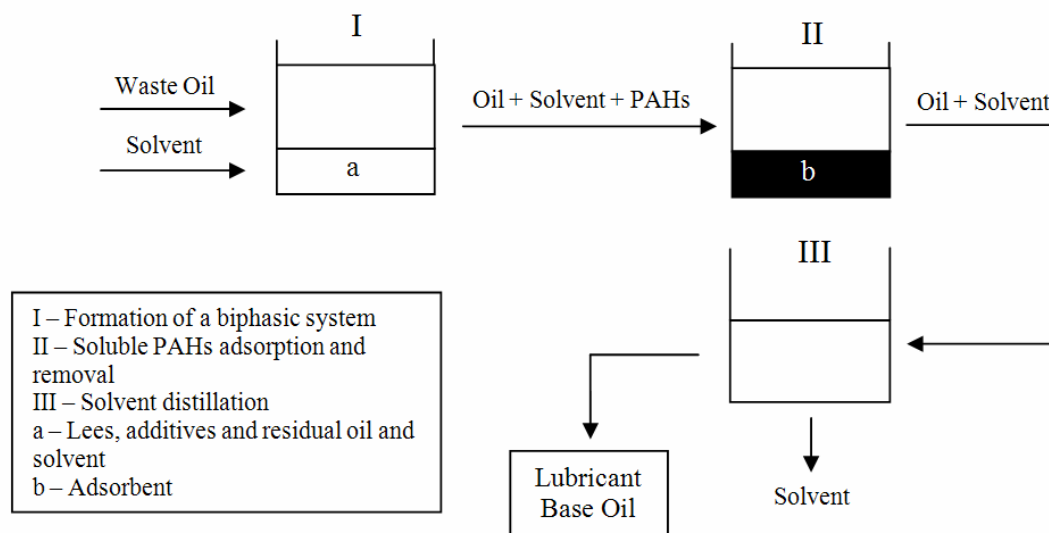

Figure 1: Lubricant base oil recovery process: extraction by solvent, adsorption on solids and solvent evaporation.
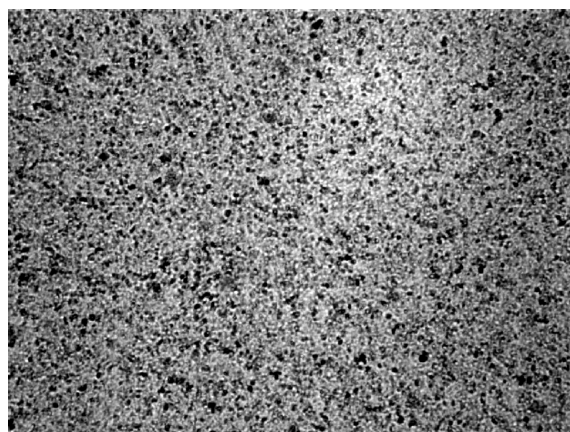
Figure 2: Digitalized image of used lubricant oil with particles of average diameter of $1.0\pm0.1\mu$. Temperature $28\pm1°C$ and magnification of 400 times.

Solvent Extraction

Fig. 3 shows the extracted lubricant oil percentage, calculated by applying Equation (1), as a function of the solvent:used oil ratio. The behavior found was similar for all systems containing used oil and the solvents 2-propanol, 1-butanol, tert-butanol and ethanol, but each one of them had its own characteristics.
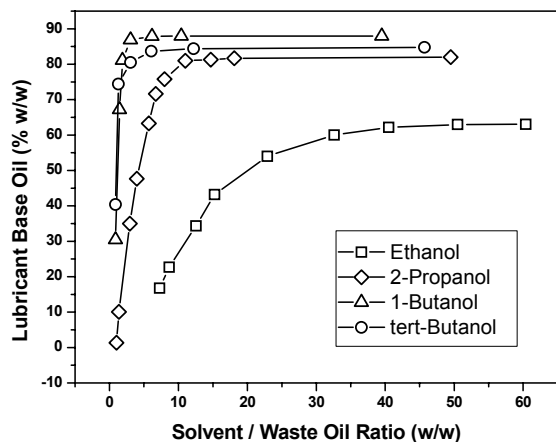
Figure 3: Lubricant base oil percentages extracted by various solvents as a function of the solvent:waste oil ratio.

