Pd-Impregnated activated carbon and treatment acid to remove sulfur and nitrogen from diesel

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ABSTRACT

Removal of sulfur and nitrogen compounds from national commercial diesel through adsorption onto activated carbon was studied. Brazilian commercial activated carbon samples (AC) were modified by acid oxidation and, alternatively, were impregnated with palladium chloride. Modified carbon samples showed a significant increase in the quantity of acid sites, particularly those AC submitted to impregnation with palladium. Adsorption capacity of the carbon samples increased proportionally to the increase in the acid groups. Adsorption efficiency of the activated carbon impregnated with palladium chloride was over 85% for nitrogen compounds and over 60% for sulfur compounds. The treatment studied was found to be an efficient option for the removal of sulfur and nitrogen compounds present in commercial diesel, and thus it could be an alternative pretreatment in the conventional hydrotreatment process.

Keywords: Adsorption; Activated carbons; Sulfur compounds adsorption; Nitrogen compounds adsorption; Diesel

1. INTRODUCTION

On a global scale the reduction of atmospheric emissions has encouraged environmental institutions to establish ever stricter legislation, principally in relation to the sulfur content of automotive fuels [1].

Currently, refineries in Brazil are facing the challenge of producing commercialized fuels which adhere to the sulfur limit of 10 ppmw, set for 2016 according to Resolution of the Brazilian National Council on the Environment. With the existing hydrodesulfurization (HDS) technologies it is expensive to achieve production with such low sulfur levels, since extreme operating conditions are required. Thus, new alternatives to remove sulfur compounds have been studied in order to achieve the low levels stipulated in the new specifications without altering the quality of the product [2]. In this regard, the removal of contaminants by adsorption using modified materials has gained relevance due to their good performance in relatively simple processes with mild operating conditions.

In recent studies, emphasis has been given to the preparation of modified activated carbon surfaces using different procedures to increase the adsorption capacity for specific contaminants. Several treatments have been reported including the use of acids, bases, impregnation, ozone, surface treatments with plasma and microwaves [3].

In the search for alternative adsorption materials were used industrial residue sludge and waste material to prepare activated carbon [4]. Kumagai *et al*. [5] studied the production of rice husks adsorbents that were carbonized and then activated with CO_2. The material produced was characterized chemically through the quantification of acid and basic sites at the surface. It was noted that the number of acid and basic sites increased as a function of the time and temperature of activation. An improvement in the adsorption associated with acid groups was observed by Ania and Bandosz [6], Zhou *et al*. [7] and Singha *et al*. [8].These groups are probably centers for the adsorption of Dibenzotiophene DBT via oxygen-sulfur or sulfur-sulfur interaction.

Adsorption of sulfur species resistant to the hydrotreatment using activated carbon as the adsorbent was studied [9, 10]. Sano *et al*. [11] proposed for the desulfurization of diesel oil a process consisted of two stages: hydrodesulfurization followed by adsorption onto activated carbon fiber in order to obtain a product

with sulfur content lower than 10 ppmw.

Wang *et al*. [12] and Wang and Yang [13], using π-complexation adsorbents, such as Cu(I)-Y zeolite, CuCl and PdCl$_2$ supported on activated carbon and PdCl$_2$ supported on alumina, performed an investigation about adsorption of sulfur present in aviation fuel (JP-5) and the greatest capacity and selectivity were observed for PdCl$_2$ supported on activated carbon.

In the traditional desulfurization process (HDS), nitrogen compounds present in petroleum derivatives have a considerable adverse effect on the sulfur removal. Due to their chemical nature, nitrogen compounds adsorb onto the acid sites of the catalyst, in some cases in an irreversible manner. Adsorption of nitrogen compounds before the HDS process would increase both the hydrodenitrogenation and the hydrodesulfurization of the middle distillates in the production of ultralow sulfur diesel.

Three types of nitrogen compounds are generally present in diesel: heterocycles with 6-member rings, heterocycles with 5-member rings and non-heterocyclic compounds. The heterocycles with 6-member rings are basic (acridine and quinoline) and those with 5-member rings are non-basic (carbazole, indole). According Kotai *et al*. [14] the inhibitory effect of basic nitrogen is stronger.

