INSTITUTO POLITÉCNICO DE BRAGANÇA
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# Oxidative Degradation of Aniline Derived Compounds over Carbon Based Materials

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**Orientada por:**

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**Abstract**

The objectives of this work were: the preparation of different forms of carbon materials (AC, ACSA, CX, CXSA and GBCM), assessment of their catalytic efficiency in the CWPO of the azo dye Chromotrope 2R.

Initially the materials were characterized by several techniques, afterwards adsorption and reaction runs were done and lastly the samples obtained from the adsorption/reaction runs were tested using the COD to calculate the organic matter in solution.

Reactions were carried out with 100 mg/L C2R solution at 50ºC, pH = 3, hydrogen peroxide of 34.6 mM (5 mL) and 0.5 g/L of carbon material. Several samples (5 mL) were removed from the reactor during 2.5 hours to evaluate the evolution of the dye removal by analysis with UV-VIS (spectrophotometer). The adsorption runs were done the same way, but without hydrogen peroxide.

The best results were obtained with Activated Carbon, this material was the best adsorbing material and catalyst, removing 64 % of C2R after 150min of reaction and 74 % the adsorption run.

As the reaction results weren´t better than the adsorption ones, iron was incorporated in two of the materials. Incorporating iron in the carbon materials increased radically their catalytic behaviour, with 100 % removal being attained after 150 min of reaction.

**Key Words**: CWPO; Hydrogen Peroxide; Activated Carbon.

**Resumo**

Os objectivos deste trabalho foram: a preparação de diferentes materiais de carbono (AC, ACSA, CX, CXSA e GBCM) e testar a eficiência destes no CWPO do corante Chromotrope 2R.

Inicialmente os materiais foram caracterizados através de várias técnicas, seguidamente foram realizados os ensaios de adsorção e reacção, e no fim, determinou-se a Carência Química do Oxigénio (CQO) das amostras resultantes dos ensaios.

As reacções foram feitas numa solução de Chromotrope a 100 mg/L, a 50º C, pH = 3, peróxido de hidrogénio a 34.6 mM (5 mL) e com 0.5 g/L de material de carbono. Foram retiradas várias amostras (5 mL) do reactor durante 2.5 horas, para avaliar a evolução da degradação do corante através da análise com UV-VIS (espectrofotómetro). Os ensaios de adsorção foram feitos da mesma forma, mas sem o peróxido de hidrogénio.

Os melhores resultados foram obtidos com o carvão activado que foi o melhor adsorvente e catalisador, removendo 64 % do Chromotrope após 150 min de reacção e 74 % no ensaio de adsorção.

Como os resultados da reacção não foram melhores que os obtidos da adsorção, foi incorporado ferro em dois dos materiais. A incorporação de ferro nos materiais de carbono aumentou radicalmente o comportamento catalítico destes, obtendo-se uma remoção de 100 % após 150 min de reacção.

**Palavras-Chave**: CWPO; Peróxido de Hidrogénio; Carvão Activado.

**Index**

## 1. Introduction

With the industry development over these last few decades there has been an outraged increase in waste products, including toxic compounds in effluents that are highly prejudicial to human health and the environment. Wastewater discharged in a river will contaminate the water causing serious environmental problems. For example, a change in the water chemistry due to surface water contamination can negatively affect all levels of an ecosystem with a strong impact in the health of lower food chain organisms and, consequently, in the availability of the food supply up through the food chain.

It´s of great importance that industry waste products are treated before being discharged to concentration values below environmentally accepted levels. Unfortunately it`s often avoided, mostly because of the expenses and time needed. Studies have been done to find efficient methods to treat these wastes existing already a great variety of methods. Factories of coal conversion, petroleum refining, iron and steel, textiles, dyes, resins, plastics, agrochemicals, explosives, herbicides, as well as many others, discharge wastewater containing organic compounds, which are very toxic and are difficult to treat by biological processes. Amongst these are aniline, phenolic compounds and nitroaromatic related compounds. These compounds are harmful to human health, with a high level of toxicity, as observed in Table 1, and are suspected to be carcinogens. Thus, they will be considered as model compounds in the studies that will be carried out in this work.

