



# Removal of Sudan IV from a simulated biphasic oily wastewater by using lipophilic carbon adsorbents



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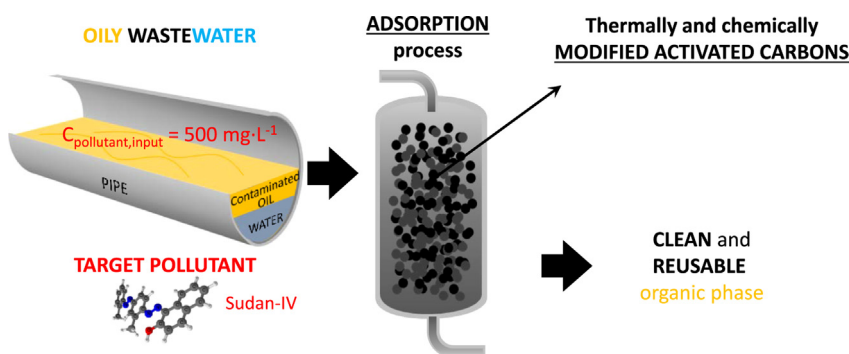
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## HIGHLIGHTS

- Commercial activated carbons are modified to act as specific adsorbents.
- A triphasic adsorption system is used to treat petroleum refinery model effluents.
- Lipophilicity and particle size of materials have significant effect on adsorption.
- The best performing adsorbent was obtained by N-doping and thermal treatment.
- Sudan-IV is completely uptaken ( $q_e = 200 \text{ mg}\cdot\text{g}^{-1}$ ).

## GRAPHICAL ABSTRACT



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## ABSTRACT

Several chemically and thermally modified activated carbons were tested in the adsorption of a lipophilic pollutant (Sudan IV) contained in biphasic oil-water mixture mimicking petroleum refinery effluents. The effect of different parameters on the adsorption performance has been assessed, such as the absence of water, particle size of the carbon material and the respective chemical and thermal modifications, initial concentration of pollutant, water/oil volume ratio, nature of the organic phase (cyclohexane, n-hexane or n-hexadecane) and the presence of an emulsifier (sodium dodecyl sulphate). Lipophilicity of the adsorbent was found to be a key parameter in the purification of the organic phase. Successive treatments of the parent commercial activated carbon Norit ROX 0.8, namely with nitric acid, urea, followed by a thermal treatment at 800 °C under inert atmosphere, developed the highest adsorption capacity ( $q_e = 200 \text{ mg}\cdot\text{g}^{-1}$ ) in the base material. A load of  $2.5 \text{ g}\cdot\text{L}^{-1}$  of this modified carbon was able to completely remove  $500 \text{ mg}\cdot\text{L}^{-1}$  of the pollutant from the organic phase after 8 h of contact time, owing to the highest specific surface area ( $S_{\text{BET}} = 1055 \text{ m}^2\cdot\text{g}^{-1}$ ) and characteristic surface chemistry with the lowest content of oxygen surface groups among the tested adsorbents.

## 1. Introduction

The industrial development is leading to an increase in the number of oily products. As consequence the oil industry, oil refining, oil

storage, transportation and petrochemical industries are generating larger amounts of oily wastewater [1–4]. Despite the technical and management evolution in this field, many oily compounds are transferred into water bodies, causing pollution. This pollution is

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detrimental in many different aspects, such as: (1) affecting drinking water and groundwater resources, jeopardizing aquatic resources; (2) affecting crop production; (3) endangering human health; and (4) causing negative impacts on the natural landscape [4,5].

Oily wastewaters, such as petroleum refinery effluents, consist on outflowing stream composed by oil, grease and other organic compounds with serious toxic hazards to the environment [6]. The removal of these organic pollutants from the oil fraction of oily wastewaters is interesting, not only to mitigate the possible environmental impact, but also to recover the oil phase, which can be a fuel, a lubricant or another potential organic raw material. In fact, increasing attention is being paid to the development of techniques aiming the recovery and reuse of the valuable oil content in oily wastewaters, such as in cutting fluid oily wastewater [7]. Nevertheless, the organic pollutants are limiting the reusability of the oil phase and, thus, must be removed. The cleaning of an oil phase is also being a subject of interest in the field of fossil fuels. During fuel combustion, molecules containing sulphur (S) or nitrogen (N) elements generate  $\text{SO}_x$  and  $\text{NO}_x$ , which are the main responsible products for acid rain. In this context, stricter legislation has been implemented all over the world to limit the S and N-contents in petroleum fuels. Due to this reason, new technologies to remove S and N-containing compounds from oily products are required [8].

Oily wastewater are conventionally treated by flotation, coagulation, biological treatment and membrane separation technologies [4]. The use of adsorption process to treat oily wastewater with activated carbon is an alternative scarcely explored, but looks like promising in the treatment of oily wastewater effluents [9,10].

The current work is focused on the removal of a lipophilic pollutant (Sudan IV) from a biphasic medium oil-water (simulating contaminated oil mixtures with water) by using different modified activated carbons as adsorbents. To the best of our knowledge, we are reporting for the first time an improved strategy for the modification of activated carbons to increase the removal of Sudan IV (S-IV) used as N-containing target pollutant ( $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}$ ), a well-known lipophilic dye contaminant with toxic hazards properties [11,12]. Sudan dyes are harmful colouring additives widely used in fuels, waxes, plastics, floor and shoe polishes, whose discharge into water could cause environmental hazards [11]. Furthermore, S-IV was selected as target pollutant owing its hazard properties and the strong lipophilic character (it is preferentially found in the oil phase) that make it a good candidate to evaluate the recovering of the desirable organic phase contaminated with N-containing substances. For this purpose, the main variable conditions of the process are evaluated, *viz.* the absence or presence of water, particle size of the carbon material and chemical and thermal modifications, initial concentration of target pollutant, water/oil ratio (W/O), nature of the organic phase and presence of an emulsifier.

## 2. Materials and methods

### 2.1. Materials and chemicals

The commercial activated carbon Norit ROX 0.8 (AC) was supplied in cylindrical pellets (0.8 mm of diameter and an average length of ca. 4.0 mm). AC is an extruded carbon material with high purity (ash content of only 3 wt%) produced by steam activation. Sudan IV, S-IV (general purpose grade), sodium dodecyl sulphate, SDS (99%), and cyclohexane (99.99%), were obtained from Fisher Chemical. Other organic solvents, as n-hexane (95%) and n-hexadecane (99%), were supplied by Sigma-Aldrich and Alfa Aesar, respectively. Hydrogen peroxide,  $\text{H}_2\text{O}_2$  (30%, w/v), was obtained from Panreac. Sulphuric acid (96–98 wt%), nitric acid (65 wt%) and urea (65 wt%) were obtained from Riedel-de-Haën. Distilled water was used throughout the work.

