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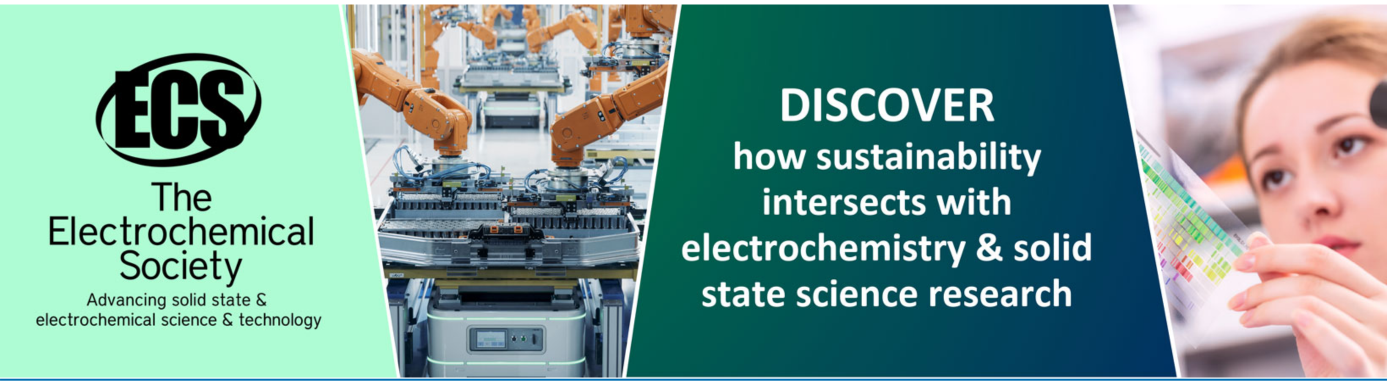

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The effect of a magnetic field and magnetite nanoparticles on the electrodeposition of asphaltenes of a Colombian 21api oil sample

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Abstract This research focuses on the effect of a magnetic field and magnetic nanoparticles on the electrodeposition of asphaltenes from a Colombian oil sample. Different electrodepositions were carried out by applying an electric field of 100V/cm. Two magnetic field systems were used: a static one and a dynamic one. They both exhibited a magnetic flux density of 0.1mT. Under the absence of fields, we observed a deposit of 7mg on the anode and 8mg on the cathode. However, presence of an electric field deposits increased to 10mg on the anode and to 13mg on the cathode. In the presence of static magnetic field (generated by a transformer), deposits further increased to 26mg and 21mg. When using the dynamic magnetic field (generated by a stator), we obtained deposits of 63mg and 54mg. Subsequently, 1% of magnetite nanoparticles were added to oil. In the absence of fields, deposits remained about the same. With an electric field, we generated deposits of 26mg on the anode and 21mg on the cathode. The transformer-increased electrodeposition to 30mg on the anode and to 24mg on the cathode, while with stator, deposits increased to 114mg and 73mg. Asphaltene deposits were confirmed by spectroscopy.

1. Introduction

Electrodeposition is currently one of the least used separation techniques of asphaltenes in the oil industry. Research on this topic was pioneered around 1960 by Wright and collaborators [1,2]. It is believed that the interaction of an electric field with the oil structure generates an alteration of the hydrocarbon equilibrium, promoting the release of the asphaltene. The charge of the free species depends on many factors, including the origin of the oil and the conditions of the electrodeposition. Afterwards, the asphaltene will be oriented and deposited in the corresponding electrode [3-5]. During the asphaltene electrodeposition process of the oil, only the electric field disturbs the hydrocarbon equilibrium, and its effectiveness will depend upon the electric field to which it is subjected, because the hydrocarbon is a non-electrical conductive medium. As this field increases, the amount of deposited asphaltene will be higher [6-9].

One of the options for improving the electrodeposition process is to increase the conductivity of the medium. This feature can be modified by including additives in the process, as long as these additives do not neutralize the charge of the asphaltene. It is relevant to mention that not all additives will

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interact with oil and asphaltene in a similar way, as this depends on their composition and origin [10-12].

Previous research has shown that the rheological behavior of hydrocarbons is affected by the presence of a magnetic field. The effect is a lowered viscosity of the oil [13]. This is consistent with the research of *Lesin* et al [14], in which they reported the presence of magnetic nanoparticles in the composition of the oil from its origin. Such nanoparticles would be responsible for the modification of the characteristics of the oil exerted by the magnetic field.