Analyzing the results presented in Fig. 3, one can verify that, in the extraction step, the solvent 1-butanol had better performance, extracting practically 86% of the lubricant base oil, followed by tert-butanol (83%), 2-propanol (80%) and ethanol (65%). These results become more notorious when we consider the amount of each solvent at the extraction limit. The difference between these percentages is related to the solubility of the base oil in these solvents.

According to Hildebrand's parameter (Hildebrand et al., 1970), the miscibility between two compounds is higher when the difference between their solubility parameters is smaller. For Elbashir et al. (2002), that difference is 6 and 7 for the 1-butanol and 2-propanol, respectively; hence, the lubricant base oil solubility was higher in 1-butanol than in 2-propanol. Their data is consistent with the results presented in this work (Fig. 3).

In this case, the efficiency of the extraction agents can also be justified in terms of the relationship between the solubility and the size of the carbon chain (Clonfero and Schieppati, 1999), in which the

solubility increases with the number of carbons in the solvent molecules. In the case of 1-butanol and tert-butanol, however, the fact that 1-butanol presented better extraction efficiency than tert-butanol is possibly related to the different interaction between the solvent and oil molecules, due to the size of the main carbon chain and the solvent molecules' configuration.

The base oil percentage increases in the solvent phase with the increase of the extraction phase ratio due to the higher affinity of the oil for the solvent, therefore agreeing, in this study, with the results of Elbashir et al. (2002). In the interval comprehended between the ratios 1 and 7, a major increase of the extracted oil was verified, while between the ratios 7 and 14, there was a moderate increase and, beyond the ratio 14, there was no significant increase in the lubricant oil extraction, thus representing the extraction limit of the system 2-propanol+used oil.

The Critical Clarifying Ratio (CCR) represents the relation solvent:used oil necessary for better destabilization of the particulate material and for obtaining a biphasic system in which the supernatant is limpid (Elbashir et al., 2002; Reis and Jerónimo, 1988). In this study, this index was determined graphically, as described by Elbashir et al. (2002), for the system 2-propanol+used oil (Fig. 4) that showed an intermediate behavior (Fig. 3).

As seen in Fig. 4, the CCR was equal to 3 for the system 2-propanol+used oil, and this value was adopted in the next experiments of adsorption aimed at establishing a comparative criteria with the other systems.
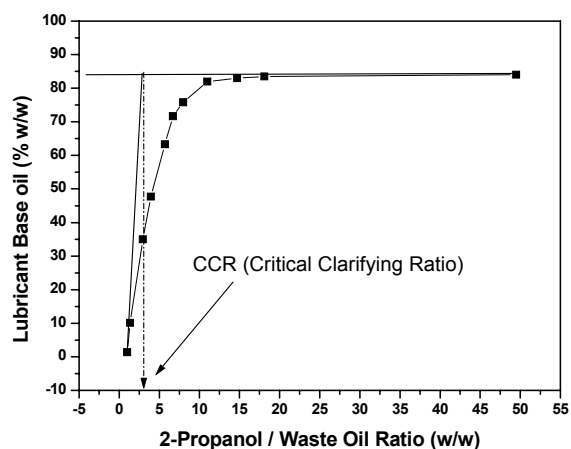
Figure 4: Percentage of lubricant base oil extracted by 2-propanol as a function of the extraction ratio at the temperature of 28±1ºC.

PAHs Adsorption onto Solid Surfaces

In order to evaluate the PAHs removal in the waste oils recovery, a calibration curve was initially made in such a way that it allows the PAHs' concentration to be monitored in the different systems.

The absorption spectra obtained between 300 and 800 nm for various PAHs concentrations in toluene are shown in Fig. 5; they point to the polydisperse character of the sample (broad band, lack of specific peaks and absorption over a wide wavelength range). However, in this case, they provide a qualitative characterization with respect to the PAHs, due principally to their spectral similarity with the polyaromatic systems already well known in the literature, as for example the asphaltenes (Ramos et al., 2001). The broad absorption band originates from the large amount of chromophores present in these compounds' chemical structure.

