

STUDY OF ADSORPTION OF DIBENZOTHIOPHENE EMPLOYING IONIC LIQUID SUPPORTED ON SILICA

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ABSTRACT: Due the problems caused by sulfur compounds in refineries, in car engines and the environment, the environmental agencies (CONAMA) established new regulations to reduce the sulfur content in fuels. This work developed a new adsorbent material, aggregating ionized organic compounds (ionic liquid, LI) in a solid adsorbent (silica) to remove dibenzothiophene present in petroleum. The dibenzothiophene was selectively removed by adsorption using N-methyl-imidazolium with $N(Tf_2)^-$ supported on silica. The synthesis of the material was made by impregnation of the cation and anion of the ionic liquid through conventional method (oil bath). The samples were characterized by classical techniques of characterization of solid materials: adsorption and desorption N_2 (BET and BJH methods), chloride titration, CHN, infrared Fourier transform spectroscopy (FTIR) and chromatographic analysis by GC- FID. The adsorption capacity of dibenzothiophene in Sil- IMI - $N(Tf_2)^-$ in equilibrium (q) increased 0.2 to 1.0 mg/g with increased initial concentration of the pollutant 25 to 100 mg/L, the adsorbent is capable of adsorbing dibenzothiophene about 58%.

KEYWORDS: Adsorption, dibenzothiophene, ionic liquid.

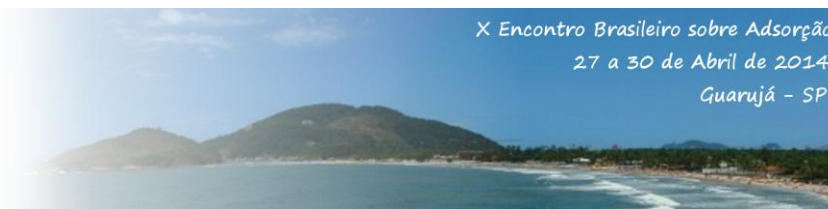
1. INTRODUCTION

The petroleum contains appreciable amount of constituents that have heteroatoms, elements as sulfur, nitrogen, oxygen and metals. These constituents, considered as impurities, may appear in all fractions of the petroleum, but has concentrated on the heavier fractions. The sulfur compounds present in greater numbers between the resins and asphaltenes, which are large molecules with high relation carbon/hydrogen and striking presence of sulfur, oxygen and nitrogen (of 6.9 to 7.3%) Thomas et al. (2004).

The sources that emit sulfur compounds for the atmosphere can be natural or anthropogenic. Human activities are responsible for the emission of large amounts of sulfur for the atmosphere, produce SO_2 and SO_3 by combustion, which form H_2SO_3 and H_2SO_4 Rocha et al. (2009).

The sulfur compounds are present in all types of petroleum, and in general, the higher the density of the petroleum, the higher the sulfur content. The sulfur compounds, addition to undesirable, because compete to increase the polarity of oil (increasing the stability of emulsions), are the responsible for the corrosivity of petroleum products, contaminate the catalysts used in transformation process and determine the color and smell of the products final Mariano (2005).

Due the problems caused by sulfur compounds in refineries, in car engines and the environment, the environmental agencies (CONAMA) established new regulations to reduce the sulfur content in fuels. Problems those also observed in the lines of processes in the petroleum sector, the coming motivating the sector for changes in their treatment processes. The market now available a diesel of cleaner sulfur S-10 launched by Petrobras currently, meaning 10 ppm sulfur in diesel.



Several studies have focused on the removal of sulfur compounds of petroleum by alternatives methods such as biodesulphurization, desulfurization by adsorption, desulfurization by ultrasound, adsorption, adsorption oxidative and liquid-liquid extraction. All of these are complementary to the hydrotreating process, which uses large amounts of hydrogen, high temperatures ($>300^{\circ}\text{C}$), high pressures ($>4\text{MPa}$) and sophisticated catalysts of molybdenum and cobalt, resulting in process high cost. Among these alternative methods, the adsorption shows up an interesting process with intent to conduct a deep removal of sulfur Irvine (1998), Marín-Rosas et al. (2010).