According to previous research related with individual electric and magnetic fields, implementing both simultaneously would generate two disturbances in the oil structure, favoring the formation of free asphaltene and its electrodeposition. Moreover, adding magnetite nanoparticles in low quantities would allow for a better performance of the magnetic field and would slightly increase the conductivity of the medium. In this work, asphaltene electrodepositions are proposed and carried out, in the presence of magnetic fields and magnetite nanoparticles, with the objective of improving the separation processes of asphaltene fractions from hydrocarbons.

2. Materials and methods

Electrodeposition processes were initially accomplished in a previously characterized Colombian oil. Subsequently, magnetite nanoparticles were added to evaluate the electrokinetic behavior of asphaltenes in the presence of electric and magnetic fields.

2.1. Oil characterization

Colombian oil from the middle Magdalena area (Yarigui) was used. Its SARA composition was obtained by chromatographic techniques according to ASTM D-4124, while its API gravity was determined according to ASTM 1298.

2.2. Characterization of magnetite nanoparticles

The magnetite nanoparticles were characterized by IR spectroscopy using the Bruker Tensor 27, by scanning electron microscopy (SEM) using the Quanta FEG 650

2.3. Extraction and characterization of asphaltenes

Asphaltenes were obtained according to ASTM D-6560 and purified by adding heptane in excess. Solubility tests were carried out in different solvents. They were characterized by IR spectroscopy using Bruker Tensor 27, by UV-Vis spectroscopy using the Shimadzu UV-240 IPC spectrophotometer.

2.4. Electrodeposition of asphaltenes

Electrodeposition processes were carried out with 1% of magnetic nanoparticles and without these, using an H-type cell with capacity for 300ml and 30cm long, while applying a constant DC voltage of 30volts, on 2.5cm x 2.5cm stainless steel electrodes, generating an electric field of 100V/m. (E=voltage/length). Blank adsorption experiments were performed without electric nor magnetic field. Two types of experiments were performed with two different types of magnetic fields. The first one used a transformer fed with 120volts in alternating current. The second one used a magnetic field that was generated by a three-phase stator fed with 4A in alternating current (Figure 1). Both of the resulting magnetic fields were of 0.1mT in amplitude, as measured by the Teslameter Leybold Mobile Cassy 2. All electrodeposition processes lasted 90min. After the electrodeposition processes, the deposited asphaltenes were obtained, taking advantage of their solubility. This procedure consisted of washing the electrodes with toluene, with the objective of dissolving the asphaltenes, followed by a filtration, to separate everything insoluble. Next step included the evaporation of toluene, the addition of heptane, and the filtration to obtain the insoluble fraction in heptane. According to the solubility of the asphaltenes, this final filtering corresponds to the asphaltenic fraction, which is purified with more

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heptane and dried for subsequent characterization with the same analytical techniques and equipment that the initial asphaltenes from the Yarigui oil.

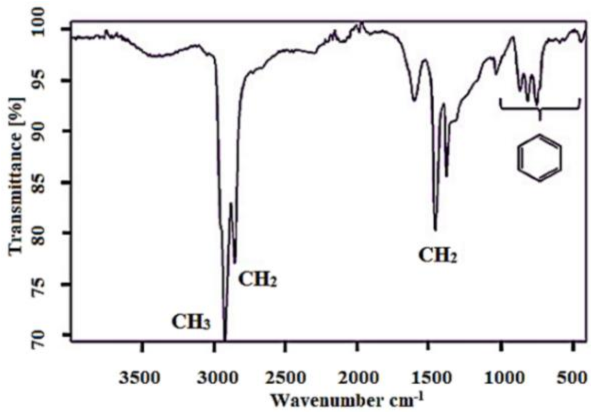
Figure 1. Asphaltene electrodeposition assembly in the presence of a magnetic field using a stator.

3. Results and discussion

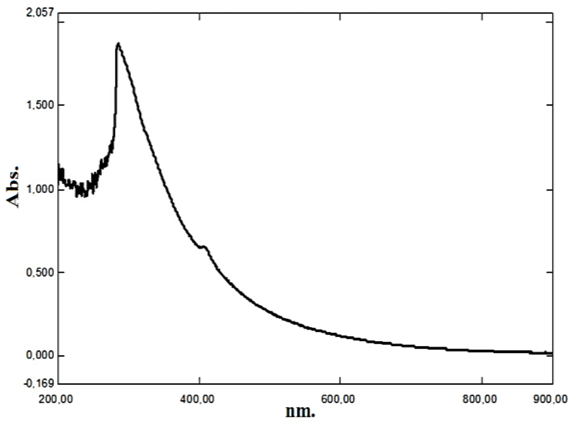
The SARA composition obtained for Yarigui oil was: saturates 34.31%, aromatics 36.71% resins 24.64 and the concentration of asphaltenes in this hydrocarbon is 4.13%. The oil presents an API gravity of 21 to 25°C. These values reveal that it is a low viscosity oil that can be classified as an intermediate oil.