Spectrophotometric measurements were taken at 350 nm, a value within the wavelength interval of 180 to 380 nm, considered to be the most expressive absorption region of polycyclic aromatic hydrocarbons (PAHs) (Brüggemann and Freitag, 1995). The initial dilution of the samples resulted in absorbances inferior to 2 units, to respect the Lambert-Beer law.

Fig. 6 presents the relationship between PAHs absorbance at the wavelength of 350nm and concentration in toluene. The curve obtained was linear in the evaluated concentration range (between 30 and 500 mg L^{-1}) with a correlation coefficient close to 1 and it was used to determine the PAHs adsorbed on the various solid surfaces in subsequent studies.
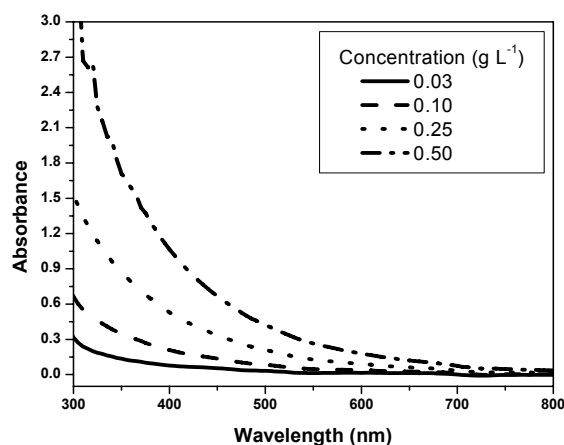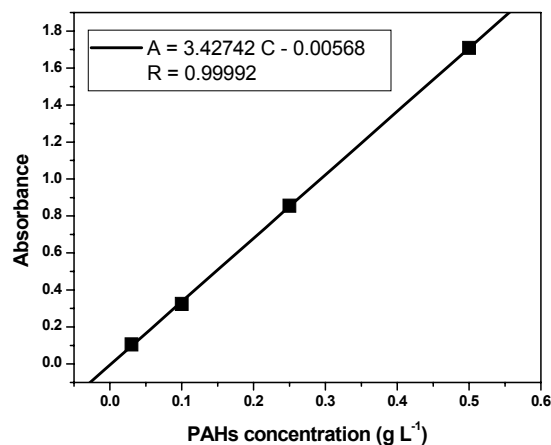
In Figs. 7 and 8, one can verify the adsorption kinetics in the various systems. Considering that the adsorption on activated carbon was higher than on chitosan and silica, these are presented separately to facilitate visualization. In the evaluated conditions, two different behaviors can be observed: the first, up to almost 45 h, represents a faster transference of the PAHs to the solid surface; while the second is characterized by a slow transfer in which there is still an increase in the adsorption, but tending to equilibrium, according to the flattening out of the curves.

Equilibrium concentration is attained in about 75 h, a relatively large time that can be justified, possibly, by surface phenomena of physical adsorption followed by multilayer formation. For adsorption, 96 h was always considered to be the necessary time for the system to attain equilibrium. It is worth noting that, both qualitatively and quantitatively, oils are distinct in their solubility in different solvents and, consequently, the PAHs removed from the oil phase by the adsorbents also change.

In Figs 7 and 8, the smaller effect on the solid loading capacity of ethanol-containing systems reflects the lower amount of PAHs available in the medium. However, to sketch an appropriate profile of the PAHs adsorption process in the different solids and solvents it is necessary to construct the adsorption isotherms, which is out of the scope of this work. Nevertheless, one can conclude that it is possible, by contact with the solids activated carbon, chitosan and silica, to remove the original PAHs from the waste oil and that, in principle, activated carbon appears to be the best adsorbent, no matter the solvent's nature.

Figure 5: PAHs Absorbance Curves in toluene as a function of the wavelength (300 to 800 nm) at the temperature of 28±1ºC.

