

Effect of the BMIM BF₄ immobilization on oxidized activated carbon in fuel desulfurization

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Abstract

Environmental consequences of high consumption of fossil fuels containing sulfur compounds have promoted research in technologies for their removal. Catalytic hydrodesulphurization currently used requires high temperature and pressure. Alternative technologies based on ionic liquids pure and anchored to matrices have shown good desulfurization properties. Composites offer advantages of reuse, less time consuming and costs, using lower IL amount. In this work, we obtained a solid composite containing [BMIM][BF₄] supported on oxidized active carbon and characterized by FTIR, BET, TGA-DSC, and SEM. We evaluated the extraction capacity of benzothiophene, thiophene, dibenzothiophene, and diphenyl sulphide from a model fuel with both pure [BMIM][BF₄] as well as the same IL on oxidized activated carbon. In the extraction process using pure IL were achieved removal percentages of up to 69.8% whereas with the composite it was possible to reduce 80 % of the sulfur content. Copyright © 2018 VBRI Press.

Keywords: Ionic liquids, activated carbon, sulfur removal.

Introduction

Oil refineries are under pressure due to the strict regulatory requirements related to fuel sulfur content. Advanced technologies based on the catalytic conversion of the S- compounds with sulfur elimination. Hydrodesulfurization (HDS) is one established technology for removal of thiols, sulfides, and disulfides, but it does not efficiently eliminate aromatic S-compounds. Also, this technology works under harsh conditions including high temperatures and pressures, and high operating costs. This situation demands the development of new technologies capable of performing under greener conditions, with high yields of removal and low energy consumption and costs; in the last years have been reported alternative technologies involving physicochemical separations and transformations [1]. Among these alternatives, extractive desulfurization is interesting as it is carried out at ambient temperature and pressure and it does not require hydrogen. Ideal candidates for the extractive and oxidative desulfurization are ionic liquids which are low melting point salts with negligible vapor pressure and can be easily regenerated [2]. Several studies [3–15] have reported the effects of different cations and anions on the selective extraction of sulfur compounds from fuel oils without removal of aliphatic and aromatic hydrocarbons

to maintain the fuel under specifications; next paragraphs summarized some of those studies. IL extraction processes focus on the extraction of the aromatic sulfur compounds, which are difficult to remove, by common HDS at traces level. This kind of direct extractive desulfurization has higher percentages of removal than conventional organic solvents but still low desulfurization efficiency (10-40%) in a single extraction, so it requires several continuous extraction steps to reach the ideal S-contents. Study of oxidative methods [4–8] based on IL technology started with systems using IL as extractant, with acetic acid as catalyst and H₂O₂ as oxidant. This kind of systems allow removal of up to 99%, but the use of acetic acid make difficult the separation or regeneration of the catalyst, and there is oil contamination by dissolution of the catalyst at trace levels. A better alternative is the use of Lewis and Brönsted acidic ILs, which have a double function as extractant and catalyst allowing removal percentages as high as 100% with recycling of up to six times the IL; however, there is no report about the properties of the fuel oils after the oxidative extracting process.

Recently, for S-compounds removal, the ILs are being supported on solid materials like silica, polymers, graphite and activated carbon (AC) to obtain materials easier to handle and regenerable [16–21]. AC has high

surface area and porosity, low cost and their surface can be modified [17]. Oxidative desulfurization reported in the solid state with graphene-hexagonal boron nitride (G-h-BN) as a matrix of tungsten ionic liquid. The synthesized material showed to be thermostable and chemically stable; reaction conditions were very mild, and sulfur removal of DBT from model oil could reach up to 98.5% at 60°C. The catalyst could be recycled five times without significant loss of catalytic efficiency demonstrating a new strategy of designing high activity heterogeneous catalyst for organic reactions [19]. In this research in a preliminary test, we studied liquid-liquid extractions of sulfur compounds (thiophene, benzothiophene, dibenzothiophene and diphenyl sulfide) achieving removal percentages of up to 61.2% and 69.8% for thiophene and dibenzothiophene by using the pure ionic liquid [BMIM][BF₄]. To improve this percentage of removal and to obtain a cheap solid material, regenerable and reusable, we prepared a composite supporting this IL on oxidized activated carbon. We characterized properties including thermal, morphological, physical and structural by TGA-DSC, SEM, BET and FTIR techniques, respectively. Also, results of the extraction of thiophene and benzothiophene from both model and enriched fuel at the optimal conditions have shown that extraction efficiency can be raised up to 80% using significantly less amount of IL.