The solubility tests reported that the asphaltenes are soluble in toluene, chloroform and dichloromethane, but insoluble in Heptane that results correspond to the expected behavior for the asphaltenic fraction, soluble in aromatic and polar solvents, and insoluble in linear alkane solvents.

Figure 2(a) corresponds to the infrared spectrum of the asphaltenes obtained from Yarigui oil. According to the literature, it corresponds to an infrared spectrum for asphaltenes, where we can see the signals for CH_3 between 2800cm^{-1} and 3000cm^{-1}, can also observe signals for CH_2 in two regions: between 1400cm^{-1} and 1600cm^{-1}, and between 500cm^{-1} and 900cm^{-1} the signals corresponding to the aromatic groups the Figure 2(b) shows the UV-Vis spectrum of asphaltenes extracted from the oil. Two main signals are observed: one around 400nm and another one at 300nm. These correspond to the chromophore groups present within asphaltenes.



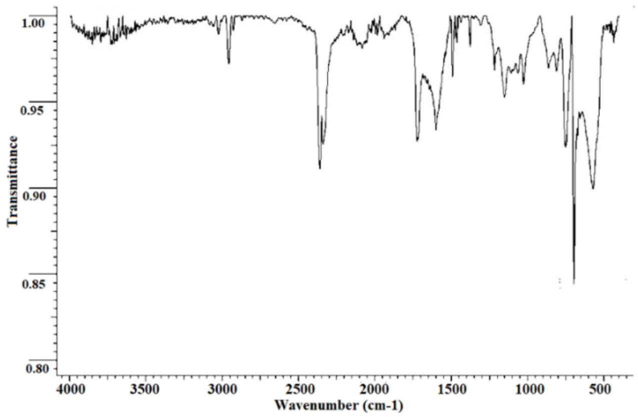
(a)

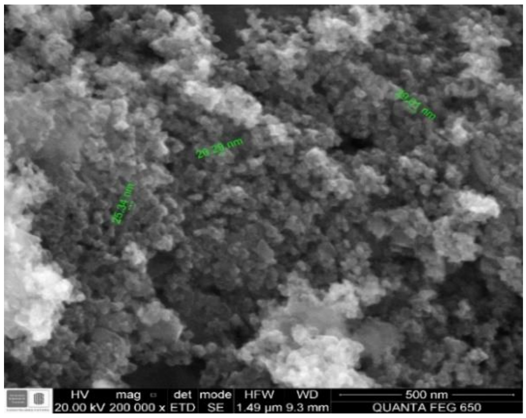


(b)

Figure 2. IR spectrum of asphaltenes extracted from Yarigui oil (a). UV-Vis spectrum of asphaltenes extracted from crude Yarigui (b).

Figure 3(a) shows the infrared spectrum of the magnetite nanoparticles, where characteristic signals can be observed at 750cm^{-1}, 700cm^{-1} and 500cm^{-1}. Figure 3(b) shows the SEM micrograph of the magnetite nanoparticles. As can be observed, their size is about 20nm.





(a) (b)

Figure 3. (a) Infrared spectra of magnetite nanoparticle (b) SEM micrograph of the magnetite nanoparticles.

Figure 4 shows the effect of electric and magnetic fields on the electrodeposition of asphaltenes, including an adsorption blank performed in the absence of fields. In this case, 7mg of deposit was obtained on the anode and 8mg of deposit on the cathode. As established in previous investigations of different authors [15], asphaltenes are sensitive to the electric field, allowing them to be electrodeposited. Our data corroborates this. As shown in Figure 4, deposits increased to 10mg and 13mg (on the anode and the cathode, respectively) by using the electric field. Moreover, applying a magnetic field further increased the performance of the process. In particular, by using the static magnetic field from the transformer, we increased deposits by approximately 50%, yielding 26mg and 21mg (the anode and the cathode, respectively). Even so, the most promising results came with the application of the dynamic field from the stator, when deposits rose to 63mg and 54mg (the anode and the cathode, respectively). This represents an increase of about six times when compared to the values observed with just the electric field.