**Table 1** – Toxicity of some organic compounds

| **Products** | **Toxicity** | |
|---|---|---|
| Nitrobenzene | 200 $mg.kg^{-1}$ | $LD_{LO}$[a] (oral route) |
| Aniline | 250 $mg.kg^{-1}$ | (rat: oral route) $LD_{50}$[b] |
| | 61 $mg.L^{-1}$ | (fish toxicity) $CL_{50}$[c] |
| Phenol | 23.5 $mg.L^{-1}$ | CE (I) 50-48h[d] |
| 4-nitrophenol | 20 $mg.L^{-1}$ | CE (I) 50-48h |

[a] American standard which defines the smallest amount that can kill by one of the administering route.

[b] Corresponds to the limit amount by oral or skin route that can lead to death 50% of the tested population.

[c] Medium lethal concentration.

[d] Corresponds to the initial concentration that kills in 48h 50% of daphnia magna.

## 1.1 Aniline

Aniline is an organic compound with the formula $C_6H_7N$ also known as phenylamine or aminobenzene. It´s an aromatic amine that has an aromatic ring in the molecular structure. These compounds range from a simple molecule as aniline to highly complex molecules such as azo dyes, among others.

Aniline is a poisonous, carcinogen, neurotoxin and one of the most important aromatic amines, being used as a precursor to more complex chemicals. For instance, it is used in the manufacture of polyurethane. Aniline and its derivatives are usually produced as by-products in certain industries, especially chemical. They are biorefractory (can`t be degraded biologically) and highly toxic, being able to convert haemoglobin into metahaemoglobin reducing the intake of oxygen.

Previous studies have also reported that hydroxyaniline induces allergies in humans, in addition to other known neurotoxicities. Like most volatile amines, aniline has an unpleasant odour of rotten fish and a burning aromatic taste. It´s a highly-acrid (sharp, corrosive) poison and ignites readily burning with a smoky flame.

Aniline can be formed the following way through the mechanism shown in figure 1.

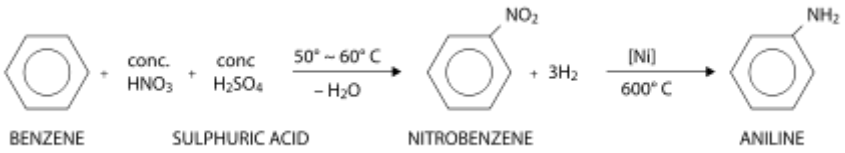


**Figure 1** – Synthesis of aniline

As can be observed on figure 1, benzene is initially nitrated, using a concentrated mixture of nitric acid and sulphuric acid at 50 to 60ºC, producing nitrobenzene. Afterwards, the nitrobenzene is hydrogenated at 600ºC in the presence of a nickel catalyst to form aniline. Alternatively, aniline can also be prepared from phenol ($C_6H_5OH$) and ammonia. Accordingly, typical aniline industrial producers generate liquid effluents containing not only aniline in its composition, but also other phenolic and nitroaromatic compounds. Aniline is also a precursor of other compounds such as azo dye colourings which will be studied in this work due to their large application in the industrial fields and also to account certain health risk concerns which have appeared or are suspected from the usage of the colouring. For instance, certain amines are currently included in several hazardous chemicals release inventory and restriction regulations, at international and national level,

which reflect the current knowledge of their hazardous character, with particular emphasis on their carcinogenity [1].
They account for approximately 60 - 70 % of all dyes used in the manufacture of a vast variety of food and textile products.

### 1.1.1 Azo Dyes

Azo dyes constitute the largest and most versatile class of synthetic dyes used in the textile, pharmaceutical, food and cosmetics industries.
They are characterized by nitrogen to nitrogen double bonds and are a major source of aromatic amines having in their molecular structure one or more aromatic rings with one or more amino substituents. The colour of the dyes is due to the azo bond and associated chromophores [2, 3].
Due to electron delocalization through the nitrogen to nitrogen double bond group, these compounds have vivid colours, such as red, orange, or yellow. Depending on the number of azo groups there are mono-, di- and triazo dyes [4].
The biological reduction of an azo bond is responsible for the appearance of dangerous aromatic amines in liquid effluents, such as aniline and sulphanilic acid which are carcinogenic [5]. Strong colour imparted by the dyes poses aesthetic problems and serious ecological problems such as inhibition of benthic photosynthesis and carcinogenicity [1, 6]. In some cases they can be harmful compounds and can originate dangerous compounds through oxidation, hydrolysis and other chemical reactions [7], being thus of particular environmental concern. Due to their biological recalcitrance, conventional biological treatment processes, such as activated sludge process, are ineffective to remove these dyes from wastewater [8, 9] being necessary to develop different methods such as the one studied in this work based on wet peroxide oxidation.