Experimental

Materials

Activated charcoal (granular, 8-20 mesh, Sigma-Aldrich). 1-butyl-3-methylimidazolium tetrafluoroborate (for synthesis, Merck), nitric acid (p.a., ≥65%, Sigma-Aldrich). Thiophene (for synthesis, Merck). 1-benzothiophene (for synthesis, Merck), dibenzothiophene (for synthesis, Merck), diphenyl sulfide (for synthesis, Merck), and tetrahydrofuran (for analysis, Merck). Isooctane (for analysis, Merck).

Material synthesis

Immobilization of [BMIM][BF₄] on OAC, OAC/IL

Oxidation treatments of AC fix oxygen surface groups including carboxyl, lactone, carbonyl, quinone, phenols, alcohols, and ether that make the carbon material more hydrophilic and acidic. Commercial AC (particle size ≤ 300 μm), was oxidized with nitric acid and H₂O₂ at 65°C (±0.2°C) for three, six, eight and ten h. Then the OAC was washed with distilled water and dried at 115°C (±0.2°C) for 24 h. Evaluation of the oxidation efficiency was monitored by FTIR and by titration with NaOH. We immobilized the ionic liquid on OAC, (ratio of OAC: IL calculated with the number of acidic active sites determined previously). We dissolved the ionic liquid in tetrahydrofuran and stirred at 60°C (±0.2°C) for 4 hours; then the solid composite was filtered and washed with isooctane and THF; we monitored the process by FTIR and UV Spectroscopy.

Characterizations and response measurements

We evaluated the leach stability of the material IL/OAC, by rinsing it with two different solvents: THF and isooctane. The composite was weighted before and after the leaching process (leach %) and analyzed by UV Spectroscopy through absorbance measurements at 313 nm (λ_{max} of absorption) for the imidazolium ring. TGA analysis allowed to determine the thermal stability of the composite by using a TA Instrument SDT-Q600 system from 40 to 500°C at a rate of 10°C/min. We used a TA Instrument DSC-Q20 from -90 to 200°C at a heating rate of 10°C/min for differential scanning calorimetry (DSC) curves determination. The surface area of AC, OAC, and OAC/IL, were determined through nitrogen adsorption/desorption processes using a Micrometrics series 3Flex system with isotherms at 77 K; we previously degassed the samples with a degasser Micrometrics series Vacprep. Calculations performed according to Brunauer–Emmett–Teller (BET) equation. Using a Field Emission Scanning Electron Microscopy (FESEM), Inspect F50 equipment (FEI Instruments) on secondary electrons mode determined the biomaterials morphology.

Liquid-liquid extraction of sulfur compounds from model fuels with [BMIM][BF₄]

Solution preparation: A mix of thiophene (T), benzothiophene (BT), diphenyl sulfide (DPS) and dibenzothiophene (DBT) prepared at 100 and 200 ppm to obtain two different total concentrations of 96.43 and 192.84 mg S/L, respectively. We performed the liquid-liquid extraction process under the next experimental conditions, mass ratio 1:1 (IL: Oil) at 27°C (±0.2°C), during 30 minutes with a stirring speed of 845 rpm (Figure S1). All the experiments realized three times and monitored by gas chromatography using a GC-2014 Shimadzu, equipped with a DB-1 capillary column (length 30 m, diameter 0.320mm, thickness 0.25 μm) and an FID detector. Also, we evaluated the extraction capacity of the [BMIM][BF₄] after regeneration of the spent IL with methanol and active carbon; by heating the mix under reflux for three hours, then the AC was filtered and the methanol rotoevaporated.