### 2.2. Modified activated carbons

The original AC was chemically modified by liquid phase, thermal

and hydrothermal treatments, resulting in the production of five additional activated carbon samples, following the procedures reported elsewhere [13–16]. Three of the samples were modified directly from the original AC by liquid phase treatments with hydrogen peroxide (ACHP), sulphuric acid (ACSA) and nitric acid (ACNA). The treatment with hydrogen peroxide was performed wetting 25 g of AC with 500 mL of hydrogen peroxide solution 30% (w/v) at room temperature for 24 h. In sulphuric acid oxidation, 25 g of AC was immersed in 500 mL of 18 M acid solution for 3 h at 423 K. Oxidation with nitric acid was carried out boiling 25 g of AC in 500 mL of 5 M nitric acid solution for 3 h. After the liquid phase treatments, all samples were thoroughly washed with distilled water until the neutrality of the rinsing waters and further dried in oven for 18 h at 383 K, resulting in samples ACHP, ACSA and ACNA, respectively. The other two samples were obtained in successive treatments of the ACNA material. 2 g of ACNA was immersed in 50 mL of 1 M urea solution and kept in a 125 mL stainless steel high pressure batch reactor under its own atmosphere at 473 K for 2 h, the recovered solids being thoroughly washed with distilled water until the neutrality of the rinsing waters, and further dried overnight in oven at 383 K, resulting in the ACNAU material. Then, a gas phase thermal treatment was applied, in which 1 g of ACNAU was heated, under a  $\text{N}_2$  flow ( $100 \text{ cm}^3 \text{ min}^{-1}$ ), at 393 K, 673 K and 873 K during 60 min at each temperature and then at 1073 K for 240 min, resulting in the ACNAUT material.

In order to obtain adsorbents with smaller particle size, another set of materials was produced starting with powdered activated carbon (PAC) obtained by grinding and sieving the original AC to particle sizes ranging from 0.106 to 0.250 mm. The same chemical modification methods described above were applied to PAC leading to PACHP, PACSA, PACNA, PACNAU and PACNAUT, respectively. Significant changes in the particle size of the original AC were not observed after being chemically modified by the liquid phase, thermal and hydrothermal treatments.

### 2.3. Characterization of activated carbon samples

The textural properties of the materials were determined from  $\text{N}_2$  adsorption–desorption isotherms at 77 K, obtained in a Quantachrome NOVA 4200e adsorption analyser. The specific surface area ( $S_{\text{BET}}$ ) was calculated using the BET method [17]. The external surface area ( $S_{\text{ext}}$ ) and the micropore volume ( $V_{\text{mic}}$ ) were obtained by the *t*-method (thickness was calculated by employing ASTM standard D-6556-01) [18]. The total pore volume ( $V_{\text{Total}}$ ) was calculated at  $p/p^0 = 0.98$ . The microporous surface area ( $S_{\text{mic}}$ ) was determined as the subtraction of  $S_{\text{ext}}$  from  $S_{\text{BET}}$  and the average pore width ( $W_{\text{mic}}$ ) by approximation ( $W = 4V_{\text{mic}}/S_{\text{mic}}$ ). The microporosity was assessed by employing two methods, *viz.* empiric micropore analysis method (MP) of Mikhail et al. [19] and theoretical Horvath-Kawazoe (HK) method [20]. In addition, Barrett-Joyner-Halenda (BJH) analysis was applied for  $\text{N}_2$  adsorption and desorption ( $p/p^0 > 0.35$ ) to assess the mesoporosity of the materials [21]. Calculations of those methods were all done by using NovaWin software v11.02. Elemental analysis was performed in a Carlo Erba EA 1108 Elemental Analyser in order to quantify C, H, N and S contents.

### 2.4. Static adsorption studies

Batch adsorption experiments were performed in a 250 mL well-stirred glass flask, equipped with a condenser and a thermocouple. The flask was loaded with a previous selected quantity of organic phase (cyclohexane, n-hexane or n-hexadecane) contaminated with a target pollutant (the lipophilic dye S-IV) and water. A total volume of 100 mL within the two phases was considered and the W/O ratio was varied from 5:1 to 1:10. Then, the flask was heated to 50 °C by immersion in a water bath at controlled temperature. Upon stabilization at the desired temperature, 2.5 g·L<sup>-1</sup> of adsorbent was loaded, defining this instant as

the initial time of the run ( $t_0 = 0$ ). All experiments were conducted during 24 h.

Selected experiments were performed in triplicate, in order to assess reproducibility and error of the experimental results. The experiments were monitored by taking samples periodically from the flask to determine the concentration of S-IV in the organic phase by using UV/Vis spectrophotometry (Jasco V530).

The amount of dye taken up by the adsorbent was calculated by applying Eq. (1):

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

where  $q_t$  is the adsorption amount at the time  $t$  ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_0$  is the initial dye concentration in the organic phase (OP) ( $\text{mg}\cdot\text{L}_{OP}^{-1}$ ),  $C_t$  is the dye concentration at the adsorption time  $t$  ( $\text{mg}\cdot\text{L}_{OP}^{-1}$ ),  $W$  is the adsorbent mass (g) and  $V_{OP}$  is the volume of the organic phase ( $\text{L}_{OP}$ ).

### 3. Results and discussion

#### 3.1. Textural and chemical characterization of the adsorbents

The  $\text{N}_2$  adsorption-desorption isotherms of the studied powdered activated carbon samples are depicted in Fig. S1. Similar  $\text{N}_2$  sorption isotherms were obtained for these materials, with an hysteresis loop of the H4 type (according to the current IUPAC [22], following the revisions of 1985 IUPAC recommendations on physisorption isotherms), which is typically found for micro-mesoporous carbon materials. This sort of hysteresis loop is ascribed to a composite of isotherms of type I and II, where the more pronounced uptake at low  $p/p^0$  is associated with the filling of micropores. The textural properties, determined from the  $\text{N}_2$  sorption analysis as described in Section 2.3, are summarized in Table 1 (only for powder materials) and the  $t$ -plots are represented in Fig. S2. The thermal and chemical treatments increased or maintained the specific surface area ( $S_{\text{BET}}$ ,  $S_{\text{ext}}$  and  $S_{\text{mic}}$ ) of the pristine material (PAC), with an exception for the treatment with sulphuric acid (PACSA). The treatment with urea (PACNAU) has a more significant effect on the specific surface area. The adsorbents are essentially microporous materials ( $V_{\text{mic}}/V_{\text{Total}}$  higher than 0.5), with an average width of micropore ( $W_{\text{mic}}$ ) of ca. 1.72 nm. Apparently, the micropore width was not affected by these treatments, although differences on the specific surface areas and micropore volumes were observed.