The organic sulfur compounds and the nitrogen compounds, with the exception of dodecylamine, contain a heteroatom bound to an aromatic hydrocarbon structure. These molecules have a high nucleophilicity due to the electron cloud of aromatic compounds and the non-bound electron pair in the sulfur or nitrogen atoms. Thus, adsorbents with acid (electrophilic) characteristics have a greater capacity to adsorb the sulfur and nitrogen compounds present in diesel.

This paper describes a study on the adsorption of compounds containing sulfur and nitrogen in commercial diesel using different types of activated carbon. The increase of the adsorbent electrophilic power was carried out with inorganic acids and with impregnating palladium. The quantity of acid and basic groups present in the different types of carbon and their influence on the adsorption process studied was discussed.

2. MATERIALS AND METHODS

Samples of brazilian commercial activated carbon (AC) and of modified AC were employed in this study. Commercial samples were provided by Fábrica Brasileira de Catalisadores Ltda. The commercial samples modifications were carried out as follows: oxidation with three different inorganic acid; impregnation with palladium. Besides having different granulometric characteristics, the AC samples used were derived from different raw materials, babassu (*Attalea speciosa)* coconut shell and pine wood.

Were used commercial diesel fuel AS500 samples, contained 305 ppmw of sulfur and 133 ppmw of nitrogen compounds, donated by REPAR Petrobras. All reagents with analytical grade were used, hydrochloric acid (Merck), nitric acid (Merck), sulfuric acid (F Maia) and sodium hydroxide (Merck). For the neutralization, impregnation and adsorption a Marconi shaker (model MA-410) was used. The quantification of sulfur and nitrogen compounds in the diesel was carried out using an Elementary sulfur analyzer (model Trace SN cube). Scanning electron microscopy analysis was carried out on a Jeol microscope (model JSM 6360LV).

Carbon samples were identified as CAC coconut shell activated carbon and PAC pine wood activated carbon. CAC1 and CAC2 samples have the same granulometric classification, although they are obtained from different activation processes. The granulometric classification to the samples is 0.42 mm to 1.68 mm to CAC1 and CAC2. CAC3 is 0.84 mm to 1.68 mm, PAC1 is 0.30 mm to 1.68 mm and PAC2 is 0.71 mm to 1.68 mm.

The surface area, pore volume and pore size of the five activated carbon samples were determined employing the methodology proposed by Brunauer, Emmett and Teller (BET method) in a N$_2$ adsorption test carried out on a QuantaChrome instrument (model NOVA 1200).

Quantification of the acid and basic surface groups of the two carbon samples was carried out in triplicate employing the methodology proposed by Boehm [15]. For the determination of the quantity of basic groups given in milliequivalents per gram of carbon, approximately 0.5 g of each carbon sample was maintained in contact with 50.0 mL of a solution of 0.1 mol.L^{-1} HCl. The mixture remained under shaking for 24 h at 40°C. After this period, aliquots (10.0 mL) of the resulting solution were titrated employing 0.1 mol.L^{-1} NaOH.

The determination of the acid surface groups was carried out leaving the carbon sample in contact with a solution of 0.1 mol.L^{-1} NaOH for 24 h with shaking. Aliquots (10.0 mL) of the resulting solution were then acidified with 20.0 mL of 0.1 mol.L^{-1} HCl. The excess of HCl was titrated with a solution of 0.1 mol.L^{-1}

NaOH.

Samples CAC2 and CAC3 were modified by impregnation with palladium chloride and oxidation with nitric acid, hydrochloric acid and sulfuric acid. The impregnation solution was prepared by solubilizing 4.0 g of palladium chloride per liter of 1.0 mol.L^{-1} hydrochloric acid solution. An aliquot (5.0 mL) of the palladium solution was then transferred to a flask containing 2.0 g of carbon. The carbon was left in contact with the palladium chloride for 24 h under shaking and with the temperature maintained at 40 °C. After this period the carbon was filtered.