Evaluation of the composite for sulfur removal

An experimental setup as shown in Figure S2 was used to evaluate the composite for removal of S-compounds from the model oil (MO) consisting in a mix of T, BT, DPS and DBT at 200 ppm of each one to obtain total concentrations of 192.84 mg S/L in isooctane. For the experiments, we used a mass of composite (0.052, 0.105 and 0.3 g (±0.1 mg)) in a fixed bed quartz reactor with an internal diameter of 4 mm). Tests performed with reactor temperatures of 25, 45 and 60 °C (±1°C) (Lindberg Blue Tube Furnace, Thermo Scientific). The model oil (MO) (5 mL) pumped into the sample container with a peristaltic pump (Masterflex easy-load) at a feed flow of 0.5 mL/min (±0.01 mL/min). The total

sulfur content was found using a wavelength dispersive X-ray Fluorescence S8 TIGER Bruker spectrometer. After three cycles of extraction, the composite was regenerated by thermal desorption process at 100°C ($\pm 0.2^\circ\text{C}$) for 24 hours. The regenerated material was re-tested under the same experimental conditions to examine its reusability. At last, a commercial fuel with an initial total concentration of 320 mg-S/L, was desulfurized using 0.150 g (± 0.1 mg) of composite and 5 ml of fuel, at 45°C ($\pm 0.2^\circ\text{C}$) and 0.50 mL/min (± 0.01 mL/min).

Results and discussion

Characterization of the material OAC/[BMIM][BF₄]

The process of AC oxidation over time was monitored using FTIR; the spectra it shows in **Fig. 1**. Analysis of IR spectra of AC and OAC showed a strong band at 1720 cm^{-1} related to C=O stretching vibrations of carboxylic groups after oxidation. The band centered at 1544 cm^{-1} is associated with aromatic ring stretching coupled to highly conjugated carbonyl groups (C=O)[22]. Broadband from 1050 to 1100 cm^{-1} is assigned to C-O stretching in acids, alcohols, ethers or esters groups[23]. IR confirmed the effectiveness of the oxidation reaction for the formation of oxygen species on the AC surface. The spectrum of the composite OAC/[BMIM][BF₄] shows the characteristic bands of the [BMIM][BF₄]. At 3136 cm^{-1} quaternary amine salt and 1017 cm^{-1} BF₄ asymmetric stretching, at 2947 and 2870 cm^{-1} the signals of CH₃ and CH₂ asymmetric and symmetric stretching, and at 1560, 1450, 1151 and 840 cm^{-1} the signals attributed to the imidazole ring [24–26]. The disappearance of the signal at 1720 cm^{-1} and the substantial reduction in the height of the signal at 1544 cm^{-1} in the composite material indicates the electrostatic interaction between carbonyl groups in OAC with the IL.

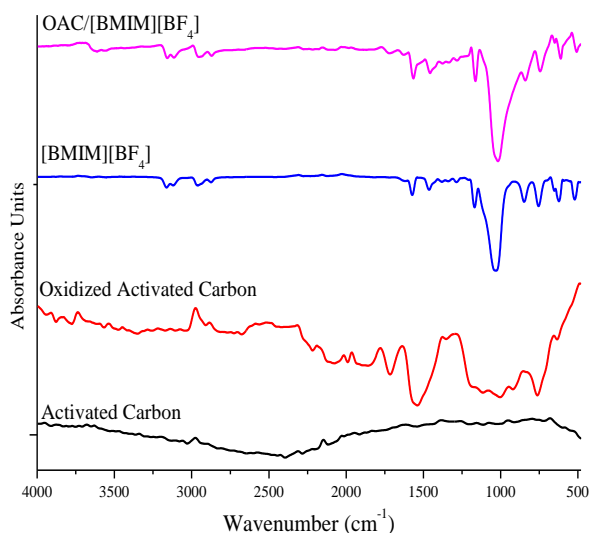


Fig. 1. FTIR spectra of AC, OAC, [BMIM][BF₄] and OAC/[BMIM][BF₄].