To the best of our knowledge, the cross-sectional area or the maximum atom distance of the S-IV molecule is unknown, but a naphthalene molecule, whose maximum atom distance is of ca. 0.72 nm, can be used as reference molecule. The size of the naphthalene molecule can be determined by different methods, *viz.* semi-empirical, composite, Hartree–Fock, density functional and Møller–Plesset perturbation, from the website of Computational Chemistry Comparison and Benchmark DataBase (CCCBDB) of NIST, where the chemical formula of S-IV is not recognized. According to the average micropore width (1.72 nm), the adsorption of S-IV on the adsorbents may be limited by the size of the S-IV molecules and to slow diffusion of them in the micropores. Fig. S3 shows a relation scale between S-IV, naphthalene and the average micropore size of the adsorbents (the 3D optimized representations of S-IV and naphthalene was done by ACD/Labs/Chemsketch Freeware

v14.00).

The pore distribution of the powdered activated carbons samples, determined by the HK, MP and BJH methods, are depicted in Fig. 1. The methods regarding microporous range (HK and MP) predict that the microporous volume is mainly due to microporous with ca. 0.6 nm. The BJH method used to assess the mesoporous range reveals that the majority of the pores have a diameter less than 10 nm (Fig. 1B only shows the results from  $\text{N}_2$  adsorption-desorption analysis of PAC, PACNAU and PACNAUT in order to illustrate the highest difference among all adsorbents).

The elemental composition of the fresh adsorbents are summarized in Table 2. The treatment with hydrogen peroxide was found to be the method that less affects the composition of the adsorbent (PACHP) when compared to the original PAC. The treatments with sulphuric (PACSA) and nitric (PACNA) acids increase the S and N-contents, respectively, and both decrease the C-content, more significantly in the case of nitric acid. In a previous study [13], an increment of the surface oxygen, due to the incorporation of O-containing groups, mainly carboxylic acids, was observed by temperature programmed desorption (TPD) analysis of all materials modified by treatment with nitric acid, sulphuric acid or hydrogen peroxide. Thus, partial oxidation of the materials can justify the decrease of the C-content as well as the increment of the remaining elements (ashes and likely oxygen). The remaining elements (nonCHSN-content) increase from 18.9% (PAC) to 20.9% (PACSA) and 25.2% (PACNA), which can be ascribed to the oxidation of the carbon material. As expected, the N-content of PACNA additionally increased by the successive treatment with urea (PACNAU), reaching 3.2% of N in the composition. However, the thermal treatment applied to obtain PACNAUT decreases the N-content (to 2.8%) and, especially, the nonCHSN-content (from 18.4% to 5.9%), likely due to desorption of the weakest O- and N-containing surface groups. This means that the remaining content in PACNAUT is due likely to O-content (the ashes of the commercial carbon is 3%). Characterization of the materials, regarding the acidity, basicity, PZC and the concentration of CO, CO<sub>2</sub> and SO<sub>2</sub> released during Temperature Programmed Desorption (TPD) analysis, can be found in previous studies [13–15]. According to those results, the chemical properties of PACNAUT are found to be quite different when compared with the other materials (*i.e.* lower oxygen content, higher basicity and PZC).

#### 3.2. Adsorption studies

##### 3.2.1. Effect of the presence of water

Preliminary adsorption experiments were carried out in the presence and absence of water in order to study the distribution of the adsorbent on the biphasic system phases as well as its adsorption capacity when the contaminated oily phase is mixed with water. The results obtained in the adsorption of S-IV with the original and with the modified activated carbons can be found in Fig. 2. The adsorption capacities after 24 h experiments with AC and ACNAUT samples were found to be in the range from 20.9 to 21.6 mg of S-IV per gram of adsorbent, either in the adsorption experiments carried out with or without water. On the opposite, ACHP, ACSA, ACNA and ACNAU lead to low S-IV removals by adsorption, namely presenting adsorption capacities of 0.1–6.1  $\text{mg}\cdot\text{g}^{-1}$  after 24 h. Furthermore, the adsorption

**Table 1**  
Textural properties of the powdered activated carbons determined from BET and  $t$ -Plot methods.

	$S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$S_{\text{ext}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$S_{\text{mic}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$V_{\text{mic}}$ ( $\text{mm}^3\cdot\text{g}^{-1}$ )	$V_{\text{mic}}/V_{\text{Total}}$ (%)	$W_{\text{mic}}$ (nm)
PAC	885 ± 10	160 ± 2	725 ± 12	314 ± 1	58	1.73 ± 0.03
PACSA	862 ± 9	150 ± 2	712 ± 11	308 ± 1	59	1.72 ± 0.03
PACHP	893 ± 10	159 ± 2	734 ± 12	319 ± 1	58	1.73 ± 0.03
PACNA	889 ± 10	170 ± 2	719 ± 12	311 ± 1	57	1.72 ± 0.03
PACNAU	960 ± 11	181 ± 2	778 ± 12	336 ± 1	58	1.72 ± 0.03
PACNAUT	1055 ± 11	197 ± 2	858 ± 12	367 ± 1	58	1.71 ± 0.03

