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Recycling of the used automotive lubricating oil by ionizing radiation process

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Abstract

The recycling process of the used mineral oils has been gaining a very important gap in the context of environmental protection. Among mineral oils from petroleum, the lubricating oils are not entirely consumed during their use; therefore, it is necessary to apply a treatment for recuperation seeking their reuse. Moreover, the environmental legislation of countries does not allow their discard in any type of soils, rivers, lakes, oceans or sewerage systems.

The conventional treatment has shown certain difficulties in the recuperation process for used oils. The ionizing radiation process is renowned in the industrial effluents treatments due to its high efficiency in the degradation of organic compounds and in the removal of metals by the action of $OH^{\bullet}$, $^{\bullet}H$ and e_{aq} radicals.

In this work, used automotive lubricating oil was treated by the ionizing radiation process for metal removal and degradation of organic compounds. The samples were irradiated with 100 and 200 kGy irradiation doses. Determination of the elements Mg, Al, P, S, Cl, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Mo, Nb, Cd, Sn, Ba, Bi and Pb, before and after the irradiation, was done by X-ray fluorescence technique and the organic profile was obtained by infrared spectroscopy.

Keywords: Ionizing radiation; Used oil treatment; Metal removal

1. Introduction

The automotive lubricant oils require for their applications some additives, such as organic compounds and metals. Usually, the chemical elements B, Mg, P, Ca, Cr, Ni, Zn, Se, Mo, Cd, Sn, Sb, Ba, and Hg are found in automotive oils. These additives have several functions, such as antioxidants, dispersants and detergents. Normally, they are diethylcarbamates and sulphonates of organometallic compounds, and may be present in Fe, Zn, Cd, Bi and Pb diethyl phosphates, Ti, Mn, Fe, Co and Ni acetylcetonates and also Ca, Fe, Ni, Zn, Ag, Cd, Sb, Pb and Bi alkyl aryl diethyl phosphate (DDP) complex forms (Sychra et al., 1981). Other metallic elements could be in the oil by wearing mechanisms or corrosion process. Therefore, the removal of these metallic elements is very important for the recycling of the used automotive lubricating oil.

Generally, the technologies for used oil recycling utilize the following steps: cyclonic distillation with dehydration, flash distillation, clarification, neutralization and filtration. Each step provides products that receive adequate treatments, mainly metal removal to be then reutilized as raw material or in other products. (Ambiente Brasil, 2001—www.ambentebrasil.com.br).

The ionizing radiation process has been used for different applications, especially for industrial and domestic effluents treatment (organic and biologic compounds degradation, metal removal) due to its high efficiency and clean technology application (Slegers et al., 2005; Ribeiro et al., 2004; Getoff, 1986).

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In this work, the ionizing radiation was used to verify the removal level of Mg, Al, P, S, Cl, Ca, Y, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Mo, Nb, Cd, Sn, Ba, Bi and Pb elements, with and without the addition of hydrogen peroxide in a used automotive lubricating oil sample.

The elemental concentration was determined by X-ray fluorescence technique, using the Fundamental Parameters Method. The values obtained were compared with the values from one sample recycled by conventional process.

2. Experimental

2.1. Sampling

A 1000 mL sample of used automotive lubricating oil from a gas station was collected. This sample was fractioned by following two steps:

Step 1: Five millilitres from the sample was transferred into three glass vials of 5 mL each, and labeled as step 1, samples named A1–A3.
Step 2: Four milliliters from the sample was transferred into three glass vials of 5 mL each. In each vial, 1 ml of the hydrogen peroxide (H_2O_2: 30%; MERCK) was added. These samples were then mixed for 10 min in a mixer (SPEX-MILL, CAT. NO. 76156), and the samples were named B1–B3.

2.2. Processing

The irradiation was performed in a ^{60}Co irradiator (GAMMACELL-220—12 kCi). The A2, A3, B2 and B3 samples were irradiated with the following absorbed doses: 100 and 200 kGy, respectively. The A1 and B1 samples were used as "blank".