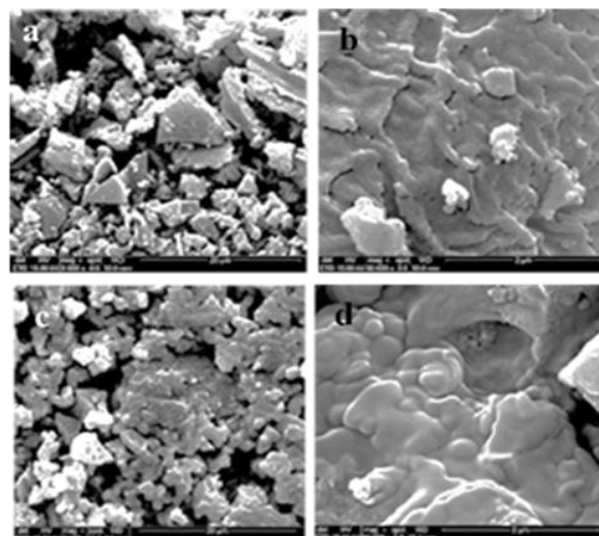


Fig. 2. SEM images of OAC and the composite: a and b, OAC at 8.000x and 80.000x, respectively; c and d, composite at 8.000x and 80.000x, respectively.

Fig. 2 shows SEM images of both OAC (a and b) and the composite (c and d) at 8000 x and 80000x, respectively. In these images the OAC looks like a dispersed material with a laminar morphology and irregular shapes. In the images of OAC/BMIM BF₄, the material looks agglomerate with spherical particles. The surface looks wholly occupied by the IL molecules which as reported for nanostructured carbon materials [27]. The results of EDS analysis (**Fig. S3** and **Table S1**) showed the corresponding peak of fluorine confirming the presence of BF₄⁻ anion.

Thermogravimetric analysis was performed to determine the thermal stability of the materials. **Fig. 3** presented the TGA thermograms of AC, OAC, OAC/IL and BMIM BF₄. In the first stage, the loss of mass up to 120°C attributed to water was 5% for AC, 15% for OAC (indicating that the oxidation process led to a more hydrophilic material) and 1% for OAC/IL (indicating a hydrophobic behavior). The mass of BMIM BF₄ remained constant. For OAC there was a second stage (loss of mass of 9%) from 150°C until the final temperature of 500°C assigned to decomposition of oxygenated type groups [28,29].

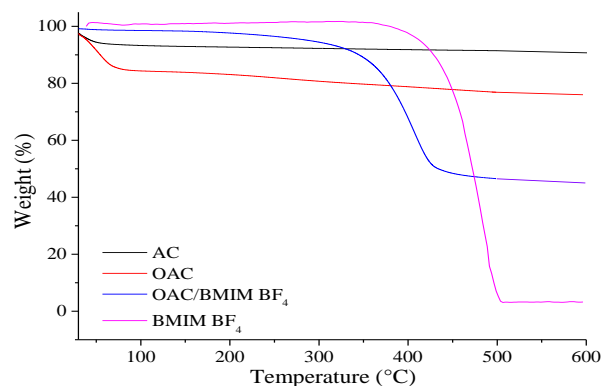


Fig. 3. TGA thermograms of AC, OAC, [BMIM][BF₄] and OAC/[BMIM][BF₄].

In the second stage of OAC/[BMIM][BF₄], a loss of mass from 150°C to 320°C was lower than that of OAC which may be related to a lower loss of oxygenated groups due to the electrostatic interaction with the IL. In the third stage between 320 and 500°C, a mass decrease of 50% is related to the BMIM BF₄ loss which decomposes between 361 and 505°C. The difference on the onset temperature between OAC/[BMIM][BF₄] and [BMIM][BF₄] confirms the IL/matrix interaction, since this affects the ILs structure and therefore its thermal stability [30,31]. **Fig. 4** shows DSC curves for activated carbon, BMIM BF₄, and composite. For the OAC an endothermic pick was observed at 88.19°C with an integrated area of 163,3 J/g, attributed to water desorption from its surface.