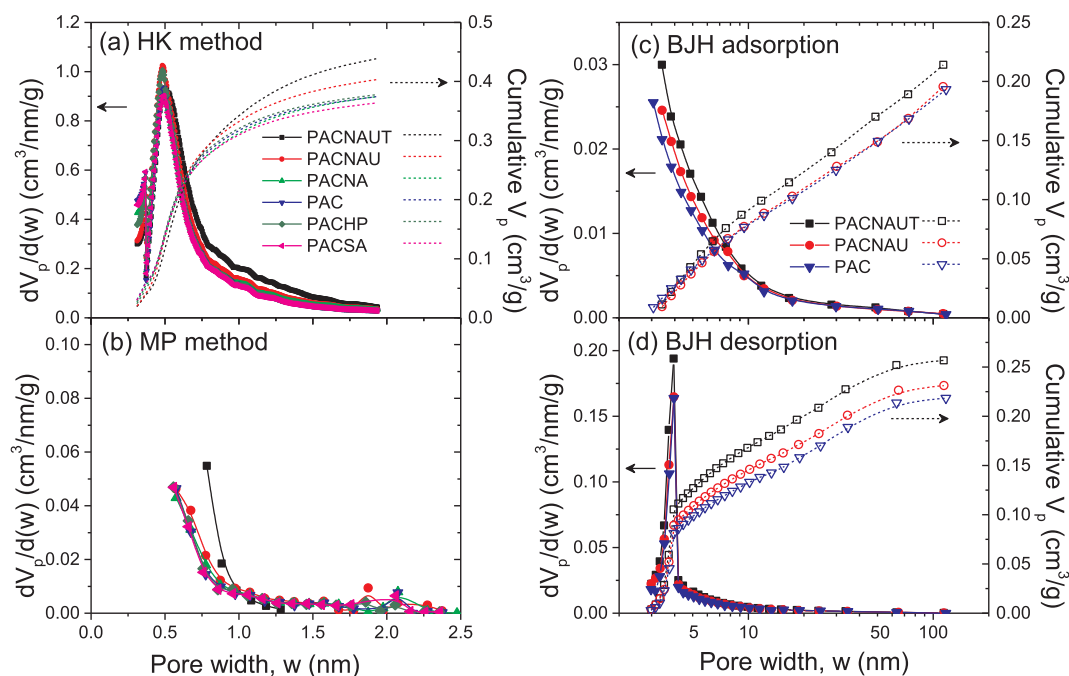


Fig. 1. Pore distribution in the powdered activated carbons from  $N_2$  adsorption-desorption analysis and determined by (a) HK and (b) MP methods for microporous range, and BJH method in (c) adsorption and (d) desorption of  $N_2$  for mesoporous assessment.

**Table 2**  
Elemental analysis of the adsorbents before and after (in brackets) adsorption.

	C (%)	H (%)	S (%)	N (%)	Remaining (%)
PAC	79.0 (82.7)	1.5 (1.9)	0.6 (0.8)	0.0 (1.4)	18.9 (13.2)
PACSA	76.1	1.8	1.2	0.0	20.9
PACHP	81.4	1.4	0.6	0.0	16.5
PACNA	70.6 (74.9)	2.4 (1.7)	0.4 (0.4)	1.4 (2.7)	25.2 (20.3)
PACNAU	75.3 (77.6)	2.7 (1.8)	0.3 (0.3)	3.2 (4.1)	18.4 (16.1)
PACNAUT	88.6 (84.1)	2.2 (1.5)	0.4 (0.4)	2.8 (3.7)	5.9 (10.4)

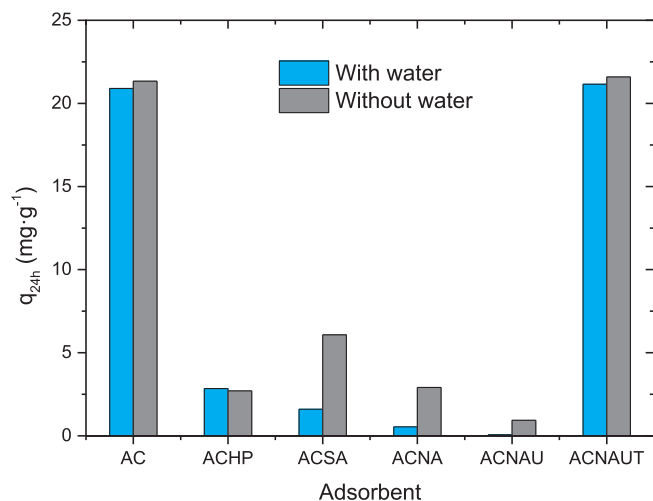


Fig. 2. Effect of the presence of water on the adsorption of S-IV from cyclohexane with different activated carbons. Experimental conditions: natural pH,  $T = 50^\circ\text{C}$  and  $C_{\text{adsorbent}} = 2.5\text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).

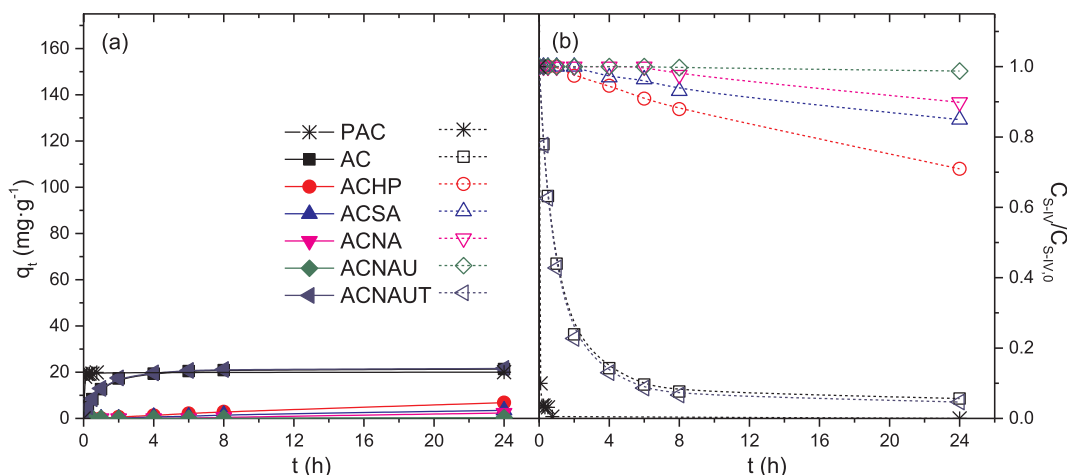
capacities of ACSA, ACNA and ACNAU samples are significantly different when the contaminated oily phase is mixed with water. This behaviour may be ascribed to a decrease of the contact area between the adsorbent and the organic phase, very likely due to the higher hydrophilic character of ACSA, ACNA and ACNAU, when compared to

the lipophilic-character of AC and ACNAUT. In this sense, these results prove the importance to develop adsorbents with high lipophilic-character when adsorption of lipophilic pollutants, as S-IV ( $\log P_{\text{octanol/water}} = 6.66 \pm 0.43$ , estimated with ACD/Labs/Chemsketch Freeware v14.00), from an organic phase is targeted.