Figure 6: Absorbance as a function of the PAHs concentration in toluene (wavelength of 350 nm). Temperature of 28±1ºC.
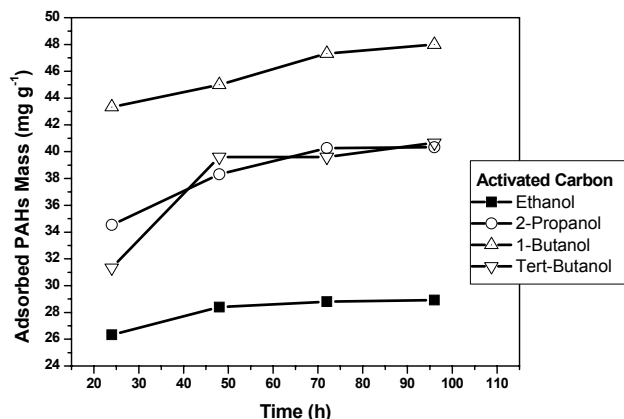
Figure 7: PAHs adsorbed on activated carbon in the supernatants oil+ethanol, oil+2-propanol, oil+1-butanol and oil+tert-butanol. Temperature 28±1ºC.
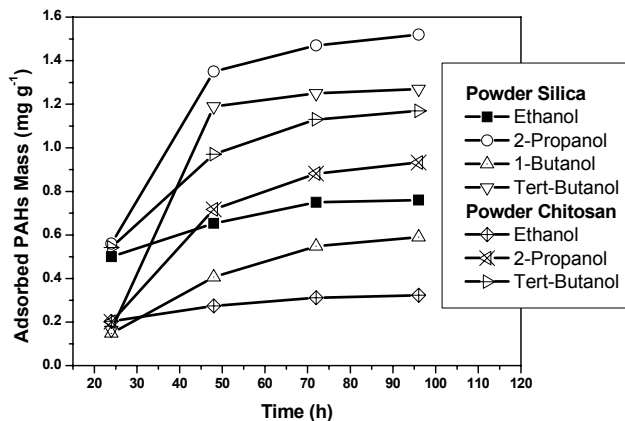
Figure 8: PAHs adsorbed on silica powder and chitosan powder in the supernatants oil+ethanol, oil+2-propanol, oil+1-butanol (except for chitosan powder) and oil+tert-butanol. Temperature 28±1ºC.

Solvent Removal

After the adsorption on solids, the solvents were removed from the supernatants by distillation (section 2.5) and then the recovered base oil in each system was characterized.

Characterization of the Recovered Oils

In this section, several systems were selected, aiming at evaluating the global used oil recovery process, starting from some specific quality control properties of these products.

The recovered oils were obtained through the procedure detailed in this work using the ratio of 3:1 (solvent: used oil), as established in the study of the Critical Clarifying Ratio of the system 2-propanol: used oil.

The recovered lubricant base oils were designated in terms of the solid and solvent utilized, as shown in Table 1. In the adsorption step, we started by excluding solid chitosan since the results using that solid were quantitatively similar to those obtained with silica. In Table 1, the kinematic viscosity at 40ºC, the index of total acidity and the water content of the selected systems are also given. The water content in the recovered lubricant base oils was small compared with that of the waste lubricant oil.

Table 1: Denomination of recovered lubricant base oils according to the solvent (ratio solvent: used oil equal to 3:1) and solid employed in the process, and their classification ANP, experimental values, ASTM kinematic viscosity, acidity index, and water percentage.

Oil	Solvent	Solid	Classification ANP n 005/99	Kinematic viscosity at 40ºC (cSt)		Acidity index (mg KOH/g)		Water content (%)
				Experimental	ASTM D445	Experimental	ASTM D974	Experimental
Waste oil	-	-	-	107.87	-	0.665	-	0.0048
A1	ethanol	activated carbon	Heavy Neutral	125.84	without reference	10.932	0.05	0.0020
A2	ethanol	powdered silica	Heavy Neutral	96.52	without reference	7.129	0.05	0.0038
B1	2-propanol	activated carbon	Light Neutral	27.49	26 – 32	2.814	0.05	0.0038
B2	2-propanol	powdered silica	Light Neutral	31.59	26 – 32	2.262	0.05	0.0023
C1	1-butanol	activated carbon	Spindle	15.25	8 – 18	1.079	0.05	0.0023
C2	1-butanol	powdered silica	Spindle	16.79	8 – 18	1.147	0.05	0.0031

Fig. 9 presents a digitalized image, obtained by optical microscopy, of the recovered oil sample C1, from which one can verify that the sample C1 is clean and free of suspended particles, a fact that confirms the efficiency of the process for eliminating insoluble compounds. The same visual characteristics were checked with the other systems.