In the OAC/IL curve, is observed that peak at 83.45°C with an integrated area of 34.5 J/g, which is significantly lower than that of OAC. The lower area is related to a less amount of water absorbed on its surface. The hydrophobic character of OAC/IL is due to an interaction between the acid groups of the matrix and the IL as well as the hydrophilic IL molecules soaked into the pores [32].

BET analysis confirmed this affirmation since the surface area of OAC (676.8104 m²/g), which was similar to that of AC (662.0570 m²/g), was almost suppressed after the immobilization of the IL (1.7998 m²/g). This decrease indicates that the IL filled the micro and mesopores and produced some pore blockage as confirmed by SEM. This agglomeration is consistent with the lower surface area determined by BET analysis. Palomar *et al.* [33], proposed the presence of blocked porosity in the case of IL adsorb (from aqueous effluents) on commercial activated carbon and Rufete-Beneite [28] detected the same phenomena studying immobilization of IL on different kinds of porous carbons. We studied the stability of the IL/OAC against leaching by rinsing the composite with solvents with variable polarity as shown in **Fig. S4**. This behavior determines the field of application of the material. Monitoring of mass loss after each rinse allowed determining the leached %. It was stated by [28] that the kind and extension of the oxidation process for AC as well as the amount of IL loaded were crucial factors to prepare stable materials.

Sulfur extraction with pure ionic liquid [BMIM][BF₄]

The extraction of model oil led to the S-sulfur removal percentages shown in **Table 1**. We include reference data reported by Dharaskar [10] for comparison purposes. As expected, starting with a concentration of 96.43 mg S/L led to higher removal percentages when compared to the initial concentration of 192.84 mg S/L. This behavior indicates that the IL gets saturated at concentrations above 92.43 mg S/L using a ratio of IL/MO of 1:1. Removal of DBT is the highest for both initial concentrations, in agreement with the Nernst partition coefficients (K_N). It is usual to observe matrix interference when the extraction process performs with

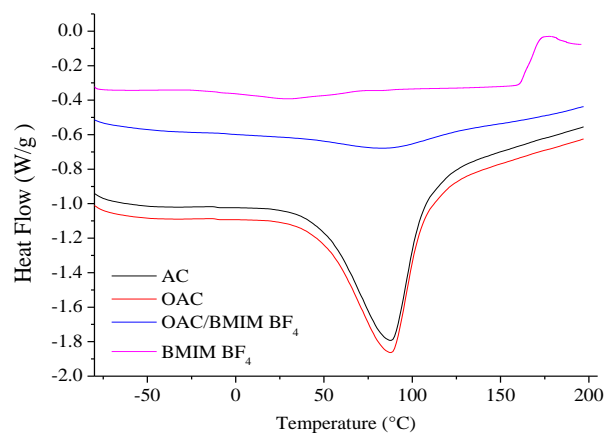


Fig. 4. DSC curves of AC, OAC, [BMIM][BF₄] and OAC/[BMIM][BF₄].

mixes. However, we do not detect this effect in our experiments compared with that reported by Dharaskar [10]. It has to be remarked that Dharaskar's tests started with a higher concentration (500 mg/L) but they used a 3:1 IL/MO ratio while in our experiments we used a lower initial concentration with a 1:1 IL/MO ratio. The greater DBT removal is due to that this one has the highest electron density when compared to BT, and T, DPS, which led to the highest π - π interaction capacity [10]. Removal percentages are not the same for all the aromatic S-compounds as shown in **Table 1**, indicating that the structure (extension of the π - π electronic interaction) and geometry of the S-compounds determine the extension of the interaction with the imidazolium ring of the ionic liquid. Planar structures favor the interaction with the imidazolium explaining the lowest removal percentage for the diphenyl sulfide. In general terms, our results are in agreement with those reported. [3,11].

Table 1. Sulfur removal percentages from model oil solutions.