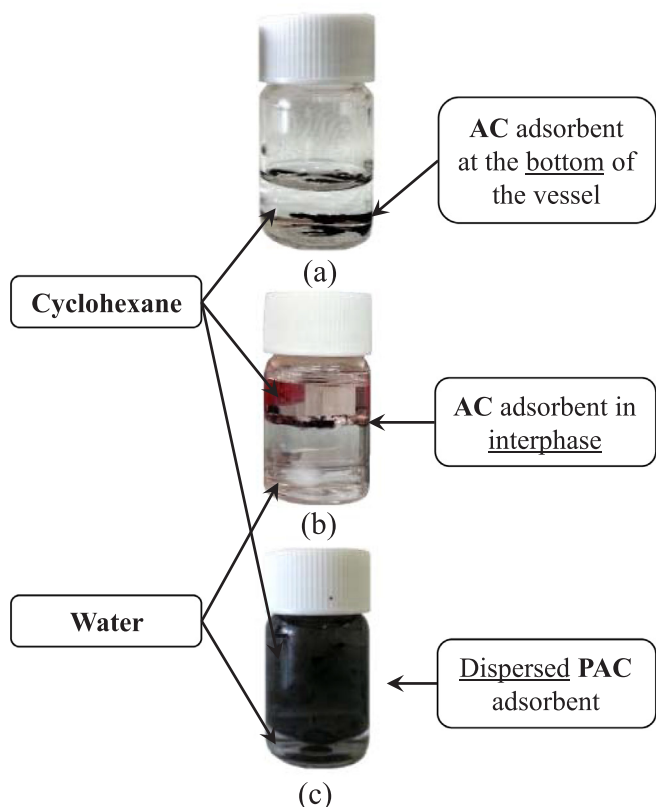
### 3.2.2. Effect of particle size

To study the effect of particle size, the commercial activated carbon (AC) was tested in the biphasic system ( $W/O$  ratio = 1:1) considering two different particle sizes: a diameter of 0.8 mm and average length of 4.0 mm, corresponding to the original size of the materials, and a particle size between 0.106 and 0.250 mm, as resulted from grinding and sieving of AC to PAC. The results achieved in the runs carried out with AC and PAC, and with the modified activated carbons (ACHP, ACSA, ACNA, ACNAU and ACNAUT), obtained with the same particle size as the commercial AC, are depicted in Fig. 3. The plot shows the adsorption values ( $q_t$ ) upon the contact time ( $t$ ) and the S-IV removal, measured as the ratio of the concentration of S-IV ( $C_{S-IV}$ ) at a given time and the concentration of S-IV ( $C_{S-IV,0}$ ) at the beginning of the adsorption run (with experimental values shown as symbols and the tendency shown as curves). The adsorption capacity of the original AC and ACNAUT samples are both found to be  $20\text{ mg}\cdot\text{g}^{-1}$ , after 8 h of adsorption time. The chemically modified activated carbons ACHP, ACSA, ACNA and ACNAU present an adsorption capacity in the range from 0.3 to  $6.8\text{ mg}\cdot\text{g}^{-1}$  at 24 h, lower than the value obtained with the commercial adsorbent AC. Moreover, the maximum adsorption capacity value ( $20\text{ mg}\cdot\text{g}^{-1}$ ) is reached in less than 1 h of contact time for PAC, revealing the strong influence of particle size on the performance of the adsorption process. In fact, the adsorption performance of the material with the lower particle size (PAC) is far faster than that obtained with any modified and unmodified sample with the original particle size of the commercial adsorbent. As can be observed (Fig. 3), the chemical modification of the commercial activated carbon (ACHP, ACSA, ACNA, ACNAU, ACNAUT) does not improve the adsorption performance when compared to the decrease of the particle size of the original activated carbon (PAC). The adsorption of S-IV was expected to increase while decreasing the adsorbent particle size, as observed in other instances [23], thus increasing removal with the reduction of the particle size of





**Fig. 3.** Effect of contact time and particle size on (a) adsorption capacity and (b) normalized concentration evolution in the adsorption of S-IV on the activated carbon samples. Experimental conditions:  $W/O$  ratio = 1:1, natural pH,  $T = 50\text{ }^{\circ}\text{C}$ ,  $C_{S-IV,0} = 50\text{ mg}\cdot\text{L}^{-1}$  and  $C_{\text{adsorbent}} = 2.5\text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).



**Fig. 4.** Effect of water and particle size of adsorbents by photographs of vessels with a mixture of (a) oil-AC sample, (b) water-oil-AC sample and (c) water-oil-PAC sample.

the carbon substrate. In the present study, the increase was remarkable, namely growing from 25% to 96%, for AC and PAC samples (in 15 min), respectively. The higher performance of PAC may be explained by three reasons: (a) a higher external surface area of the adsorbent owing to higher ratio of surface ( $S$ ) to volume ( $V$ ) of adsorbent particles, assuming spherical (sieved samples, SS) and cylinder (pristine material, PM) shape for particles (Eqs. (2) and (3)); (b) a lower mass transfer limitation enabled by the smaller particle size; and (c) a better dispersion of the adsorbent in the organic phase as a consequence of smaller particle size, reducing settling effects at the interphase, when compared to the higher settling of the adsorbent AC at the interphase

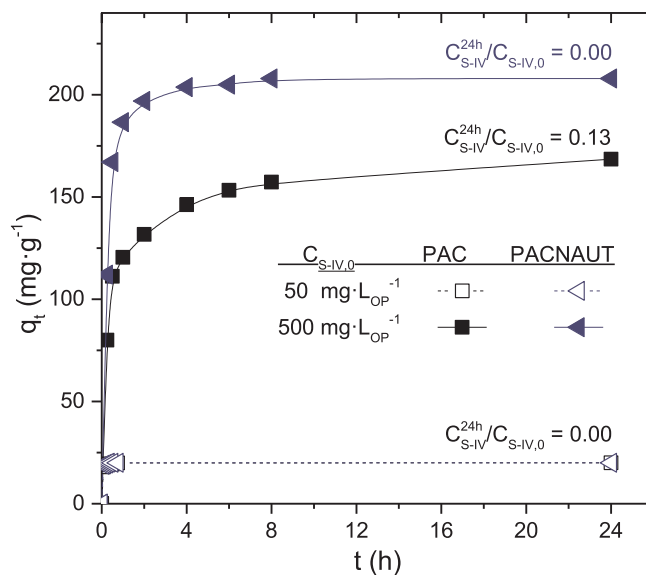
between the aqueous and organic phases, due to the larger particle size, as observed in Fig. 4.

$$[S/V]_{PM} = \frac{D_P + 4L}{D_P L} = 20\,200\text{ m}^{-1} \quad (2)$$

$$[S/V]_{SS} = \frac{6}{D_P (1.06 \times 10^{-4} \sim 2.50 \times 10^{-4}\text{ m})} = 24\,000 \sim 56\,600\text{ m}^{-1} \quad (3)$$

### 3.2.3. Effect of initial pollutant concentration

An increase of the initial pollutant concentration was considered to study the effect on S-IV removal with PAC and PACNAUT. Fig. 5 shows the adsorption capacity and removal towards the S-IV obtained during 24 h runs for the selected initial concentrations: 50 and 500 mg of S-IV per liter of organic phase. The complete adsorption of S-IV was achieved before 1 h at the lower initial pollutant concentration (50 mg per liter of organic phase) regardless of the adsorbent, resulting in a maximum possible uptake capacity (Eq. (4)).