Oxidation of the carbon surface was performed through contact with nitric acid, hydrochloric acid and sulfuric acid at a concentration of 1.0 mol.L^{-1}, following a procedure analogous to that described for the impregnation of palladium chloride.

Tests for the adsorption of sulfur and nitrogen compounds in commercial diesel were carried out in triplicate employing the samples of commercial and modified activated carbon. The adsorption was conducted with a shaker maintaining 2.0 g of each carbon sample in contact with 20.0 mL of diesel for 24 h at 70 °C, selected conditions in previous studies. After that an aliquot of diesel was removed in order to determine the quantity of sulfur and nitrogen adsorbed. The analytical method was based on the catalytic combustion of the sample followed by analysis of the gases generated during burning in a UV fluorescence detector.

3. RESULTS

3.1 Carbon Characterization

The physical chemical properties of the activated carbon samples used in this study and provided by the manufacturer are given in Table 1.

Table 1: Physical chemical properties of activated carbon samples provided by the manufacturer.

SAMPLE	IODINE NUMBER (mg of I$_2$)	MOLASSES NUMBER (%)	pH	HUMIDITY (%)	ASH (%)	HARDNESS (%)	APPARENT DENSITY (g/cm^3)
CAC1	809	15	10	4.5	10.8	94	0.50
CAC2	919	25	10	5.0	11.3	93	0.47
CAC3	1005	55	10	5.5	17.9	88	0.43
PAC1	754	55	10	3.5	6.8	92	0.41
PAC2	801	75	10	6.0	7.6	91	0.37

CAC1 and CAC2 coconut shell (0.42 mm to 1.68 mm); CAC3 coconut shell (0.84 mm to 1.68 mm); PAC1 pine wood (0.30 mm to 1.68 mm) and PAC2 pine wood (0.71 mm to 1.68 mm).

The results shown in Table 2 indicate that samples CAC2 and CAC3 had the largest surface area and higher values for the micropore area and volume. These characteristics are important in the physical adsorption of sulfur and nitrogen compounds.

Table 2: Characterization of pores of activated carbon samples.

ADSORBENT	BET AREA (m^2 g^{-1})	EXTERNAL SURFACE AREA (m^2 g^{-1})	MICROPORE AREA (m^2 g^{-1})	MICROPORE VOLUME (cm^3 g^{-1})	AVERAGE DIAMETER (Å)
CAC1	665	47	619	0.32	22.3
CAC2	728	63	665	0.34	22.6
CAC3	784	86	698	0.36	23.1

| PAC1 | 557 | 58 | 499 | 0.26 | 23.2 |
| PAC2 | 651 | 85 | 565 | 0.29 | 24.4 |

After the characterization of the carbon samples, it was select two of them (CAC2 and CAC3) for further study of oxidation and impregnation with palladium.
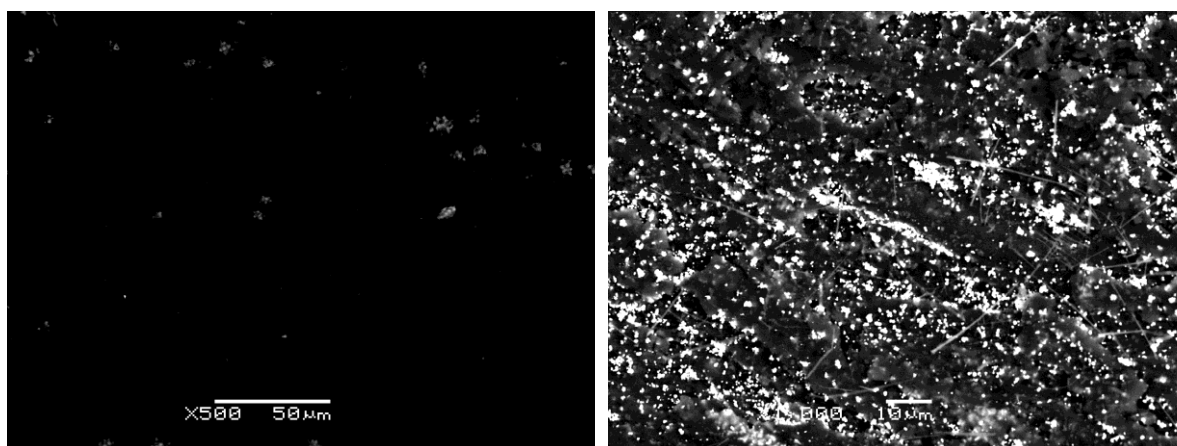
3.2 Carbon impregnation