The elemental concentration was determined by wavelength dispersion X-ray fluorescence spectrometer (RIGAKU Co., model RIX 3000) using the fundamental parameters method (Lachance and Claisse, 1995). For elemental analysis, 50 μl of the samples were deposited onto a 2.0 cm diameter filter paper fixed on the double face adhesive ribbon. It was dried at 25–35 °C and re-covered by polyethylene film (Mylar) (Scapin and Sato, 2002). Following the same procedure, six samples from ALFA AESAR reference material (stock 36740, lot 703527D) were prepared. The precision and accuracy of the method were evaluated applying statistical tests according to EUROCHEM/CITAC Guide (second ed.).

The irradiation treatment efficiency was evaluated by chemical analysis of the duplicate samples before and after irradiation.

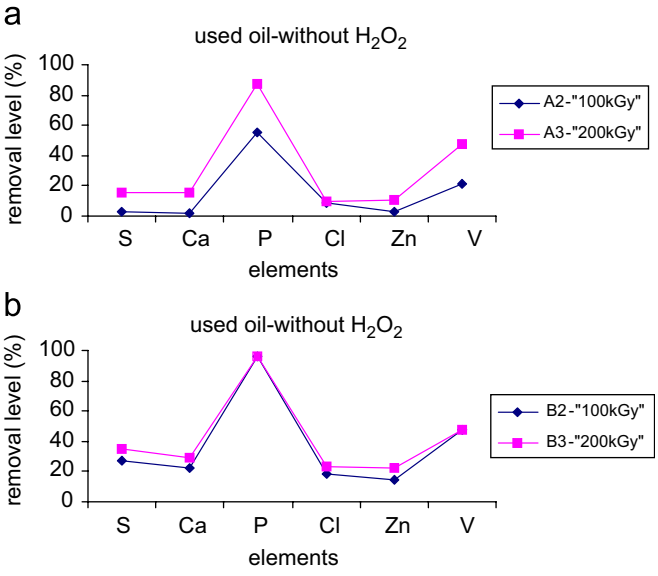

Fig. 1. Removal level percentage of used oil sample without and with H_2O_2.

Table 1
Metal removal level for different irradiation doses

Elements	Without H_2O_2			With H_2O_2			CRP
	"Blank" A1 sample	100 kGy A2 sample	200 kGy A3 sample	"Blank" B1 sample	100 kGy B2 sample	200 kGy B3 sample	Recycled sample
S (%RL)	0	3.2	16.0	25.5	27.6	34.5	–
($\mu g\,ml^{-1}$)	6349 ± 30	6144 ± 30	5334 ± 30	4733 ± 30	4598 ± 30	4156 ± 30	5495 ± 30
Ca (%RL)	0	1.5	15.3	20.5	22.3	28.9	–
($\mu g\,ml^{-1}$)	2651 ± 20	2612 ± 20	2245 ± 20	2107 ± 20	2060 ± 20	1884 ± 20	90 ± 20
P (%RL)	0	55.8	87.0	37.0	>96	>96	–
($\mu g\,ml^{-1}$)	231 ± 10	102 ± 10	62.3 ± 10	85.5 ± 10	<10	<10	23 ± 10
Cl (%RL)	0	8.6	10.0	15.3	18.7	23.4	–
($\mu g\,ml^{-1}$)	209 ± 10	191 ± 10	188 ± 10	177 ± 10	170 ± 10	160 ± 10	20 ± 10
Zn (%RL)	0	2.7	10.7	12.5	14.3	22.3	–
($\mu g\,ml^{-1}$)	112 ± 5	109 ± 5	100 ± 5	98 ± 5	96 ± 5	87 ± 5	15 ± 5
V (%RL)	0	21.1	47.7	0	>48	>48	–
($\mu g\,ml^{-1}$)	19 ± 5	15 ± 5	10 ± 5	19 ± 5	<10	<10	<10

% RL: removal level percentage.
CRP: conventional recycled process.