**Fig. 5.** Effect of initial pollutant concentration on adsorption of S-IV on modified activated carbons. Experimental conditions:  $W/O$  ratio = 1:1, natural pH,  $T = 50\text{ }^{\circ}\text{C}$  and  $C_{\text{adsorbent}} = 2.5\text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).

$$q_{24h} = \frac{50 \text{ mg L}_{OP}^{-1} - 0 \text{ mg L}_{OP}^{-1}}{2.5 \text{ mg L}_{OP}^{-1}} = 20 \text{ mg g}^{-1} \quad (4)$$

Specifically, the thermal and chemically modified adsorbent PACNAUT lead to complete removal of S-IV after 30 min at 50 °C, with an initial pollutant concentration of 50 mg·L<sub>OP</sub><sup>-1</sup> and 2.5 g·L<sub>OP</sub><sup>-1</sup> of adsorbent. At a similar initial pollutant concentration, 3 h were needed to obtain the complete removal of pollutant by other techniques [24]. The adsorption capacity from the solution with an initial pollutant concentration of 500 mg·L<sup>-1</sup> was found to be 168.5 and 200.0 mg·g<sup>-1</sup> at 24 h with PAC and PACNAUT, respectively. At higher concentration of S-IV, the removal obtained with PACNAUT is relatively higher when compared with the removal obtained with the original PAC. The complete adsorption of S-IV was found with PACNAUT after 6 h of contact time at these conditions, whereas 87% of S-IV is removed from the organic phase after 24 h of adsorption with PAC adsorbent.

### 3.2.4. Effect of W/O ratio and pH of aqueous phase

Three adsorption experiments were performed considering an initial pH (pH<sub>0</sub>) of 7 in the presence of PAC with a water/oil volume ratio (W/O) of 5:1, 1:1 and 1:10, keeping the total volume of the system always equal to 100 mL. Additionally, an experiment with a W/O ratio of 5:1 was performed at pH<sub>0</sub> = 3. The quantity of adsorbent needed to operate at 2.5 g<sub>ads</sub>·L<sub>OP</sub><sup>-1</sup> was maintained in all the experiments. The results obtained in the adsorption of S-IV are reported in Fig. 6, evidencing that the removals reached with the PAC adsorbent are not significantly affected by the W/O ratio, neither with the pH of the aqueous phase. The removals of S-IV were always near 90% and the adsorption capacity was found to be in the range from 168.5 to 184.9 mg·g<sup>-1</sup>. Both PAC adsorbent and the target pollutant S-IV have lipophilic-character, so the removal is mainly governed by the parameters in the organic phase, leading the S-IV adsorption to be independent from the water volume and pH of the aqueous medium.

### 3.2.5. Effect of chemical modifications

The uptake capacities of the modified adsorbents prepared with particle size ranging between 0.106 and 0.250 mm are presented in Fig. 7. It is observed that the uptake capacities of S-IV are 168.5, 190.8, 174.1, 160.96, 183.2 and 200.0 mg·g<sup>-1</sup> at 24 h of contact time with PAC, PACHP, PACSA, PACNA, PACNAU and PACNAUT, respectively, and the S-IV removal reach respective values of 86.9, 95.4, 87.1, 87.3, 94.7 and 100.0%. The thermal and chemically modified activated carbon (PACNAUT) reveals a significant S-IV removal, leading to complete adsorption of the pollutant from the W/O biphasic mixture after 6 h and, therefore, to the complete removal of the N-content and

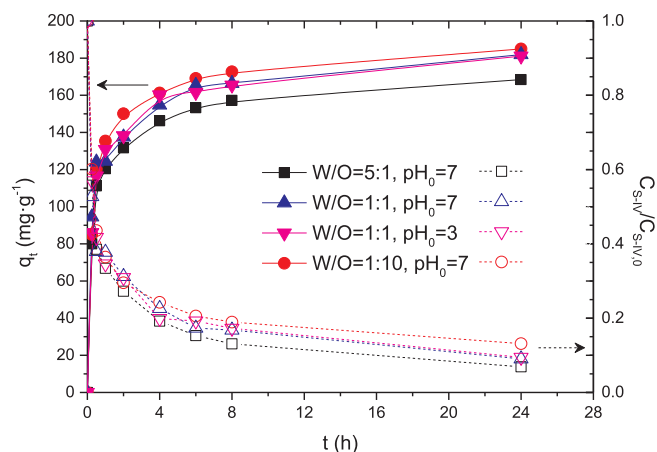


Fig. 6. Effect of W/O ratio and pH of the aqueous phase on adsorption capacity (left axis) and normalized concentration (right axis) evolution in the adsorption of S-IV on PAC. Experimental conditions:  $T = 50 \text{ }^\circ\text{C}$ ,  $C_{S-IV,0} = 500 \text{ mg}\cdot\text{L}^{-1}$  and  $C_{PAC} = 2.5 \text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).

colour from the organic phase. In this regard, it is possible to observe an increase of the N-content in the carbonaceous materials after their use in the adsorption of S-IV (1.40, 1.30, 0.90 and 0.99 wt% more in used adsorbent samples with respect to the fresh PAC, PACNA, PACNAU and PACNAUT materials). The theoretical increase of N-content in the adsorbents at end of the process was calculated taking into consideration the experimental uptake capacities obtained, the molar weight ratio (4-N/S-IV), the previous N-content in the fresh materials and the hypothesis that the remaining species found in the elemental composition analysis shown in Table 2 (likely ashes and oxygen) was kept during the adsorption process. According to these premises, the N-content of the materials after the adsorption process should be 1.47, 3.22, 4.99 and 4.85 wt% respectively for PAC, PACNA, PACNAU and PACNAUT materials, close to the N-content measured. However, the non-CNHS content of the materials decreased after adsorption, with exception of PACNAUT. This was ascribed to the oxygen content of water (H: 11.19%, O: 88.81%), cyclohexane (C: 85.63%, H: 14.37%) and S-IV (C: 75.77%, H: 5.3%, O: 4.21%, N: 14.73%) that can be chemisorbed on samples.