1.1. Adsorption

The adsorption of sulfur compounds in fossil fuels has shown the efficiency and selectivity of adsorbents tested in model systems. The acidic alumina proved capable to adsorb about 98% of the compounds and also has the property of regeneration after the calcination step, making it an adsorbent efficient and economical Yen et al. (2007). Erickson et al. (2006) used the adsorbent Cu- Al_2O_3 with the goal of removing thiophenes from a mixture of hydrocarbons. Zhou et al. (2009) employed an activated carbon adsorbent for selective adsorption of sulfur compounds refractory, with the 4-metildibenzotiofeno, dimethyldibenzo and 4,6-thiophene-diesel, and obtained a yield of adsorption greater than 90% of carbon derived from activated carbon and 35% higher than the best commercial activated carbon between all the activated carbon commercial examined.

1.2. Ionic Liquid

Zhang and Shuguang (2002) performed experiments to selectively remove sulfur from fuels using different ionic liquids at room temperature, obtaining better results for ILs, 1-ethyl-3-methylimidazolium tetrafluoroborate ($\text{EMIM}^+\text{BF}_4^-$), 1-butyl-3-methylimidazolium tetrafluoro-borate ($\text{BMIM}^+\text{BF}_4^-$) and 1-butyl-

3-methyl imidazolium hexafluorofosfato ($\text{BMIM}^+\text{PF}_6^-$). Cassol et al. (2007) using the LI with the characteristics of cations 1-n-butyl-3-methyl-imidazolium (BMI) with the bis anion (trifluoro-methanesulfonyl) imidate $\text{N}(\text{Tf}_2)^-$, where used the extraction technique liquid - liquid and obtained a result of 40% of removal of sulfur compounds.

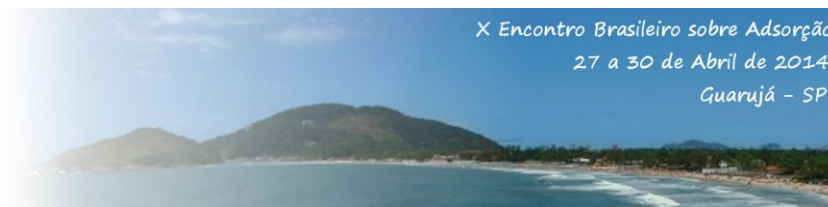
2. METHODOLOGY

2.1 Preparation of functionalized silica with Ionic Liquid

To promote removal of impurities and activation of silica gel (Macherey-Nagel), this was washed three times with acetone PA (Vetec) on ultrasound. It was subsequently taken to an oven at 110°C for 12 hours for elimination of physically adsorbed water and stored in a desiccator under vacuum.

In order to promote the widest possible coverage of the surface, was used an excess of the ligand silane 3-chloropropyltrimethoxysilane (CPTMS Sigma-Aldrich), a mass of 0.53 g (2.67×10^{-3} mol). Thus, 20 g of were added to a solution containing 10.6 g of CPTMS in 200 mL of toluene. The suspension was heated to 80°C in the solvent refluxed for 24 hours. The modified was washed with 100 mL of toluene, 80 mL ethanol, and finally 50 mL of diethyl ether (all Vetec) to assist in drying. Then the material was dried at 80°C for 8 hours. Subsequently, the silanized silica passed through a removal of excess organic compounds by the method of Soxhlet with ethanol for 24 hours, and put in an oven at 80°C for 8 hours and stored in a desiccator under vacuum. The material obtained will be called silica CPTMS.