## 1.2 Phenolic Compounds

Phenol is also designated as carbolic acid, hidroxybenzene, oxybenzene and phenylic acid. It is a white, crystalline, water-soluble, poisonous mass, $C_6H_5OH$, obtained from coal tar, or a hydroxyl derivative of benzene. It´s used in the manufacture of resins, plastics, dyes, pharmaceuticals (as aspirin) and also as a topical anaesthetic in dilute solution known as carbolic acid or hydroxybenzene. Because of its harmful effects, wastewaters containing phenolic compounds must be treated before being discharged into receiving water bodies. Phenols have been designated as priority pollutants by many countries due to their acute toxicity and long term persistence.

### 1.2.1 Nitrophenols

Nitrophenols are biorefractory organic compounds, which are widely used as important raw materials for the production of insecticides, herbicides, explosives, and various synthetic compounds [10]. They are also considered important hydrocarbons for usage in pharmaceutical, petrochemical and other chemical manufacturing processes. The U.S. Environmental Protection Agency (USEPA) has considered nitrophenols as hazardous waste and one of the 129 priority toxic pollutants. Moreover, they cannot be effectively treated by traditional technologies, such as adsorption, solvent extraction and biological degradation [10].

Nitrophenols include two chemicals, 2-nitrophenol and 4-nitrophenol, which are very similar to each other. They are manufactured chemicals that do not occur naturally in the environment. The manufacture of one almost always produces a little of the other. The number and the position of the $-NO_2$ group affects the activities of nitrophenols [10].

2-Nitrophenol is a light yellow solid with a peculiar sweet smell while 4-Nitrophenol is a colourless to light yellow solid with very little odour.

2-Nitrophenol is used mainly to make dyes, paint colouring and rubber chemicals. 4-Nitrophenol is used mainly to make drugs and fungicides, dyes, and to darken leather.

## 1.3 Nitrobenzene

Nitrobenzene ($C_6H_5NO_2$) is the simplest aromatic nitro compound. Physically it is water-insoluble pale yellow oil with the odour of bitter almonds. It is used as a solvent, especially for electrophilic reagents and occasionally it´s used as a flavouring or perfume additive. Nitroaromatic compounds are considered hazardous substances from wastewaters due to their high stability [11], being very hard to eliminate. Nitrobenzene in large quantities is highly toxic and is mainly produced as a precursor to aniline.

It is listed as a priority pollutant by the USEPA and declared as a hazardous waste when its concentration is above 2 mg/L [12].

Most nitrobenzene produced is reduced to aniline and smaller amounts can be converted to azobenzene, hydrazobenzene and phenylhydroxylamine.

## 1.4 Treatment of Industrial Wastewater

Before using any treatment on waste water, a preliminary analysis should be done, for example a bioassay, to evaluate the toxicity of the wastewater and the appropriate method to be applied.

Methods that treat wastewaters can be classified into biological methods, physical methods and chemical methods. Physical methods aren´t appropriate to remove organic compounds since they simply transfer the pollutants into other phases, thus new waste disposal problems are generated. Biological methods aren´t sufficient since reaction rates of biological processes are usually slow, normally requiring huge reactor volumes or spaces. In addition, biological methods are not suitable in the treatment of toxic compounds. Non biological technologies, such as phase separation techniques, adsorption processes and stripping techniques, followed by methods that destroy the contaminants (chemical oxidation/reduction) are mainly advantageous. The reaction rates of the chemical methods are relatively high and total mineralization is possible if the reaction conditions and reactor are adequately designed [13]. Taking in consideration wastewaters containing aniline, phenolic and nitroaromatic related compounds, as those that will be studied in this work, biological processes are inefficient, due to their high toxic character. Accordingly, suitable options to treat this type of wastewaters involve the use of advanced oxidation processes.

### 1.4.1 Advanced Oxidation Processes (AOP)

Over the last decade advanced oxidation processes have proved to be very effective on the degradation of most organic compounds converting them completely into carbon dioxide and water, although it´s not so efficient on wastes containing massive pollutants. One of the advantages of using AOP is that the chemicals used decompose the pollutants to harmless or beneficial by products. In literature, it`s mentioned that AOP can also be used as a preliminary treatment of an inexpensive biological process [14].