As shown in Section 3.1 (textural characterization), PACNAUT presents a high texture development after the treatments (the highest  $S_{BET}$ ,  $S_{ext}$ ,  $S_{mic}$  and  $V_{mic}$ ), explaining in a certain extent to the higher adsorption of S-IV. However, the highest uptake capacity of PACNAUT may be also ascribed to the absence of O-containing groups on the activated carbon surface, such as carboxylic acids (decomposed upon the thermal treatment performed under N<sub>2</sub> atmosphere), promoting adsorption interaction between S-IV and the activated carbon surface due to changes in the surface chemistry and to changes in the surface area and porosity [23,25–27]. The TPD characterization reveals that PACNAUT contain lower quantity of oxygen surface groups when compared with PACNA, as determined by the lower quantity of CO and CO<sub>2</sub> released (445 and 119  $\mu\text{mol}\cdot\text{g}^{-1}$ , respectively) [13–15]. In the opposite, the worst S-IV adsorption performance was precisely found when PACNA was used. This material presents the highest amount of oxygen surface groups, as revealed by the higher content of CO and CO<sub>2</sub> groups released by TPD (> 4000 and > 2000  $\mu\text{mol}\cdot\text{g}^{-1}$ , respectively), confirming the detrimental influence of O-containing groups in the adsorption performance of the activated carbons.

The chemical and thermal modification methods applied to the activated carbon materials in this work have been used previously in order to improve the uptake capacity of carbon xerogels towards caffeine and diclofenac [28], also supporting the need to remove O-containing groups for an improved performance. In this regard, the modified carbon xerogel obtained applying the same process used to obtain PACNAUT, was found to be the best method to maximize caffeine adsorption on carbon xerogels.

Treatment of S-IV by the heterogeneous Fenton process [8,29], attained removals from 58 to 80% (in 1 h of reaction time) from an oily phase polluted with 500 mg·L<sub>OP</sub><sup>-1</sup> of dye contaminant mixture with water, using 4 g·L<sub>OP</sub><sup>-1</sup> of a red mud based catalyst [8] or 2 g·L<sub>OP</sub><sup>-1</sup> of a Fe–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (Fe 10% and Mo 1%) [29]. In the present work, we are significantly increasing the amount of S-IV removal (90% in 1 h) by adsorption on PACNAUT (2.5 g of PACNAUT adsorbent per liter of oil phase). Furthermore, no oxidative intermediates susceptible of contaminating the oily phase are generated in the adsorption process, at variance with what occurs when using the heterogeneous Fenton reaction. The adsorption of S-IV was also studied in the above mentioned previous reports, being the materials left in contact with the substrate solutions until they reached the adsorption equilibrium. It was observed that less than 1% [29] and 5% [8] of S-IV removals were respectively obtained with Fe–Mo/Al<sub>2</sub>O<sub>3</sub> (in 3 h) and the red mud based catalyst (in 1 h). Thus, these S-IV adsorption removals are considerably lower than those achieved with PACNAUT in the present work.

### 3.2.6. Effect of organic phase

Adsorption runs of S-IV from different organic phases (cyclohexane,

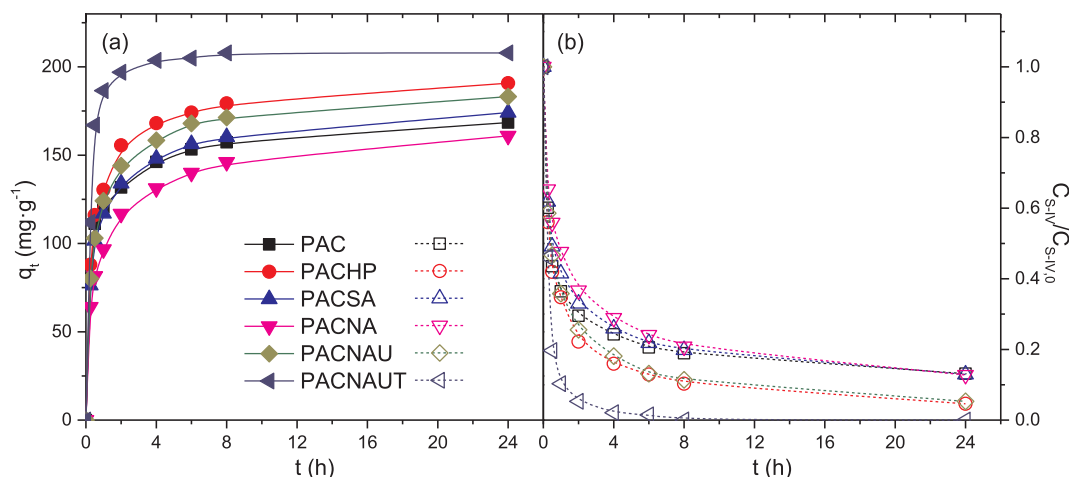


Fig. 7. Effect of the activated carbon modifications on (a) adsorption capacity and (b) normalized concentration evolution in the adsorption of S-IV on the modified activated carbons. Experimental conditions: W/O ratio = 1:10, natural pH,  $T = 50\text{ }^{\circ}\text{C}$ ,  $C_{S-IV,0} = 500\text{ mg}\cdot\text{L}^{-1}$  and  $C_{\text{adsorbent}} = 2.5\text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).

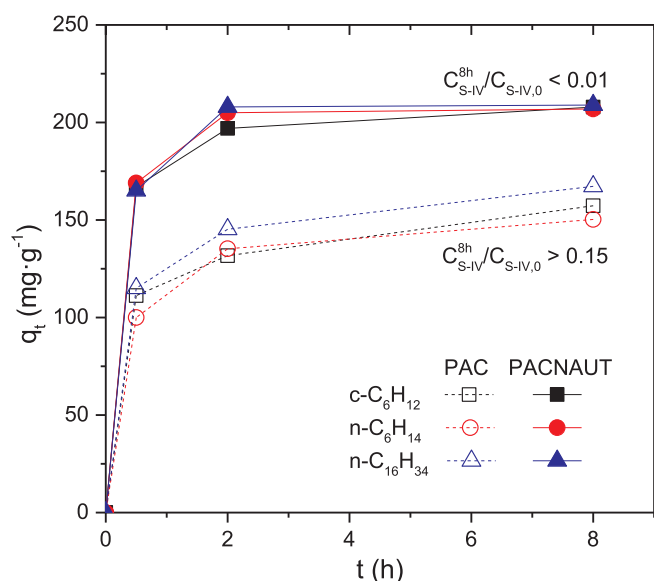


Fig. 8. Adsorption of S-IV from a biphasic mixture of water and different organic phases (W/O ratio = 1:10) at  $50\text{ }^{\circ}\text{C}$ , natural pH and  $2.5\text{ g}$  of adsorbent per liter of organic phase (cyclohexane, n-hexane and n-hexadecane).