The silica initially impregnated with the binding agent 3-chloropropyltrimethoxysilanesilane was reacted with 3.28 g of 1-N-methylimidazolium (Sigma-Aldrich, $M = 82 \text{ g mol}^{-1}$, $d = 1.035 \text{ g.mL}^{-1}$) in a glass balloon under reflux, heated at 110°C oil bath for 24 hours, as illustrated in Figure 1. The reaction product



was recovered by filtration and washed with toluene, ethanol and ethyl ether, followed by washing in a Soxhlet method for removing excess organic compounds. Subsequently,

dried at 80°C for 8 h in stoven and stored under vacuum in a desiccator. The material obtained will be called Silica-IMI-Cl.

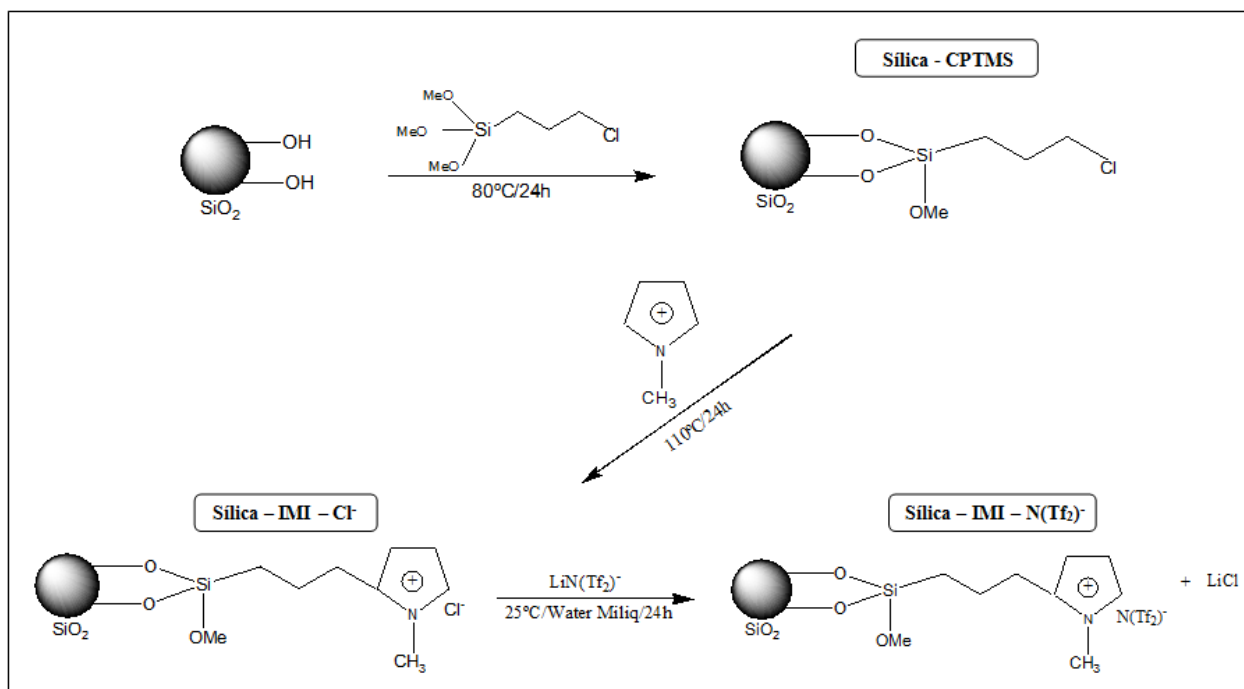
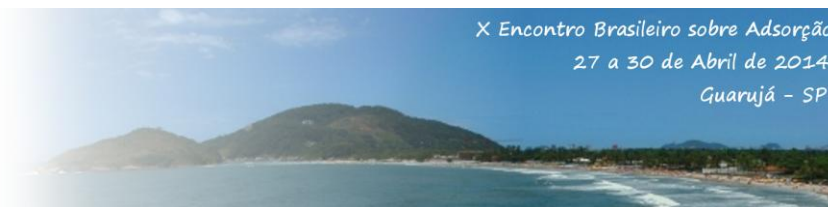


Figure 1. Scheme of step impregnation of the silica with the agent silano3-chloropropyltrimethoxysilane (CPTMS) and silica-CPTMS functionalization with 1-methylimidazolium.