The results for the quantification of the acid and basic groups present on the surface of the commercial and impregnated carbon samples with palladium chloride are given in Table 3.

Table 3: Quantification of acid and basic surface groups for the commercial and impregnated activated carbon samples.
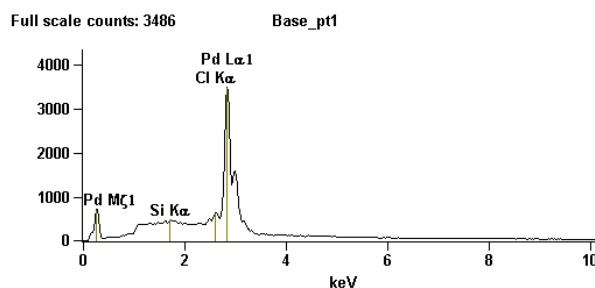
| ADSORBENT | BEFORE IMPREGNATION | | AFTER IMPREGNATION (PdCl₂) | |
	BASIC GROUPS (mEq/g of CARBON)	ACID GROUPS (mEq/g of CARBON)	BASIC GROUPS (mEq/g of CARBON)	ACID GROUPS (mEq/g of CARBON)
CAC2	0.40 ± 0.10	0.39 ± 0.05	0.22 ± 0.03	1.68 ± 0.01
CAC3	0.60 ± 0.10	0.55 ± 0.05	0.06 ± 0.03	1.72 ± 0.01

The electron microscopy analysis of the commercial AC and the samples impregnated with palladium shown in Figure 1 revealed the locations at which the palladium compounds were adhered. Figures 1a and 1b show micrograph of AC samples before and after impregnation, respectively.

(a)   (b)

(c)

Figure 1: Micrograph of AC (a) before and (b) after impregnation with PdCl₂; (c) Energy dispersive spectroscopy (EDS) spectrum of selected light area.

3.3 Carbon oxidation

The results for the quantification of acid and basic sites after oxidation are given in Table 4.

Table 4: Quantification of acid and basic groups after acid oxidation.

TREATMENT	BASIC GROUPS (mEq/g of CARBON)		ACID GROUPS (mEq/g of CARBON)	
	CAC2	CAC3	CAC2	CAC3
Oxidation with 1.0 mol.L^{-1} HCl	0.16 ± 0.03	0.07 ± 0.03	0.54 ± 0.03	0.58 ± 0.03
Oxidation with 1.0 mol.L^{-1} HNO$_3$	0.06 ± 0.03	0.00 ± 0.03	0.90 ± 0.03	1.19 ± 0.03
Oxidation with 1.0 mol.L^{-1} H$_2$SO$_4$	0.00 ± 0.03	0.00 ± 0.03	1.79 ± 0.03	2.00 ± 0.03

3.4 Sulfur and nitrogen adsorption

Table 5 shows the quantity of sulfur groups removed from a commercial diesel type A S500 using samples CAC2 and CAC3 as adsorbents.

Table 5: Mass of sulfur adsorbed by the commercial and treated samples of carbon CAC2 and CAC3.

ADSORBENT	COMMERCIAL	mg S /g CARBON			
		OXIDIZED (HCl)	OXIDIZED (HNO$_3$)	OXIDIZED (H$_2$SO$_4$)	IMPREGNATED (PdCl$_2$)
CAC2	0.47 ± 0.01	0.53 ± 0.01	0.57 ± 0.02	0.51 ± 0.01	0.88 ± 0.02
CAC3	0.66 ± 0.01	0.70 ± 0.01	0.80 ± 0.01	0.72 ± 0.02	1.64 ± 0.01

The results for the adsorption of nitrogen compounds by the commercial and treated activated carbon samples are shown in Table 6.