Figure 9: Digitalized image of the lubricant oil recovered with 1-butanol and activated carbon (C1). Temperature of 28 ± 1ºC and magnification of 400 times.

According to the ASTM values specified by ANP (1999), the different viscosities found in the various samples correspond to recovery of different oil classes. This result indicates that, in function of the initial parameters (solvent and adsorbent, ratio oil:solvent), it is possible to obtain recovered oils with different characteristics (Table 1).

Some authors reported results in the same range of kinematic viscosity at 40ºC (cSt) for oils recovered through vacuum distillation with or without previous treatment with solvents (Rincón et al., 2007); other authors, using the radiation method, also got equivalent data for the viscosity, but at 50º C (cSt) (Zaykina and Zaykin, 2002); nevertheless, these researches did not present classification concerning the type of oil produced at the end of the recovery process.

The major divergence in the analyzed properties is related to the experimental acidity index which presented even higher values compared with the ASTM D974 Norm reference index. This result, possibly explicable in terms of thermal oxidation processes, points to the necessity of more research to make clear the phenomenon.

With respect to this index, some works (Rincón et al., 2007; Zaykina and Zaykin, 2002) presented results closer to the ones demanded by the norms;

however, the addition of a neutralization step to the proposed global recovery methodology could be realized without affecting its feasibility.

In general, however, it is worth highlighting that the proposed process based upon physical steps, was efficient for the improvement of specific properties of waste lubricant oils, allowing the recovery of oils whose characteristics agree with the technical specification requirements.

However, it must be noted that the global process of recovery of used lubricant oil considered in this work is similar to the industrial process of deasphaltation with propane, differing, however, in the nature of the solvent and the step of adsorption on solids. Moreover, all the stages of the present process were carried out under ambient conditions (pressure and temperature) and posterior works must consider possible effects of these variables in the process.

CONCLUSIONS

Results presented in this work permit us to conclude that it was possible to establish a set of physical steps that allow the recovery of used lubricant oils. The stages evaluated were solvent extraction, adsorption on solids and solvent removal by distillation; at the end, products with distinct characteristics are obtained, depending on the nature of the solvents and adsorbents employed.

The step of extraction is similar to that used for oil recovery by propane extraction; however, in this case, precipitation and sedimentation of lees occur, whereas the process evaluated here promotes the formation of a biphasic system and separation of the oil based on the affinity with the solvent added.

The solvents ethanol, 2-propanol, 1-butanol, and tert-butanol were employed for the extraction of the base oil, and the solids activated carbon, silica gel, and chitosan were tested in the adsorption step. The most efficient solvent was 1-butanol, followed by tert-butanol, 2-propanol, and ethanol. Activated carbon was the most efficient solid for PAHs removal, confirming the similarity of these compounds with petroleum aromatic fractions.

Therefore, in this study, the optimum system for recovery of the used lubricant oil was 1-butanol+activated carbon, with a yield of 86% of recovered base oil in the stage of extraction for the condition evaluated, that is, employing a used oil:solvent ratio of 1:3.

The process proposed for the separation of lubricant base oils presents a high extraction

percentage in the solvent and a diversity of extracted lubricant base oils, indicating that each extraction system (solvent + adsorbent) produces different base oils, likely ready to be used in applications according to its classification.

To consider the application of this used lubricant oil recovery process on an industrial scale, however, posterior studies are necessary considering other conditions not evaluated in this work, such as different ratios of used oil:solvent, effect of the temperature in the stages of solvent extraction and adsorption, study of the economic viability of the global process and regeneration of the solvent and adsorbent, as well as exploitation of the residues.

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