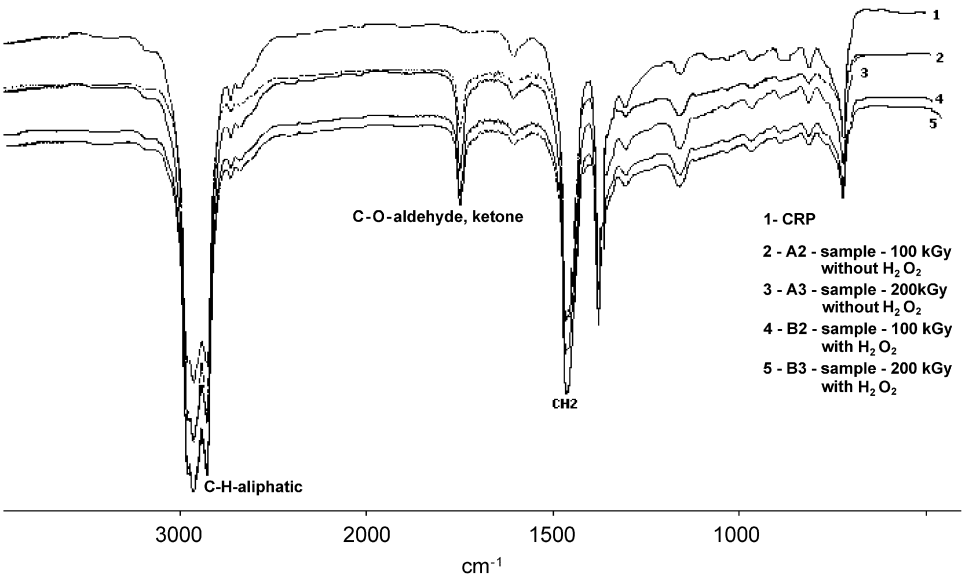

Fig. 2. FTIR spectra of the used automotive lubricating oil, submitted to 100 and 200 kGy irradiation doses.

The inorganic profile was analyzed by infrared spectroscopy (SHIMADZU, model FTIR 8400) using KBr pellets method.

3. Results and discussion

The ALFA AESAR Ground & Waste Water Pollution Standard Solution 1, Specpure® reference material data presented a precision between 1% and 5% in relation to the relative standard deviation for all the elements. The accuracy of the method presented *Z*-score values for Al, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn between −1 and +1, demonstrating the validation of the methodology for metal determination in oil samples.

The used lubricating oils showed presence of S, Ca, P, Cl, Zn and V elements (Table 1). The other ones, Mg, Al, Ti, Cr, Mn, Fe, Ni, Cu, Se, Mo, Nb, Cd, Sn, Ba, Bi and Pb, were present at concentration less than 10 $\mu g\,ml^{-1}$. Therefore, the removal level by ionizing radiation process was determined only for S, Ca, P, Cl, Zn and V.

The results showed that the ionizing radiation application removes the present elements and that the increase of the dose increases the process efficiency (Fig. 1a). There was also observed a major increase in the removal level using H_2O_2 addition, justifying its use (Fig. 1b).

The B3 sample irradiated with 200 kGy dose and added with H_2O_2 showed major removal levels for all the calculated elements. An exception was observed for P which showed >96% with 100 kGy dose also. The result shows that P is easier to be removed. S, Ca, Cl and Zn showed significant removal levels, 34.5%, 28.9%, 23.4% and 22.3%, respectively, but it may be improved by increasing the dose. V showed a removal level >48%, but the concentration is in a critical level of evaluation, thus assuming that it had been removed (Table 1).

P and S showed smaller concentration values for B3 sample when compared with the sample obtained by conventional recycled process (CRP). This result justifies the applicability of this procedure for the removal of elements. However, Ca, Cl and Zn showed higher values, thus an increased dose is needed for removing these elements (Table 1).

In Fig. 2, the infrared spectra (FTIR) of one sample recycled by conventional process (CRP) and the used automotive lubricating oil sample irradiated with 100 and 200 kGy doses, without and with H_2O_2 (A2, A3, B2 and B3), are shown.

The lubricating oil sample irradiated with 100 and 200 kGy doses, with and without H_2O_2, did not show alteration of the main organic compound groups, such as aldehydes, ketones and aliphatics. This result showed that the experimental conditions used do not degrade these compounds.

4. Conclusions

The ionizing radiation treatment revealed to be a promising process for the removal of metals in used automotive lubricant oil. Satisfactory removal was obtained for the elements P, S, Ca, Cl, Zn and V.

The FTIR spectra showed that different irradiation doses (100 and 200 kGy) and addition of H_2O_2 did not present an alteration in relation to organic compounds profile.

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