Table 6: Mass of nitrogen compounds adsorbed by the commercial and treated carbon samples CAC2 and CAC3.

ADSORBENT	COMMERCIAL	mg N /g CARBON			
		OXIDIZED (HCl)	OXIDIZED (HNO$_3$)	OXIDIZED (H$_2$SO$_4$)	IMPREGNATED (PdCl$_2$)
CAC2	0.55 ± 0.01	0.55 ± 0.01	0.59 ± 0.03	0.70 ± 0.01	0.84 ± 0.03
CAC3	0.67 ± 0.01	0.62 ± 0.03	0.63 ± 0.01	0.74 ± 0.02	0.99 ± 0.06

The Table 7 shows the results for the different types of treatment applied to the carbon sample CAC3.

Table 7: Quantity of sulfur and nitrogen adsorbed from commercial diesel according to the different types of treatment for sample CAC3.

TREATMENT	ADSORBED S (%)	ADSORBED N (%)
Activated carbon	25.68	61.47
Oxidized (HCl)	26.86	67.48
Oxidized (HNO$_3$)	31.71	68.11
Oxidized (H$_2$SO$_4$)	26.47	79.13
Impregnated with PdCl$_2$	64.70	86.51

4. DISCUSSION

The iodine number is defined as the quantity (in mg) of iodine in an aqueous solution adsorbed per gram of

activated carbon, under specific conditions determined by the method [16]. This value provides a porosity index related to small pores. On evaluating the values in Table 1 it can be observed that the carbon samples CAC3 and CAC2 had the greatest quantity of small pores. On the other hand, the capacity of the carbon to adsorb larger molecules is determined using the molasses number test, which provides an index of the decoloration measured in relation to a solution of molasses. The sample PAC2 presented the highest value and CAC3 was in second place in relation to this parameter.

The Table 2 show the results of characterization of pores from activated carbon samples, these parameters are important to adsorption of sulfur and nitrogen compounds, how much greater the available surface area and larger micropores volume is more efficient adsorption [7]. Therefore these parameters were considered to select the AC sample to continue the study. CAC2 and CAC3 samples presented the largest surface area and higher values for the micropore area and volume, beyond their larger iodine number (Table 1).

In Table 3 the sample CAC3 derived from coconut shell had the highest quantity of acid groups of the samples tested, which verifies the theoretical prediction of greater sulfur adsorption by this sample.

After impregnation process there was a significant reduction in the quantity of basic surface groups of the samples in relation to the amount present on samples. The reduction was 45% for sample CAC2 and 90% for the carbon sample CAC3. There was an increase of 76% the quantity of acid sites for CAC2 sample and 68% for CAC3 sample.

The impregnation solution of palladium chloride was prepared in acid medium and there was increase in acid groups after the treatment like expected. This increase being influenced not only by the palladium adhered to the carbon surface but also to the acidity of the solution.

Figures 1a and 1b show micrograph of AC samples before and after impregnation, the light areas in Figure 1b indicate the regions where the element palladium is concentrated. Figure 1c indicates the energy peak related to the element palladium when one of the light areas of Figure 1b is selected as a target for analysis by energy dispersive spectroscopy (EDS). It is possible confirm the presence of chlorine besides palladium, indicating that deposited palladium remains in the oxidized form (Pd^{2+}).

Table 4 shows the quantification of acid and basic sites after oxidation that the increase in acid sites for the AC samples activated with hydrochloric acid or nitric acid was not of the same magnitude compared with the samples submitted to modification through impregnation with palladium. However, the oxidation with nitric acid led to an approximately 2-fold increase in the number of acid surface groups for the activated carbon sample CAC2. A reduction in the quantity of basic groups was verified for the treatment with all acids. Oxidation with H_2SO_4 led to an almost 2-fold increase in the number of acid sites in relation to the oxidation with nitric acid.

The commercial activated carbon sample CAC3 showed the best performance for the removal of sulfur, which being the sample which had the highest number of acid surface groups. This shows that the removal of sulfur is favored by the presence of a preferentially acid surface [7, 6].