n-hexane and n-hexadecane) were carried out in order to evaluate the influence of the solvent in the process. These S-IV adsorption experiments were performed with PAC and the previous highlighted adsorbent, PACNAUT (experimental data represented in Fig. 8), revealing that the nature of the organic phase does not affect the uptake capacities of the adsorbents towards S-IV. The adsorption capacities are similar regardless of the organic phase, namely  $157.3$ ,  $150.5$ ,  $167.3\text{ mg}\cdot\text{g}^{-1}$  at  $8\text{ h}$  with PAC in cyclohexane, n-hexane and n-hexadecane, respectively, whereas the same maximum adsorption capacity values ( $200.0\text{ mg}\cdot\text{g}^{-1}$ ) were obtained with PACNAUT regardless the organic phase. This may mean that competitive adsorption between the solvent (organic phase) and the target pollutant does not exist, as long as the adsorption of the solvent take place in the medium of the system (the possible adsorption of solvents was not assessed). It is also possible that the adsorption of S-IV is benefited compared to the solvent adsorption or, in other words, that the adsorbent shows a high selectivity to the adsorption of S-IV.

Adsorption rates appear also similar regardless the organic phase for both PAC and PACNAUT, as can be observed from the represented curves. Therefore, diffusion of S-IV from the bulk organic solvent to the

external surface of the adsorbent is similar for the three organic phases or more probably, this external diffusion is not the controlling stage of this mass transfer process for any of the solvents here studied.

### 3.2.7. Effect of emulsifier and order of addition

Emulsifiers may be present in oily wastewaters, in addition to other components present in the waste [4,30]. In this sense, it is important to take into account the presence of emulsifiers in the treatment of this type of wastewater. In order to evaluate the effect of the presence of emulsifiers and the emulsion form of the biphasic medium, three S-IV adsorption runs were performed with PAC: (1) without emulsifier; (2) with sodium dodecyl sulphate (SDS) as emulsifier; and (3) with SDS, but modifying the order of addition of the adsorbent and emulsifier. Fig. 9 shows the adsorption removal of S-IV upon the contact time for the runs described. As observed, the adsorption of S-IV was found to be considerably affected by the presence of emulsifier and with the order of addition. When the adsorbent is added to the system after the emulsifier (with the consequent formation of the emulsion in the mixture water-cyclohexane), the adsorption of S-IV is substantially lower (triangle symbols), since the adsorbent probably cannot enter in contact with the oil drops formed in the bulk water. When the order of addition of the emulsifier is reversed (in this case the emulsion is formed after the addition of adsorbent), higher adsorption is observed. However, the adsorption capacity continued considerably lower than the observed in the experiments without SDS, probably due to competitive adsorption between the pollutant and the emulsifier at the adsorption sites of the material. These runs evidence the need to destabilize the emulsion before the adsorption process. In this regard, acidification is a commonly method used to destabilize an emulsion as part of pre-treated coagulation process [31,32]. Electrochemical methods can also be applied to achieve this aim [30].

## 4. Conclusions

A powdered activated carbon with characteristic lipophilic character (PACNAUT) was developed to preferentially adsorb Sudan IV (S-IV) from a simulated oily wastewater. The solubility and lipophilic character of both the adsorbent and pollutant lead the adsorption of S-IV to be independent from the water fraction of the biphasic system and pH of the medium. In addition, the application of adsorbents with low particle size improves the dispersion between the phases and strongly enhances the adsorption of S-IV.

The successive treatments with nitric acid and urea followed by thermal treatment at  $800\text{ }^{\circ}\text{C}$  under inert atmosphere, produce a complex texture development ( $S_{\text{BET}} = 1055\text{ m}^2\cdot\text{g}^{-1}$ ) developing the highest

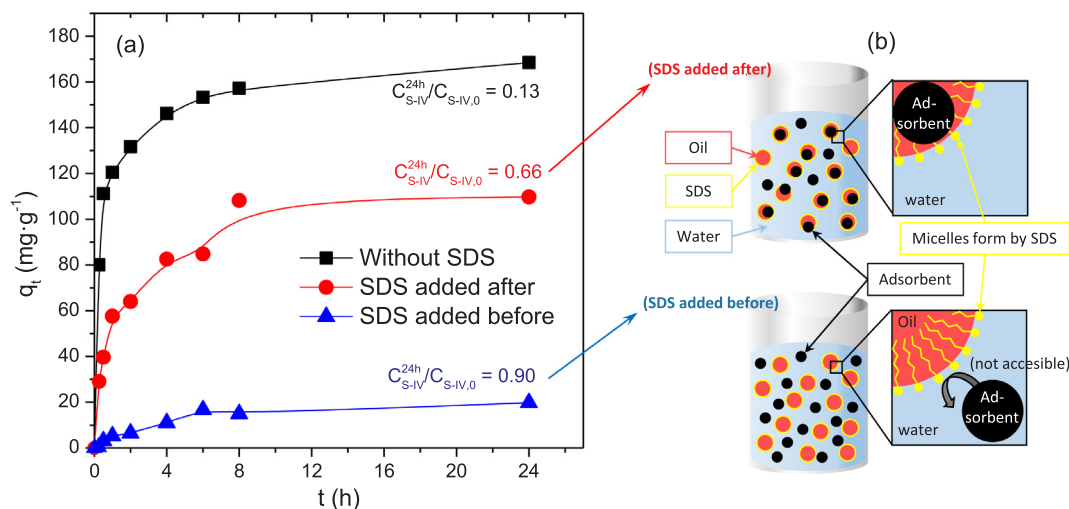


Fig. 9. Effect of the presence and addition order of SDS as emulsifier on (a) adsorption capacity evolution in the adsorption of S-IV on PAC adsorbent and (b) schematic representation of the processes taking place. Experimental conditions:  $W/O$  ratio = 1:10, natural pH,  $T = 50\text{ }^{\circ}\text{C}$ ,  $C_{S-IV,0} = 500\text{ mg}\cdot\text{L}^{-1}$  and  $C_{PAC} = 2.5\text{ g}\cdot\text{L}^{-1}$  (per liter of organic phase).

specific surface area. Furthermore, the so obtained PACNAUT adsorbent has the lowest content of oxygen surface groups owing to the thermal treatment performed.

These characteristics were found to make the adsorption capacity of PACNAUT the highest among all the prepared adsorbents. An amount of  $2.5\text{ g}\cdot\text{L}^{-1}$  of PACNAUT removes completely up to  $500\text{ mg}$  per liter of organic phase (maximum possible uptake capacity was achieved:  $200\text{ mg}\cdot\text{g}^{-1}$ ) of the target S-IV pollutant from the biphasic system in 8 h.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2018.04.105>.

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