The exchange of the compensation anion Cl⁻ of the imidazolium ring by anion bis (trifluoromethane sulfonilimida), N(Tf₂)⁻ was performed according to the procedure described by Fattori et al. (2012) 5 g of the silica-IMI were added to a solution containing 2 mmol of lithium salt bis (trifluoromethanesulfonyl sulfonilimida) (Sigma-Aldrich, M = 287.1 g mol⁻¹) in 20 ml of ultrapure water. The formed suspension was stirred for 24 hours at room temperature. The solid was recovered by vacuum filtration and washed with 200 ml of ultrapure water then placed in a stove at 80°C for 8 hours. The reaction scheme is shown in Figure 2. The material obtained will be called Sil-IMI-N(Tf₂)⁻.

2.2 Characterizations of the Functionalized Silica with Ionic Liquid

To confirm the exchange of the anion Cl⁻ for the bis (trifluoromethanesulfonyl sulfonilimida) N(Tf₂)⁻ was made an analysis of free chloride by potentiometric titration with AgNO₃. The nitrate ion displaces the chloride ion bound to the imidazolium ring, forming HCl in solution. Is then made the determination of amount of chloride in the solution by potentiometric titration with silver nitrate (AgNO₃) until precipitation of AgCl. If no AgCl precipitation in the end of the titration, revealed to have occurred in exchange for anions. Became 0.150 mg of the sample of silica functionalized and was added to 40 ml of a solution of nitric acid 0.1 mol/L.



This suspension was stirred for 30 min at room temperature. Taken up at a rate of 10 mL and titrated with AgNO₃ solution 0.1 mol/L, using a silver electrode as the indicator.

The specific surface area (S_{BET}) and pore volume distribution were determined by adsorption/desorption of N₂ at -196°C in equipment Autosorb I - Quantachrome Instruments using the BET method and BJH model (multipoint) respectively. The samples were pretreated in vacuum 2.0×10^{-3} Pa at 120°C for 12 hours to remove moisture and impurities.

The CHN analysis for the determination of the carbon, hydrogen and nitrogen was performed in Perkin-Elmer PE 2400 Analyzer. Analyses were done in triplicate.

In the infrared analysis was used a spectrophotometer with Fourier transform Perkin Elmer 1600 FTIR in the region 4000 - 400 cm⁻¹ with resolution of 2 cm⁻¹ and 64 accumulations. Were used pellets prepared from the solid dispersion in KBr at a ratio of 1:100 and analyzes were conducted at room temperature.

2.3 Chromatographic Analysis of Dibenzothiophene

The chromatographic analyzes of the dibenzothiophene samples were performed on a gas chromatograph coupled to a flame ionization detector (GC/FID) Shimadzu QP - 2010 Plus. Was used a capillary column ZB-5MS (5% phenyl and 95% methylpolysiloxane, 30 m × 0.25 mm, 0.25 mM). The chromatographic conditions were split injection mode (1:20), injector temperature 250°C, 1 μL injected volume, the mobile phase used was hydrogen gas with flow rate of 1 mL/min, interface temperature of 300°C and ramp temperature of 51°C (1 min) 3 min - 280 °C (20 min). The data were treated by GC Solution software. Before each analysis, calibration curves were made using standard dibenzothiophene at different concentrations (5, 15, 25, 50, 100, 300, 400, 500 and 1000 ppm).