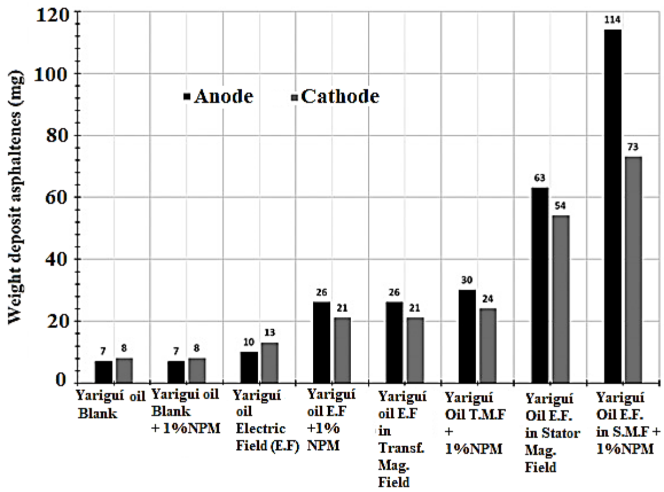


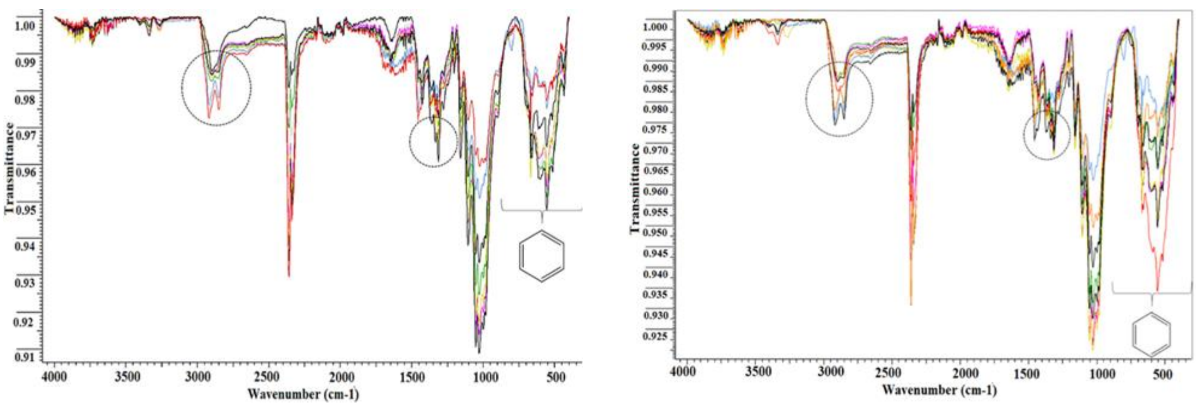
Figure 4. Amount deposited (the anode and the cathode) using Yarigui oil and Yarigui oil + 1% magnetite nanoparticles (NPM) as an electrodeposition medium.

The presence of magnetic fields improved the electrodeposition processes. In order to deposit asphaltene, it is necessary to generate a disturbance in the equilibrium of the hydrocarbon matrix, which allows the free asphaltene to be deposited. When an electric field is applied it affects the structure of the oil, leading asphaltenes with positive and negative charges to be deposited on the electrodes. The transformer generates a magnetic field around its coils, and additionally an electric field perpendicular to it. In this way three fields will be altering the equilibrium of the oil, two electric and one magnetic. Previously *Lesin* and collaborators reported the presence of magnetic nanoparticles in petroleum, a fact that has also been evidenced in investigations around rheological tests in the presence of magnetic fields [13]. This could explain the disturbance of the structural equilibrium of the hydrocarbon exerted by this type of fields. Moreover, and in contrast to the static field generated by the transformer, the stator produces a dynamic magnetic field. Hence, the magnetic field will not retain its fixed components. On the contrary, it will keep them in motion during the entire process. This movement improves the electrodeposition processes of the asphaltenes in the electrodes. The presence of the three fields will destabilize the equilibrium of the oil, freeing asphaltene and affecting it with the electric field, thus pointing it to the electrodes. According to some authors [15], charge of the asphaltene depends on the functional groups found on its surface and its heteroatoms, which involve carboxylic acids, and amines, among others. This affects the charge of the asphaltene according to the chemical environment in which it is. Thus, we may have species with positive, negative or neutral charge. In our data (Figure 4), there was not much difference between the anodic and cathodic deposits across different conditions. This fact agrees with the results previously obtained by other authors.