Seeing that CAC carbons originated from the same applied process and the same activation conditions, the differences in the quantity of acid and basic groups must be related to the surface area provided by the activated carbon sample. Sample CAC3 which had the greatest quantity of acid surface groups also had the largest BET area. This observation is to be expected, with a larger available area could be more favorable to formation of groups with oxygen on the carbon surface during oxidation process.

Oxidation of samples CAC2 and CAC3 with acid solutions of HCl, HNO_3 and H_2SO_4 increased the adsorption capacity for sulfur compounds. The effect of the modification of activated carbon through oxidation with HNO_3 applied to the liquid phase adsorption of sulfur compounds in diesel fuel was examined by Zhou *et al*. [7]. In his study the oxidation with HNO_3 was found to be an efficient method for improving the adsorption performance of commercial activated carbon in relation to sulfur compounds. This finding can be mainly attributed to the increase in the acid functional groups containing oxygen in the carbon structure, which provides an increased selectivity of the adsorbent for sulfur compounds, comparing the untreated carbon with oxidized carbon.

The carbon CAC3 was more susceptible to oxidation with acids which could also be related to the increase in the available surface area. It was verified that the carbon samples oxidized with sulfuric acid had greater surface acidity than those oxidized with nitric acid, although the samples exposed to nitric acid adsorbed a greater quantity of sulfur compounds. The impregnation of carbons with palladium chloride led to a significant improvement in their capacity to remove sulfur compounds from diesel. According to studies carried out by Bedia *et al*. [17], palladium is physically adsorbed at the carbon surface and is present in the

2+ oxidation state (Pd^{2+}) and acts as an electrophile. Thus, the palladium increases the surface acidity of the carbon. It is also important to note that the number of acid surface groups observed for the samples CAC2 and CAC3 impregnated with palladium is lower than that for the same samples oxidized with sulfuric acid, although the impregnation led to a more efficient removal of sulfur. This finding demonstrates that presence of palladium on the carbon surface plays a significant role and acts together with the acid groups in the interaction with the sulfur compounds.

The desulfurization of synthetic diesel with low contents of refractory compounds (20 ppmw) was studied by Seredych *et al*. [18]. Results indicated that the acid groups present on the carbon surface increase the capacity of the adsorbent for the removal of DBT and 4,6 DMDBT (Dimethyldibenzothiophene). Although the amount of sulfur adsorbed is governed by the volume of micropores, the acid groups located in larger pores can attract molecules of DBT and 4,6 DMDBT via specific interactions. The authors concluded that to achieve a good performance the carbon samples need to have specific characteristics, that is, a high volume of pores lower than 1 nm and the presence of acid groups in the larger pores, which leads to better results. Besides, they noted that an appropriate proportion of the adsorption must occur via acid groups in order to avoid blocking the accessibility of small pores.

Table 5 shows the behavior of CAC2 and CAC3 samples to oxidation and impregnation treatment. To CAC2 sample the capacity adsorption did not increase with oxidation acid, although shows best performance with impregnation. CAC3 sample shows improvement to both treatments.

In Table 6 carbon samples modified by impregnation with palladium showed the best performance in the removal of nitrogen compounds present in the commercial diesel S500. Of these, CAC3 was the sample originating from coconut shell with gave the highest value for adsorbed nitrogen, this value also being higher than those observed for the AC samples modified by oxidation with H_2SO_4 and impregnated with palladium. Treatments with HCl or HNO_3 did not improve the adsorption capacity. The behaviors of CAC2 and CAC3 were the same for the treatment with HCl and HNO_3.

On comparing the results for the adsorption of sulfur (Table 5) and nitrogen compounds (Table 6) of the modified samples it can be observed that for the samples oxidized with hydrochloric acid or nitric acid there was an improvement in the performance in the case of sulfur compounds but not in the case of nitrogen compounds. This finding indicates that the sulfur compounds have a stronger attraction toward the acid sites than nitrogen compounds. Another observation is that the presence of the element palladium on the carbon surface favors the adsorption of nitrogen compounds. These results show that it is possible to produce ACs with selective characteristics to enhance the adsorption of sulfur or nitrogen compounds.