2.4 Study of Adsorption

The adsorption experiments were performed sequencing batch mode using a refrigerated incubator (Marconi MA-830A). The adsorption kinetics of dibenzothiophene was determined using 300 mg of adsorbent in 10 ml of hexane (Aldrich) in sealed flasks of 15 ml containing different concentrations of dibenzothiophene of 25, 50 and 100 ppm at 40°C. Aliquots of 1 ml were collected at pre-established times (0, 15, 30, 45, 60, 90, 120, 180, 240, 300 min) for further chromatographic analysis.

The evaluation of data for the adsorption capacity of the adsorbent Sil-IMI-N(Tf₂)⁻ was taken by the adsorption isotherms according to equation (1).

$$q_t = \frac{V(C_0 - C_t)}{W} \quad (1)$$

where:

C₀ and C_t (mg/L) are the concentrations of the liquid phase of the initial dibenzothiophene solution and t is time, respectively;

V - is the volume of the solution (L);

W - is the mass of adsorbent (g).

The percentage removal of dibenzothiophene was obtained by the equation (2).

$$(\%) = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Characterization of Functionalized Silica with Ionic Liquid

The materials showed similar profiles of N₂ adsorption characteristic of isotherm type IV, with distinct regions: one at low relative pressures ($P/P_0 < 0.2-0.3$) corresponding to the N₂ adsorption in the monolayer and in the second region ($P/P_0 = 0.5 - 1.0$) is characteristic of capillary condensation of mesoporous materials Lowell and Shields (1979). All



desorption curves presented hysteresis of type H₂ related to pores cylinder open at both defined ends Gregg and Sing (1982), Storck et al. (1998). The distribution of pore volume, can be observed that the samples had similar distributions, with an average pore size around

4-5 nm. Table 1 show the values obtained in pure and textural analysis of the functionalized silica. The Figure 2 shows the isotherm adsorption/desorption N₂ and the pore size distribution the Pure Silica, Sil-IMI, IMI and Sil-N(Tf₂)⁻.