Contaminants can be oxidized through four typical different reagents: ozone, hydrogen peroxide, oxygen and air or their combination.

AOP consist in the generation of hydroxyl radicals ($HO^{\bullet}$), which are highly reactive to initiate oxidation reactions with organic compounds. So being, the hydroxyl radical is the main oxidizing agent of organics causing their mineralization and conversion to $CO_2$, water and inorganic matter [15].

There are several AOP such as ozonation, photocatalysis, electrochemical oxidation that use electron beams, UV light or ultrasound pulses to obtain high oxidation

rates through the generation of free $HO^{\bullet}$ radicals [16], along with hydrogen peroxide based processes (Fenton, photo-Fenton and Fenton-like processes) [14].
Among the AOP, Fenton's reagent combines ferrous salts (Fe(II)) with hydrogen peroxide (HP) whereas Fenton-like processes involve a series of thermal reactions catalyzed by transition metal salts (frequently ferric salts, represented hereafter as Fe(III)) that lead to HP decomposition. AOP usually operate at ambient temperature and pressure. Studies found in literature, such as one done by Goi and Trapido [17], where several AOP were compared, refers that the Fenton reagent was the most effective and the least expensive method for nitrophenol degradation and at the same time the resultant solutions were not toxic. Walling and his co-authors [18-20] also investigated the mechanism and kinetics of organic substances reacting with the Fenton reagent, which will be described in detail in section - 1.4.6.

### 1.4.2 Photocatalysis

Photocatalysis processes normally use a semiconductor metal oxide as catalyst ($TiO_2$ in the anastase form) and oxygen as oxidizing agent. The catalyst $TiO_2$ is mostly used because of its high stability, good performance and low cost.
The process consists in several steps, described in the following.
Initially there is absorption of the radiation with the formation of electron-hole pairs:

$$TiO_2 \rightarrow e^- + h^+ \qquad (1)$$

Formed electrons reduce some metals and dissolved oxygen forming a superoxide radical ion $O_2^{\bullet -}$ whereas remaining holes are capable of oxidizing adsorbed $H_2O$ or $HO^-$ to reactive $HO^{\bullet}$ radicals:

$$TiO_2(h^+) + H_2O_{ad} \rightarrow TiO_2 + HO^{\bullet}_{ad} + H^+ \qquad (2)$$
$$TiO_2(h^+) + HO^-_{ad} \rightarrow TiO_2 + HO^{\bullet}_{ad} \qquad (3)$$

These reactions are of great importance in oxidative degradation processes due to the high concentration of water and $HO^-$ adsorbed on the particle surface. Some adsorbed substrate is directly oxidized by electron transfer:

$$TiO_2(h^+) + RXa \rightarrow TiO_2 + RX_{ad}^{\bullet +} \qquad (4)$$

In the mean time, several pairs of electron-hole recombine reducing the quantum yield.

Intensive researches have been done, but no indications have been found for their application on industrial scale.

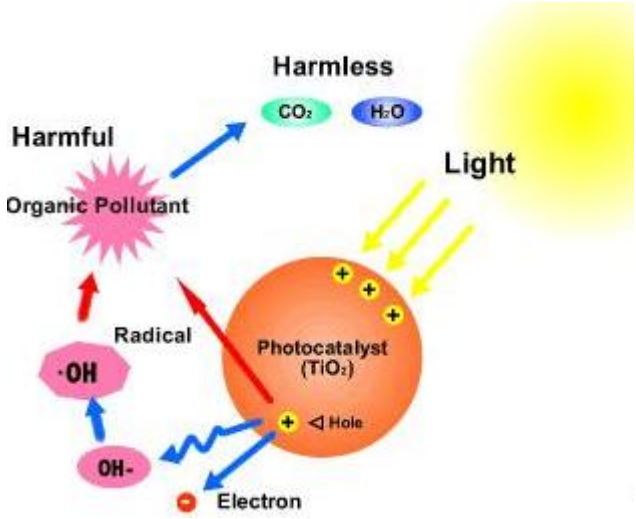


**Figure 2 -** Photocatalytic process

Figure 2 shows schematically a photocatalytic process.

