USING ESI(-) FT-ICR MS TO EVALUATE THE EFFICIENCY OF DIFFERENT ADSORBENTS TO REMOVE NAPHTHENIC ACIDS FROM CRUDE OILS

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Introduction

The crude oil and petroleum distilled fraction may contain naphthenic acids (NA), that is a mixture of carboxylic acids, that can contributes to the acidity of crude oils and can cause corrosion problems. Removing NA is a industrial practice but this approach is unsatisfactory and have high operating costs.[1] So, a non-destructive process, like adsorption is a option.[2] In this context, this study evaluated the efficacy of using some adsorbents, such as shale, activated charcoal, commercial clay (bentonita), silica gel, sandstone and sawdust modified with KOH, to remove NA from two different crude oils (C13 and C20). To evaluate this acid removal efficiency we monitored the O_2 class abundance obtained by FT-ICR MS using negative ion mode electrospray ionization (ESI), for which the crude oils and residual oils (2 mg) were previously dissolved in 1 mL of toluene and then diluted with 1 mL of methanol, containing 0.1% of ammonium hydroxide. The samples were analyzed before (crude oil) and after the adsorption (residual oil) process to all evaluated adsorbents.

Results

From the FT-ICR MS analysis it was detected for both crude oils the heteroatom classes N, NO, NO_2, O_2, O_3 and S, in which the O_2 class was the most abundant. The relative intensity of O_2 compounds to the C13 and C20 samples were 50 and 40 %, respectively. After the adsorption process, it was observed a diminishing in the relative intensity of O_2 compounds to all used adsorbents as shown in Table 1.

**Table 1.** Percentage of relative intensity of adsorbed O_2 class compound by adsorbents

Relative intensity of adsorbed O_2 class (%)	Adsorbents					
	Shale (Sh)	Activated Charcoal (AC)	Bentonita (B)	Silica Gel (SG)	Sandstone (Sa)	Sawdust Modified (SM)
Oil C13	11	43	NI*	47	5	7
Oil C20	34	35	33	37	15	15

*NI = not informed

According this table the AC and SG were the best adsorbents because they got the higher relative intensity of absorbed O_2 compounds than others for both oils. This occurs because of their large surface area and the presence of functional groups on their surface, which makes the adsorbents more competitive and efficient in the adsorption process.[3] In general, oxygenated compounds, especially those of O_2 class, were preferentially adsorbed in relation

to the nitrogen compounds, so that the relative abundance of these N class compounds increased after the adsorption process.

The distribution of DBE relative abundance for O_2 class present in residual oil samples (after adsorption process), according Figure 1, shows that the C20 sample has less amount of acidic compounds (class O_2) than the C13, since it showed lower intensity in its analysis. The compounds with DBE 3-7 were found in higher relative intensity in oils C13 and C20 and were apparently the most adsorbed compounds. The preference for these compounds may be related to the sizes of the active sites of the adsorbents. In addition, it can be observed that the SG and the AC also showed better results for adsorption of compounds of every DBE.
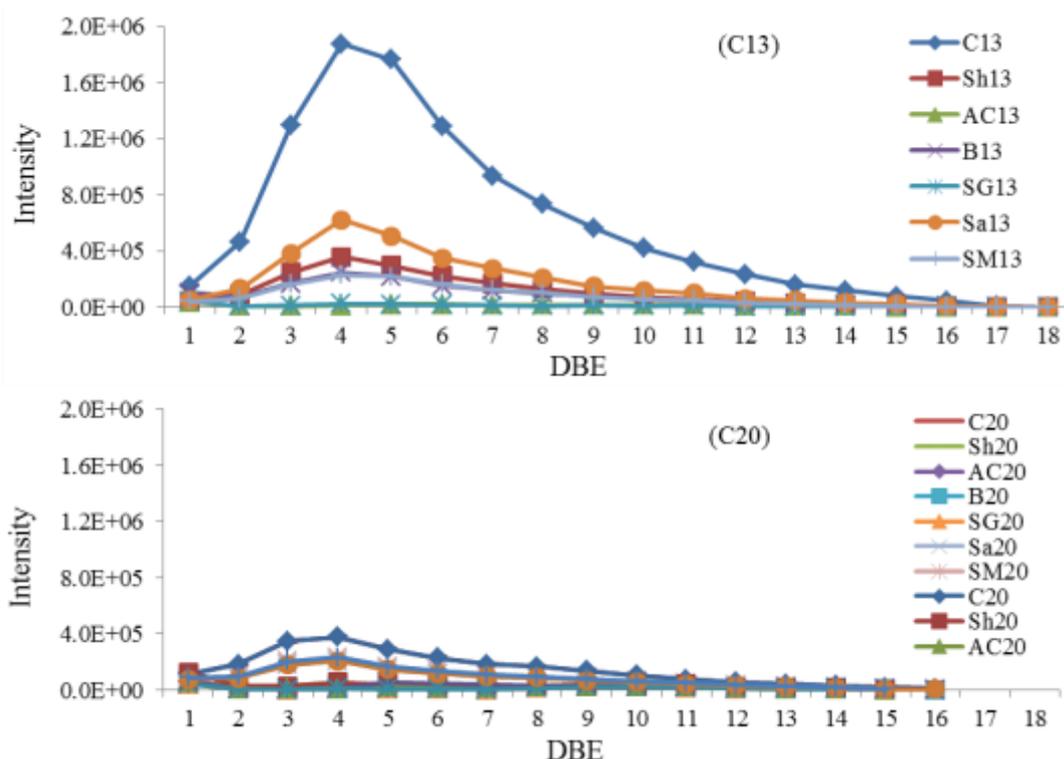
Figure 1. *Distribution of DBE relative abundance for O_2 class compounds present in residual oil samples*

Conclusions

This work shows the adsorption potential of the tested adsorbents for naphtenic acids removal in crude oils, in which silica gel and activated carbon were more efficient. Short chain acids are adsorbed preferentially in these materials.

References

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