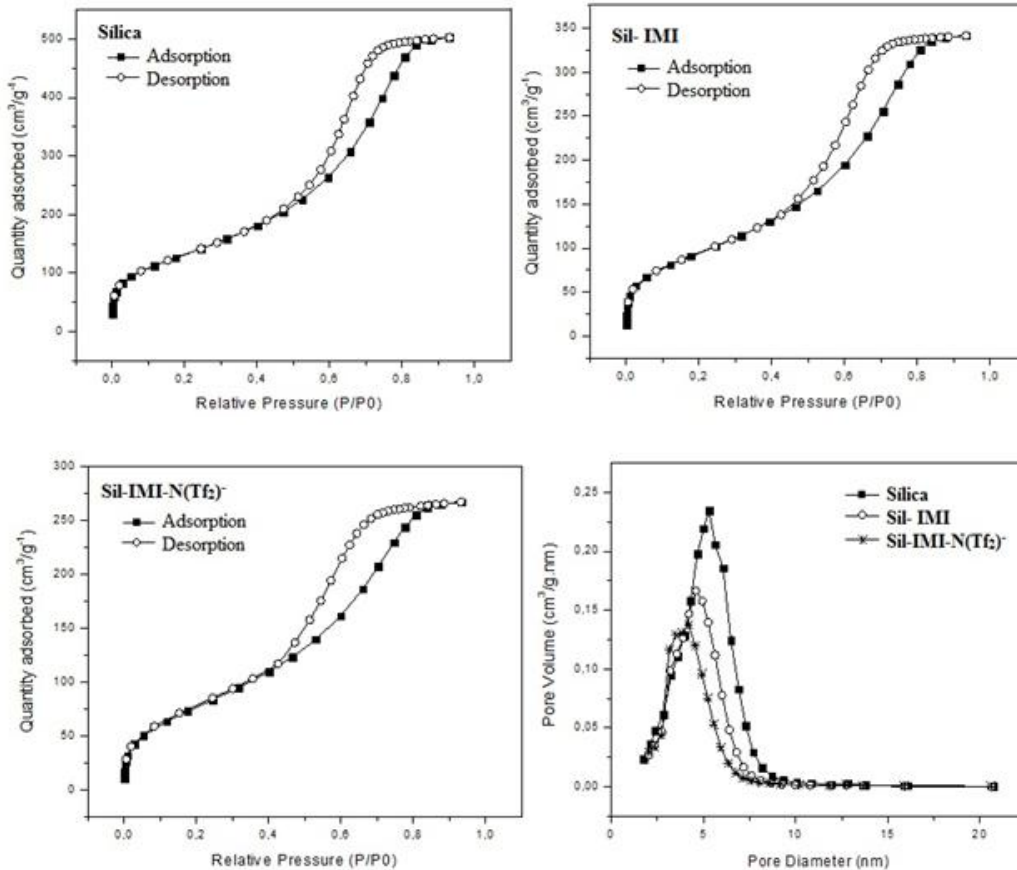


Figure 2 - (A) isotherm adsorption / desorption N₂ and (B) the pore size distribution of Pure Silica, Sil-IMI, IMI and Sil-N(Tf₂)⁻.

Table 1. Textural analysis of pure and functionalized silica.

Sample	Area BET (m ² /g ⁻¹)	Pore Volume (cm ³ /g ⁻¹)	Diameter (nm)
Silica	482	0,76	4,68
Sil-IMI	349	0,50	4,35
Sil-IMI-N(Tf ₂) ⁻	294	0,38	4,01

Is observed that functionalization with the ionic liquid gradually decreased area of the silica, their volume and pore diameter. But the functionalizing effects was most important for the surface area (40% reduction) and pore

volume (reduction of 50%), affecting little the pore diameter.

3.2 Elemental Analysis (CHN)

The results of the CHN elemental analysis, shown in Table 2 indicate that the IMI- silica was satisfactorily, they observed a much higher carbon content (6.02 mmol.g⁻¹) to that found in pure silica, (0.07 mmol.g⁻¹). After addition of the organic group N(Tf₂)⁻ there was a small increase in the content of this element to 6.79 mmol.g⁻¹, which allows to say that occurred the anchoring of the anion



bis (trifluoromethanesulfonyl sulfonilimida) in silica.

Table 2. Elemental Analysis

Sample	Elemental Analysis ^a			Analysis of Chloride ^b (mmol g ⁻¹)
	Carbon (mmol g ⁻¹)	Hydrogen (mmol g ⁻¹)	Nitrogen (mmol g ⁻¹)	
Silica	0,07	0,97	0,17	-
Sil-IMI	6,02	1,64	1,85	2,7
Sil-IMI-N(Tf ₂) ⁻	6,79	0,93	1,18	0,0

a – analysis CHN; b – obtained by potentiometric titration with AgNO₃.

Regarding the analysis of chloride, the results show the functionalization of silica with 1-methylimidazolium. The amount of 2.7 mmol.g⁻¹ corresponds to exchangeable chloride ions in the material IMI-Sil (equivalent to the amount of imidazolium groups available in the material). After the ion exchange reaction of the anion chloride by anion N(Tf₂)⁻ no longer was detected free chloride titration, indicating that all were replaced by anion N(Tf₂)⁻.

3.3 Vibrational Spectroscopy of Infrared with Fourier Transform (FTIR)

The Figure 3 shows the infrared spectrum of pure and functionalized silica. The bands vibration of the anion if manifest in 571, 617 and 741 cm⁻¹ corresponding symmetrical angular deformation in plan CF₃, CF₃ and SO₂ respectively. The vibration band of cation at 652 cm⁻¹ refers to the vibrations of deformation the axial of methyl of imidazolium ring. At 812 cm⁻¹ shows the vibration of Si-C. In 1230 and 1352 cm⁻¹ corresponding deformation axial symmetric of CF₃ and asymmetric axial deformation, SO₂ respectively. The silica appears in vibrations of 1191 and 1632 cm⁻¹ corresponding to Si-O and absorption of skeleton of silica. A broadband relative the vibration of water hydroxyl in 3000-3700 cm⁻¹.