A comparison of adsorption values for commercial AC and impregnated AC shows that the impregnation increased the adsorption capacity for different types of carbon samples, although CAC3 showed the most pronounced effect. Table 5 and Table 6 indicates that CAC3 sample shows the greatest different between the adsorption capacity for sulfur compounds in relation to nitrogen compounds, the former being almost twice as high as the latter.

The treatment with H_2SO_4 led to a better performance for the adsorption of nitrogen compounds in relation to the treatment carried out with nitric acid or hydrochloric acid. This trend was not observed in relation to sulfur compounds, where the improvement in the performance was almost the same for the three acids.

Table 7 shows the results for the different types of treatment applied to the carbon sample CAC3. On comparing the results for the purification of diesel in relation to nitrogen and sulfur compounds, it was observed that the percentage removing of nitrogen compounds was much higher than that of sulfur compounds. Although selectivity in the adsorption of nitrogen compounds can be observed for all of the carbon samples, AC oxidized with sulfuric acid showed the greatest difference in the quantity (percentage) of sulfur adsorbed in relation to nitrogen. The AC oxidized with H_2SO_4 showed a slight increase in the adsorption of sulfur compounds, although it demonstrated a high capacity for the adsorption of nitrogen compounds. This characteristic observed for the adsorbents tested could be used as a tool to aid the treatment of diesel in HDS units.

According to Koriakin *et al*. [19], the catalysts used in the HDS process show greater ability to adsorb nitrogen compounds when compared with aromatic thiophene derivatives. In addition, hydrodenitrogenation (HDN) is more difficult and slower reaction to perform than HDS and thus the residues of nitrogen compounds remain at the active sites of the catalyst competing with the molecules of sulfur compounds and making the reactive sites unavailable to them.

5. CONCLUSION

Brazilian commercial and modified activated carbon samples can be used for the removal of sulfur and nitrogen compounds from commercial diesel.

Percentage nitrogen removed from the commercial diesel (S500) tested by sample CAC3 (carbon produced from coconut shell with medium particle size) impregnated with palladium chloride was above 85%. Although the palladium occupies some of the micropores required for the nitrogen and sulfur adsorption, the increase in the affinity of the sites containing palladium for these compounds compensates for the micropore deficiency.

Treatment with palladium chloride provided the best results (> 60%) for the removal of sulfur compounds from commercial diesel (S500). However, the acid treatments did not improve the performance in relation to the adsorption of sulfur compounds.

Treatment with sulfuric acid was the form of oxidation which showed the best performance (> 75%) in relation to the adsorption of nitrogen compounds. The oxidation promotes the development of acidic sites on the adsorbent surface. These acid sites provide attraction properties to organic molecules containing nitrogen.

The results were obtained for diesel fuel and the process involved uses national raw materials in abundance. The study demonstrates that adsorption process can be an alternative for conventional treatment of diesel. To introduce the adsorption step prior hidrodesulfurization will become the process more efficient.

6. ACKNOWLEDGMENT

7. BIBLIOGRAPHY

[1] SHAHADAT HUSSAIN, A.H.M., TATARCHUK, B.J. "Adsorptive desulfurization of jet and diesel fuels using Ag/TiO$_x$-Al$_2$O$_3$ and Ag/TiO$_x$-SiO$_2$ adsorbents", *Fuel*, v. 107, pp. 465-473, May 2013.

[2] STANISLAUS, A., MARAFI, A., RANA, M.S., "Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production", *Catalysis Today*, v. 153, n. 1-2, pp. 1-68, Jul 2010.

[3] BHATNAGAR, A., HOGLAND, W., MARQUES, M., SILLANPÄÄ, M., "An overview of the modification methods of activated carbon for its water treatment applications", *Chemical Engineering Journal*, v.219, pp. 499-511, Mar 2013.