S-compounds in model oil	Sulfur removal (%)			K _N Extraction ability of [BMIM][BF ₄] [10]
	T _i S ^a 96.43 mg S/L	T _i S ^a 192.84 mg S/L	Sc ^b 500 mg S/L [10]	
T	52.41±2.88	50.03±1.14	53.8	1.16
BT	64.79±2.14	53.12±0.95	63.9	1,77
DPS	44.80±1.59	23.78±1.20	---	---
DBT	69.81±2.57	59.17±2.03	66.0	1,94

^a T_iS: Total initial S concentration (mix of S compounds). ^b S-compound concentration tested individually.

After the first cycle of extraction using the solution at 192.84 mg S/L, it is clear from **Fig. S5** that the IL is saturated. However, the extraction capacity is remarkable higher for DBT even at the third cycle. The regeneration method evaluated on the spent IL after three cycles of extraction showed a negligible loss of extraction capacity under reuse as shown in **Fig. S6**. Change *et al.* [34] reported that NMR and Molecular Fluorescence analysis showed that regeneration of the IL

with methanol caused changes associated with IL-IL interactions. That facilitates dissociation of cations and anions ending with structural changes in the IL, due to new interactions methanol-imidazolium. However, we did not detect any effect of methanol on IL extraction capacity.

Evaluation of the composite for sulfur removal using model oils

The extraction was performed at 25, 45 and 60°C to evaluate the effect of temperature. Results show that by increasing the extraction temperature from 25 to 45°C the removal extraction increases from 58.94 ± 1.19 to $64.45 \pm 1.61\%$ but at a temperature above 60°C decrease to $59.88 \pm 1.80\%$ may be due to evaporation/concentration effect. Results agree with the behavior of an exothermic extraction process [35]. The effect of temperature has been attributed to the reduction of the IL viscosity at 45°C improving its flexibility and mobility within the pore. We evaluate the composite amount on S-removal. The obtained S-removal percentages after three cycles of extraction appear in Fig. 5.

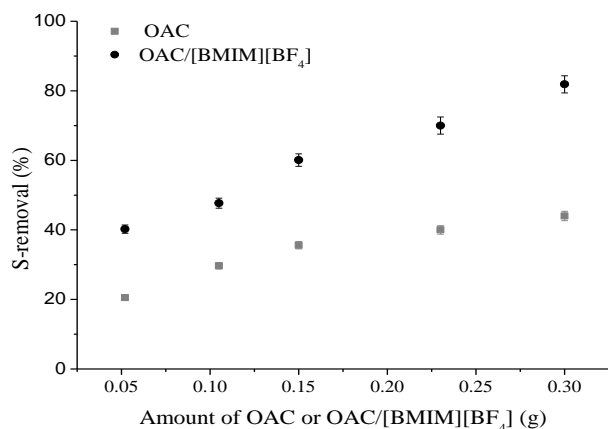


Fig. 5. Effect of OAC and OAC/IL amounts on S-removal (%). Experimental conditions: 5 mL of solution 500 mg-S/L, 0.5 mL/min, 0.05, 0.1, 0.15, 0.25 and 0.3 g of OAC or OAC/IL, 25°C and 3 cycles of extraction.

The OAC extracts S-compounds by itself, however, as has been reported [36], and it is possible to observe that increasing the amount of oxidized activated carbon or OAC/IL material S-removal percentages increase. However, as SEM and BET analysis showed, in the material OAC/IL the pores are fully occupied by the IL molecules so in this case the removal capacity should be attributed exclusively to the [BMIM][BF₄]. Using 0.3 g of the composite, the S-removal increased to 81.86%; this value is higher than the value reported by Carvalho et al. [18] 58%. They used a model oil solution of DBT (10 ml of MO at 50mg/L and 45°C) using 0.3 g of a composite of N-methyl-imidazolium with NTF₂⁻ supported on silica.

Table 2 shows the comparison of the results for the extraction capacity of the pure IL and the solid material OAC/IL using a model mix. It is remarkable the enhanced extraction capacity using the composite

material that has less amount of IL. It has to take into account that using the pure ionic liquid there is a restriction of mass transference due to its high viscosity by the other side in the solid state when the IL covers the OAC more surface area interaction is possible. In this case, we observed that the π - π interaction between the S-compound and the imidazolium ring is equal to T and DBT [37].