### 1.4.3 Ozonation

Ozonation is a suitable AOP applied to the treatment of aniline, phenolic and nitroaromatic related compounds. Ozone is considered a powerful oxidizing agent under acidic conditions and very efficient to mineralize refractory organic compounds. In the mean time it reacts slowly with aromatic organic compounds and doesn´t reach complete oxidation unless in the presence of a catalyst or in combination with UV or $H_2O_2$. Ozonation can be applied to organic compounds as referred above, but it´s very limited on waste water treatment due to high energy demands. It can be performed under heterogeneous or homogenous catalytic system conditions, having the heterogeneous the advantage of an easy catalyst retrieval from the reaction media. Phenols are claimed to be quite reactive with molecular ozone not being necessary any catalyst to oxidize these compounds. Literature even refers that oxidation of phenols was carried out in the absence and in the presence of a catalyst being no susceptible difference observed after 90 min and both having the same TOC removal. The same article outlines/specifies that

heterogeneous catalytic ozonation permits a good extent of phenol degradation and other recalcitrant compounds [14].

### 1.4.4 Electrochemical Methods

In the last years, there has been a great interest in the development of practical electrochemical methods, such as anodic oxidation and indirect electro oxidation, for the destruction of toxic and biorefractory organic pollutants for wastewater treatment. It`s an attractive technology because of its simplicity in operation, robustness in system configuration and reliable performance [21].

In anodic oxidation, adsorbed $HO^{\bullet}$ radicals are produced from water oxidation at the anode

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \qquad (5)$$

This radical is the main oxidizing agent of organics causing its mineralization, then conversion to $CO_2$, water and inorganic ions. Alternative methods based on indirect electrooxidation involve the electrogeneration of other strong oxidants, such as $ClO^-$ obtained from anodic oxidation of $Cl^-$ in alkaline medium or $H_2O_2$ formed from the two-electron reduction of $O_2$ at a graphite cathode. This last reaction in acid medium can be written as follows [15]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (6)$$

It has also been demonstrated that gas diffusion cathodes may also be used to reduce oxygen to hydrogen peroxide in acid solutions at rates which are appropriate to the needs of effluent treatment. This behaviour has also been confirmed by Harrington and Pletcher (1999) using similar cathodes.

### 1.4.5 Wet Air Oxidation

This technique is efficient on wastes with massive pollutant contents. It consists of using oxygen or air to achieve pollutant oxidation at high temperatures (130-300ºC) and pressures (0.5 – 20 Mpa). Several studies are reported in the literature about the application of Wet Air Oxidation processes to degrade aniline, phenols and nitroaromatic related compounds.

In order to reduce the operating conditions normally employed in WAO, it is considered the use of a suitable catalyst and the process is thus named Catalytic Wet Air Oxidation (CWAO) [14]. CWAO can be used to degrade organic compounds

such as phenol, carboxylic acids and nitrogen-containing compounds, and has shown to be an effective technique for eliminating organic compounds at relative mild pressures and temperatures, although these can be above 140ºC and 2 MPa [22].

An inconvenience of this method is that ammonia is usually formed during oxidation of nitrogen containing organic pollutants, which happens to be a pollutant. Another inconvenient is the cost of the operating conditions, which is quite expensive.

During the process several reactions take place and depending on the reaction conditions it will either achieve complete mineralization of organic pollutants into $CO_2$, $N_2$ and $H_2O$, or just an increase of the effluent biodegradability by orientating the conversion of hydrophobic or/and toxic organic matter to the formation of biodegradable by-products such as carboxylic acids [23].

Another alternative process is Catalytic Wet Peroxide Oxidation (CWPO). In CWPO the redox properties of dissolved transition metals (e.g. Fe, Cu, Ce) are used to generate hydroxyl radicals under mild reaction conditions in the presence of hydrogen peroxide. When iron (II) salts are considered as catalysts the process is also known as Fenton Process. It´s been used to treat wastewater streams with high organic (TOC) content, but it`s limited because of the restricted pH range and the need for the recovery of the homogenous catalyst. The use of heterogeneous catalysts overcomes these drawbacks [24]. The characteristics of CWPO, either using iron (II) salts as catalysts (Fenton process), or heterogeneous catalysts, will be discussed in the following two sections, since they are pertinent to the present work.