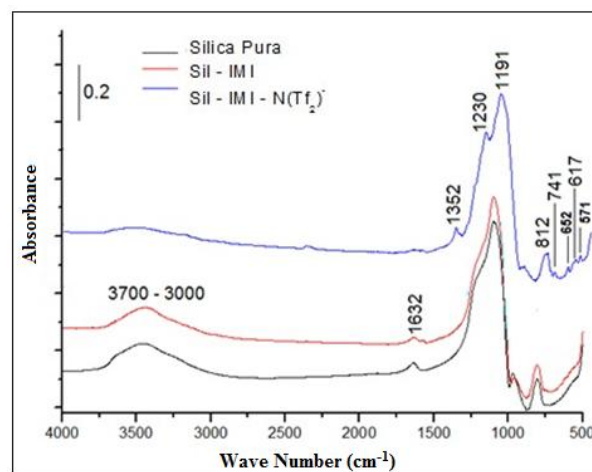


Figure 3. Infrared spectrum of pure silica and functionalized into tablet of KBr.

3.4 Experiments of adsorption of the Sil-IMI-N(Tf₂)⁻

3.4.1 Effect of mass of adsorbent

The effect of varying the amount of adsorbent Sil-IMI-N(Tf₂)⁻ (10, 20 and 30 g/L) for an initial concentration of constant dibenzothiophene (25 mg/L) is shown in Figure 4. It is observed that as the amount of adsorbent increases the initial speed of too degradation increases. The highest initial speed of adsorption of dibenzothiophene was achieved for determination of Sil-IMI-N(Tf₂)⁻ of 30 g/L.

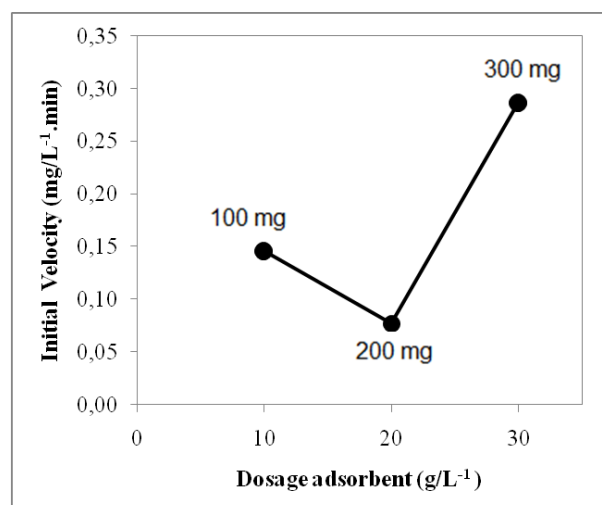


Figure 4 - Effect of the adsorbent mass on the adsorption initial speed us first 30 minutes of reaction.

3.5 Adsorption Capacity

The Figure 5 shows the adsorption capacities versus of time adsorption in different initial concentrations of dibenzothiophene on Sil-IMI-N(Tf₂)⁻. The increase in the adsorption capacity showed increased amount of dibenzothiophene adsorbed in a function of time until the adsorption equilibrium was reached.

The initial concentration provides an important driving force to overcome all mass transfer resistances of the adsorbate between the liquid phase and solid phase ALKAN et al. (2007). It was found that the adsorption was greater with the initial concentration increase of dibenzothiophene. The amount of dibenzothiophene adsorbed in balance reflects the maximum capacity adsorption of the Sil-IMI-N(Tf₂)⁻ in the studied conditions. The adsorption capacity of dibenzothiophene in Sil-IMI-N(Tf₂)⁻ in equilibrium (q) increased 0.2 to 1.0 mg/g with increasing initial concentration by 25 to 100 mg/L⁻¹.