Table 2. Comparison of S-removal (%) of sulfur compounds with pure IL and OAC/IL.

S-compounds in MO	Sulfur removal (%)	
	Pure [BMIM][BF ₄]	OAC/[BMIM][BF ₄]
T	52.41±2.88	81.53±1.68
BT	64.79±2.14	71.17±2.68
DPS	44.80±1.59	52.89±2.17
DBT	69.81±2.57	82.19±1.97

Pure IL: [Initial]: 96.43mgS/L, 1:1 ratio IL/MO, 25°C, 3 cycles. OAC/IL: 5 mL of [initial]: 500 mgS/L, 0.5 mL/min, 0.30 g of material, 25°C, 3 cycles

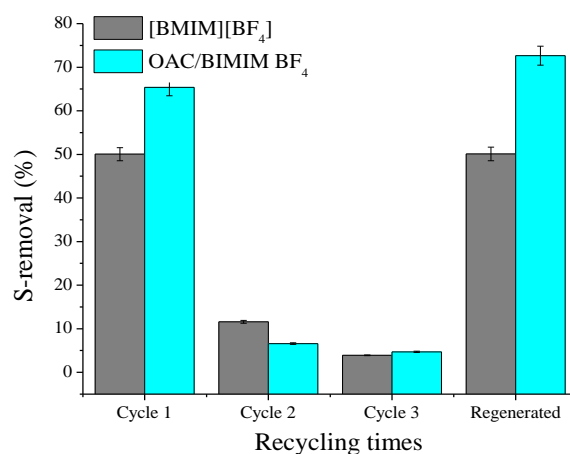


Fig. 6. Recycling tests of [BMIM][BF₄] and OAC/[BMIM][BF₄]. Pure IL: [Initial]: 96.43mgS/L, 1:1 ratio IL/MO, 25°C, 3 cycles. OAC/IL: 5 mL of [initial]: 500 mg S/L, 0.5 mL/min, 0.30 g of material, 25°C, 3 cycles.

Recycling and regeneration of the composite

All materials loss extraction efficiency after each cycle, as can be observed in Fig. 6, because of saturation. However, an advantage is that both the pure ionic liquids as well as the composite can be regenerated and re-used with even better efficiency in the case of the composite. These results are in agreement with those reported by Jiang et al. [37] who reported the same values of extraction of DBT with the initial and the regenerated IL [C₄MPIP][FeCl₄].

Desulfurization of commercial fuel

Research performed with [BMIM][BF₄] have reported that desulfurization of fuels with this particular ionic liquid does not affect the oil matrix which is desirable as the process should not change the octane number [9,38].

Observations indicate that the fuel complex mix affects the extraction efficiency as compared with model oil solutions, the extraction efficiency for fuel samples is lower than for model oils samples. However, our % S-Removal values are higher as compared to the values reported by Chu *et al.* [11] with pure ionic liquids having into account that in this research we used a remarkable less amount of ionic liquid as can be observed in Table S2.

Conclusion

In this research, a composite has been prepared to immobilize the ionic liquid [BMIM][BF₄] on oxidized active carbon, both the pure [BMIM][BF₄] and the composite tested for desulfurization of both model and real commercial fuels. The liquid-liquid extraction with [BMIM][BF₄] has been evaluated, obtaining extraction percentages as high as 60% with a probed capacity of regeneration and re-used. Desulfurization with the composite has shown that using a significantly less amount of ionic liquid is possible to obtain higher S-removal percentages (up to 82%) indicating that the solid nature of the composite allows better interaction with the fuel; at the same time, the composite can be regenerated and re-used.

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Author's contributions

Conceived the plan: M.V., M.S.V., M.P., A.T., J.A., M.R., L.D.; Performed the experiments: M.V., M.S.V., M.P., A.T., J.A.; Data analysis: M.V., M.S.V., M.P., A.T., J.A., M.R.; Wrote the paper: M.R., L.D. Authors have no competing for financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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