[4] NUNTHAPRECHACHAN, T., PENGPANICH, S., HUNSON, M., "Adsorptive desulfurization of dibenzothiophene by sewage sludge-derived activated carbon", *Chemical Engineering Journal*, v.228, pp. 263-271, Jul 2013.

[5] KUMAGAI, S., SHIMIZU, Y., TOIDA, Y., ENDA Y., "Removal of dibenzothiophenes in kerosene by adsorption on rice husk activated carbon", *Fuel*, v.88, pp. 1975-1982, Oct 2009.

[6] ANIA, C.O, BANDOSZ, T.J., "Adsorption of dibenzothiophene from liquid phase by activated carbon", *American Chemical Society Proceedings, Fuel Division*. v.88, pp.1975-1982, 2009.

[7] ZHOU, A., MA, X., SONG C., "Effects of Oxidative Modification of Carbon Surface on the Adsorption of Sulfur compounds in Diesel Fuel", Environmental, v. 87, pp. 190-199, 2009.

[8] SINGHA, S., SARKAR, U., LUHARUKA, P., "Functionalized granular activated carbon and surface complexation with chomates and bi-chromates in waste water", Science of The Total Environment, v. 447, pp. 472-487, Mar 2013.

[9] SANO, Y., CHOI, K.H., KORAI, Y., MOCHIDA I., "Adsorptive Removal of Sulfur and Nitrogen Species from a Straight Run Gas Oil over Activated Carbons for its Deep Hydrodesulfurization" *Applied Catalysis B: Environmental,* v. 49, n.4 pp. 219-225, Jun 2004a.

[10] SANO, Y., CHOI, K.H., KORAI, Y., MOCHIDA, I., "Selection and further activation of activated carbons for removal of nitrogen species in gas oil as a pretreatment for its deep hydrodesulfurization", *Energy Fuels*. v.18, n.3, pp. 644-651, Mar 2004b.

[11] SANO, Y., SUGAHARA, K., CHOI, K.H., KORAI, Y., MOCHIDA, I., "Two-step adsorption process for deep desulfurization of diesel oil", *Fuel*, v. 84, n.7-8, pp. 903-910, May 2005.

[12] WANG, Y., YANG F.H., YANG R.T., *et al.*, "Desulfurization of high-sulfur jet fuel by π-complexation with copper and palladium halide sorbents", *Industrial & Engineering Chemistry Research.*, v. 45, n.22, pp. 7649-7655, Sep 2006.

[13] WANG, Y., YANG, R.T., "Desulfurization of liquid fuels by adsorption on carbon-based sorbents and ultrasound-assisted sorbent regeneration", *Langmuir*, v. 23, n. 7, pp. 3825-3831, Feb 2007.

[14] KOTAI, T., MACAUD, M., GUEVARA, A., *et al* , "Comparative inhibiting effect of polycondensed aromatics and nitrogen compounds on the hydrodesulfurization of alkyldibenzothiophenes", *Applied Catalalysis A: General*, v.231, pp.253-261, May 2002.

[15] BOEHM, H.P., "Some aspects of the surface chemistry of carbons blacks and other carbons", *Carbon*. v.32, n.5, pp.759-769, 1994.

[16] MUCCIATO, J.C., "Conceitos e aplicações do carvão ativado", *Meio filtrante*, Ano V n.22, Set/out 2006.

[17] BEDIA, J., ROSAS, J.M., RODRÍGUES-MIRASOL, J., *et al.*, "Pd supported on mesoporous activated carbons with high oxidation resistance as catalysts for toluene oxidation", *Applied Catalysis B: Environmental*, v.94, pp.8-18, Feb. 2010.

[18] SEREDYCH, M., LISON, J., JANS, U., *et al.*, "Textural and chemical factors affecting adsorption capacity of activated carbon in highly efficient desulfurization of diesel fuel", *Carbon*, v. 47, n. 10, pp. 2491-2500, Aug 2009.

[19] KORIAKIN, A., PONVEL, K.M., LEE C., "Denitrogenation of raw diesel fuel by lithium-modified mesoporous silica", *Chemical Engineering Journal*, v.162, pp. 649-655, Aug. 2010.