### 1.4.6 Fenton Process

The Fenton process was discovered by Fenton in the last century and since then it has been investigated for wastewater treatment. It is an efficient technology involving the use of iron catalysts and hydrogen peroxide, with certain advantages. Among them, it may be referred the following: iron is very abundant and non toxic, the oxidant is easy to handle and safe, the final decay products (water, oxygen and ferric hydroxide) are harmless, and the hydroxyl radicals are rapidly generated and able to oxidize a variety of organic chemicals [25].

The application of Fenton processes requires strict pH control between 2 and 4 for an efficient treatment of wastewaters. Sludge can also be formed, which is inconvenient, causing disposal problems. The Fenton process involves the equations (7) to (16).

First, hydrogen peroxide is decomposed [25]:

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + HO^{-} + Fe^{3+} \quad (7)$$

Hidroxyl radicals may react with ferrous ions to form ferric ions, or react with other organics:

$$Fe^{2+} + HO^{\bullet} \rightarrow + HO^{-} + Fe^{3+} \quad (8)$$

$$HO^{\bullet} + \text{organics} \rightarrow \text{products} \quad (9)$$

Then, the hydroxyl radicals formed can react with hydrogen peroxide producing other radicals (equation (10)) or may also combine with each other producing hydrogen peroxide as shown in equation (11).

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (10)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (11)$$

With the reactions that occur during the process, ferrous ions and radicals are produced as shown in the following equations [25]:

$$H_2O_2 + Fe^{3+} \rightarrow H^{+} + FeOOH^{2+} \quad (12)$$

$$FeOOH_2+ \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (13)$$

$$HO_2^{\bullet} + Fe^{2+} \rightarrow HO^{2-} + Fe^{3+} \quad (14)$$

$$HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^{+} \quad (15)$$

Fenton reactions can be accelerated using UV-VIS light irradiation at wavelength values higher than 300 nm, thus $Fe^{2+}$ is regenerated and Fenton reactions occur in the presence of $H_2O_2$ (Reaction 16)

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \quad (16)$$

The Fenton process is also known as traditional Fenton. Another Fenton process is electro-Fenton.

The electro-Fenton process uses a conventional anode and the oxidation power of electro generated $H_2O_2$ is enhanced by the addition of $Fe^{2+}$ to the solution, since $HO^{\bullet}$ is formed from the classical Fenton`s reaction between $Fe^{2+}$ and $H_2O_2$.

$$Fe^{2+} + H_2O_2 + H^{+} \rightarrow Fe^{3+} + HO^{\bullet} + H_2O \quad (17)$$

As $Fe^{2+}$ is regenerated by the reduction of $Fe^{3+}$ with $H_2O_2$ (reaction 18), with hydroperoxyl radical $HO_2^{\bullet}$ (reaction 19) and/or with organic radical intermediates $R^{\bullet}$ (reaction 20), the reaction is propagated.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (18)$$
$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2 \quad (19)$$
$$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^+ \quad (20)$$

The radical $HO_2^{\bullet}$ is also formed (a weaker oxidizing power than $HO^{\bullet}$), but organics are mainly destroyed by the action of $HO^{\bullet}$ radicals produced at the anode and in the medium.

Comparing the two processes, electro-Fenton can avoid the high cost of $H_2O_2$, since it allows maintaining an almost constant concentration of $H_2O_2$ and is able to regenerate $Fe^{2+}$ more efficiently. Electro-Fenton can quickly and economically oxidize organic compounds, degrading many persistent pollutants. Studies referred in the literature, such as Oturan et al, who investigated the degradation of 4-nitrophenol by electro-Fenton using carbon fibre as cathode in undivided cells, identified and quantified intermediates of hydroquinone, benzoquinone and 4-nitrocatechoel. Brillas et al [26] investigated the mineralisation of aniline by electro-Fenton using an $O_2$-diffusion PTFE cathode [27].

### 1.4.7 Heterogeneous Fenton-like Processes (Catalytic Wet Peroxide Oxidation)

Fenton-like processes benefit from using $H_2O_2$ as a liquid oxidant and a homogenous or heterogeneous catalyst, different from Fe(II) salts, to enhance the oxidation conditions [16].