Keeping this in mind, we added magnetite nanoparticles to the oil (Figure 4). The amount of asphaltenes deposited under different conditions improved by adding the nanoparticles, except for the blank sample (i.e. the one exposed to no fields). We observed improvements (the anode and the cathode, respectively) of: 160% and 61.54% (for the electric field), 15.38% and 14.28% (for the magnetic field from the transformer), and 80.95% and 35.18% (for the magnetic field from the stator). As can be seen, highest benefits relate to the anode and to the electric field tests. Moreover, the behavior under the electric field results from the interference of nanoparticles in the hydrocarbon matrix, increasing the probabilities of having free asphaltenes. Although magnetite nanoparticles are not materials of high conductivity, their presence in a medium with low conductivity (i.e. oil) slightly improves the conductivity of the electrodeposition medium, thereby improving transport of charge and therefore the electrodeposition of asphaltene. In a similar fashion to the electric field, when exposed to a magnetic field more asphaltene is freed and can thus be electrodeposited in the electrodes according to the nature of its charge.

According to the treatment that was performed on the electrodes in the isolation of asphaltenes, it can be concluded that they are soluble in toluene and insoluble in heptane, one of the main characteristics of the asphaltene fraction.

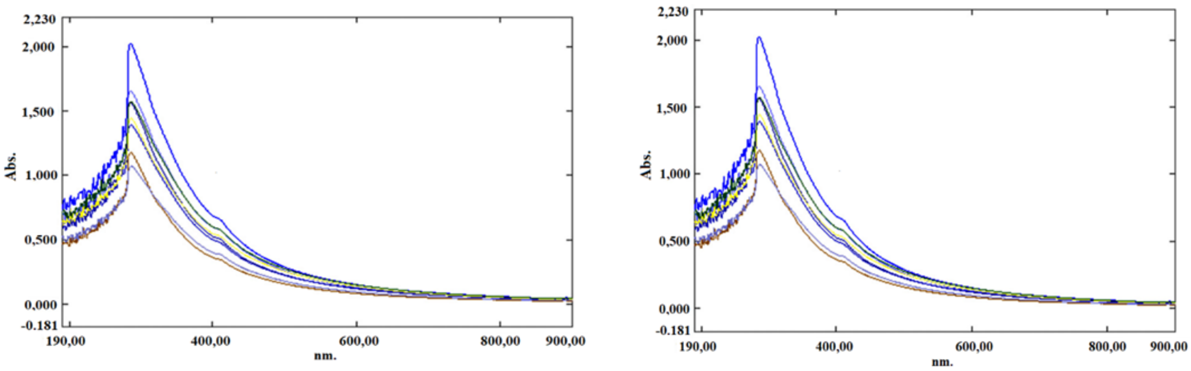
Figures 5(a) y 5(b) show the infrared spectra for anodic and cathodic deposits. Although their transmittance is low, signals of the characteristic groups for the asphaltenic fraction can be observed. The CH_2 and CH_3 sit between 2800cm^{-1} and 3000 cm^{-1}, as well as between 1400cm^{-1} and 1600cm^{-1}. Similarly, signals corresponding to CH_2 are observed between 500cm^{-1} and 900cm^{-1}, which correspond to aromatic groups. No characteristic signals of magnetite were observed in the obtained spectra. Therefore, bond formation between the asphaltenes and the magnetite is discarded during the processes of electrodeposition.



(a) (b)

Figure 5. IR spectra of asphaltenes deposited on (a) the anodes and (b) the cathodes.

Figures 6(a) and 6(b) show the UV-Vis spectra corresponding to the deposits of the electrodeposition processes, which coincide with that obtained for the free asphaltene extracted from the oil. Like with the IR spectrum, intensity varies among the spectra because they were not performed at the same concentration. Moreover, there are no signals belonging to nanoparticles (based on information available in literature) [16].



(a) (b)

Figure 6. UV-Vis spectra of asphaltenes deposited on (a) the anodes and (b) the cathodes.

4. Conclusions

Based on our experimental results, we can affirm that the presence of a magnetic field of low magnetic flux density improves electrodeposition processes of *asphaltenes* existing within the Yarigui oil. Under these conditions, having a dynamic magnetic field becomes more efficient than a static one. The interaction of the Yarigui oil with the magnetic fields in the absence of aggregated nanoparticles, suggests the presence of a natural fraction of magnetic nanoparticles according to the investigations carried out by *Lesin* in other crude oils. Adding magnetic nanoparticles further improved electrodeposition processes. It is also important to note that the interaction between asphaltenes and magnetite nanoparticles did not generate bonds, as evidenced in the chemical analysis. Thus, they can be safely used without altering the chemical properties of the crude oil.

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