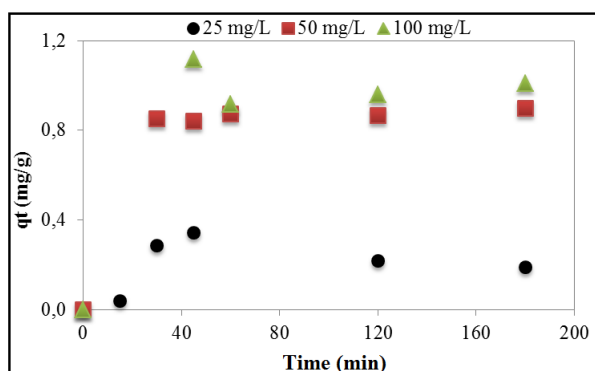


Figure 5- Capacity for adsorption of dibenzothiophene in Sil IMI-N(Tf₂)⁻ versus time adsorption at different initial concentrations. Conditions: T = 40°C, m_{adsorvente} = 300 mg.

The Figure 6 shows the percentage removal of dibenzothiophene-Sil IMI-N(Tf₂)⁻ a function of time for different initial concentrations. Increasing the initial concentration of 50 to 100 mg/L⁻¹, the percentage of removal of the sulfur-containing compound decreased from 58 to 32%. This occurred because the amount of adsorbate

increased, but the amount of adsorption sites remained the same, because the mass of adsorbent was constant and to 300 mg. Therefore, adding more adsorbate will not increase the adsorption, because sites were already occupied.

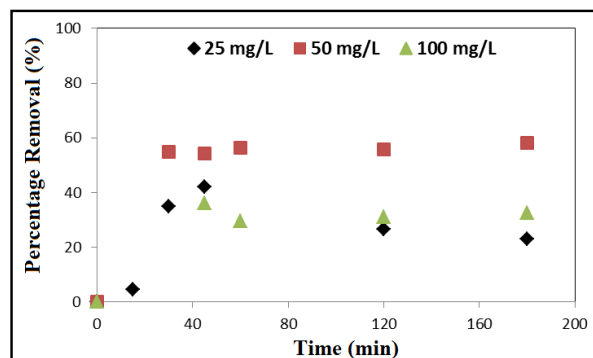


Figure 6 - Percent of removal of dibenzothiophene by adsorption on Sil-IMI-N(Tf₂)⁻ a function of time of adsorption at various initial concentrations. Conditions: T = 40°C, m_{adsorvente} = 300 mg.

4. CONCLUSION

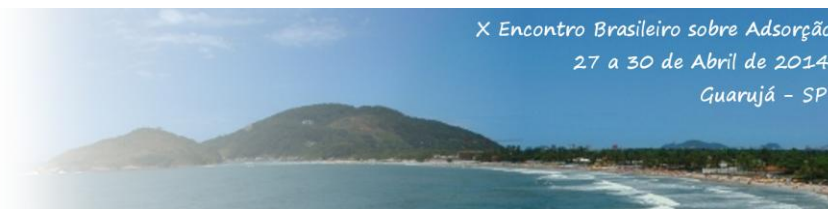
The combination of silica with ionized organic material (ionic liquid, IL), prompted the development of a new hybrid material organic - inorganic with capacity adsorbing dibenzothiophene of around 58%. The textural analysis confirmed the change in the structure of silica, influencing the area, volume and pore diameter.

The effect of temperature on the equilibrium of adsorption of dibenzothiophene in Sil-IMI-N(Tf₂)⁻ showed that the interactions occur by hydrogen bridges and apparent the stability of this binding decreases with increasing temperature between 20 and 60°C.

The expansion of this area is unlimited, due to the infinite possibilities of combinations of components and new and sophisticated applications.

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6. ACKNOWLEDGEMENTS

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