Several studies are referred in the literature concerning Fenton-like processes. For instance, one of the works used nitrobenzene (NBE) as model pollutant and aimed to study it´s oxidation kinetics in excess of $H_2O_2$ and catalytic amounts of Fe (III), to evaluate the factors that determine NBE and $H_2O_2$ degradation rates and to identify some of the key reactions that are responsible for the essential kinetic features of the process. A simple kinetic model capable of describing the initial stages was derived to precede the catalytic phase. The effects of temperature and dissolved oxygen were also studied. Among the final results it was observed that the initial reaction rates rise with [Fe(III)] and [$H_2O_2$], but decrease with organic matter loading and, depending on the temperature range analysed, different activation energies and oxygen demands are obtained [11].

In CWPO processes, the redox properties of dissolved transition metals (e.g. Fe, Cu, Ce) are used to generate hydroxyl radicals under mild reaction conditions in the presence of hydrogen peroxide [24]. However, the use of heterogeneous catalysts in the process is more convenient, since these can be easily separated from the reaction medium at the end of the treatment.

### 1.4.8 Heterogeneous Catalysts

As referred before, the use of heterogeneous catalysts can be more convenient and efficacious than homogeneous catalysts. There are several kinds of heterogeneous catalysts referred in literature applied in CWPO [14]. The representative examples include copper containing microporous or mesoporous materials, such as Cu-Al pillared clays and Cu-ZSM-5 zeolite, Cu-Y zeolite, Cu/AC, metallophtalocyanine, cerium oxide and $CeO_2$ containing materials [28], platinum supported on alumina, among others. Literature reports other studies of various heterogeneous catalysts including noble metals. It´s even described several attempts for the immobilization of transition metals, especially iron species, over different supports to find active and hydrothermally stable materials in a wide pH range.

Zeolites are also frequently referred. For instance, iron-containing zeolites are said to have remarkable catalytic activity in the presence of $H_2O_2$ under acidic solutions for the removal of phenol and other refractory organic compounds. They are also found to be efficient bringing about notable diffusion of the reactants and/or the products from its surface during the reaction [29]. In alternative, pillared clays have been modified with iron species and are also used for the treatment of phenolic aqueous solutions. Iron-containing zeolitic materials can be synthesized through hydrothermal crystallization of wetness impregnated amorphous $SiO_2$-$Fe_2O_3$ xerogels with aqueous 20 wt% TPAOH solutions [30].

Another study relates a process that was carried out to degrade phenol using Cu-Y zeolite catalyst, the process was carried out within 323-353 K and at atmospheric total pressure, varying hydrogen peroxide concentration (0.008-0.254 mol/dm$^3$) and catalyst loading (0.05-0.4 g). The initial concentration of phenol was 0.01 mol/dm$^3$ and the final results showed that the catalyst completely eliminated phenol and could be reused without significant loss of activity [31]. Another study found in the literature on the removal of phenol by CWPO with copper binding activated carbon (CuAc) catalysts, refers that these have a high oxidative ability of removing phenol or TOC conversion, which is directly related to the iron or copper content [24]. The main disadvantage of using heterogeneous catalysts in CWPO is the occurrence of iron leaching [32] into the solution, causing an additional

pollution source and requiring the elimination of the catalyst from the treated waters before discharge. In order to eliminate this drawback, the use of heterogeneous catalysts without any supported metal would be strongly desired. Recent results show that carbon materials may accomplish such criteria, such as the use of activated carbons in the oxidation of aromatic compounds [33-35], among others. In the following section this will be described in more detail.

In this work, several different carbon materials will be prepared and tested in the CWPO of aniline related compounds, more specifically in the CWPO of the azo dye Chromotrope 2R. The results obtained will be compared with those obtained using iron as active metal to conclude about future directions in this area of research.

## 1.5 Carbon Materials as Catalysts in Catalytic Wet Peroxide Oxidation (CWPO)

Carbon materials are found in a variety of forms such as graphite, diamond, fullerenes (figure 3), carbon fibres and nanotubes. Carbon assumes many structural forms due to the fact that a carbon atom can form several distinct types of valence bonds, known as hybridization bonds by physicists.

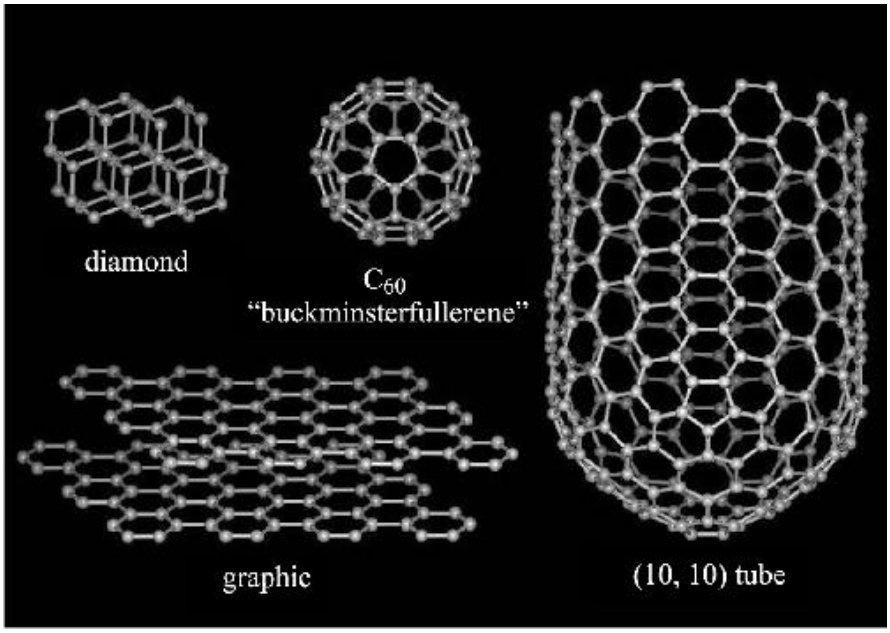


**Figure 3** – Forms of carbon slide created by Prof. Richard Smalley of Rice University.

### 1.5.1 Activated Carbons

Activated carbon is a powdered granular or pelleted form of carbon, also known as charcoal, and is produced from carbonaceous source materials like nutshells, peat, wood, lignite, coal and petroleum pitch. Due to the manufacturing process that it´s subjected, it becomes extremely porous (figure 4), pursuing a large surface area available for adsorption or chemical reactions.

The surface porosity of activated carbon results from controlled oxidation during the activation stage of manufacture, charcoal is subjected to steam and oxygen and small pores are created being designated as active carbon. It`s called "activated" because these pores are active at trapping many chemicals (figure 4), especially those that aren´t attracted to water like organic compounds. When these stick to the surface, this is known as adsorption.

Carbon can be processed by physical reactivation - carbonization or activation/oxidation:

- Carbonization (material with carbon content is pyrolized at temperatures in the range 600-900ºC, in absence of air and inert atmosphere with argon or nitrogen)
- Activation/Oxidation (raw materials or carbonized material is exposed to oxidizing atmospheres, carbon dioxide oxygen or steam, at temperature ranges of 600-1200ºC)

Otherwise, it´s produced by chemical activation, where the raw material is impregnated with certain chemicals (acid-phosphoric acid, strong base-potassium hydroxide, or a salt-sodium hydroxide) prior to carbonization. Then, the material is carbonized at lower temperatures (450-900ºC).

Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 $m^2$, as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the absorbing properties of the material.

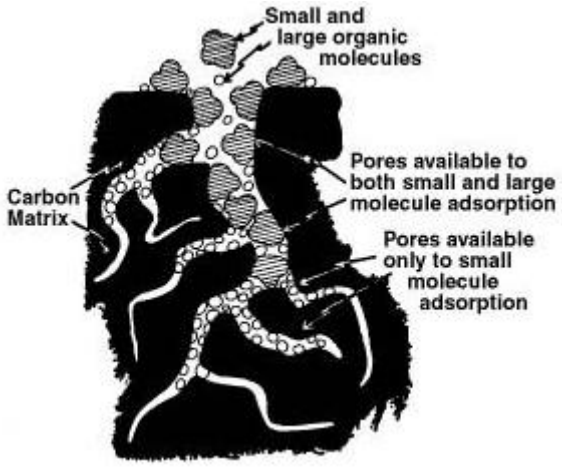


**Figure 4** - Typical Porous structure of activated carbons

- Coated-carbon:

Activated carbon can be coated with chemicals to provide better capacities to the material, this method is known as an "impregnation" method and the resultant carbon as "impregnated carbon" [36], such as a surface coating of particulate hydrophobic material like polytetrafluoroethylene, which makes the active carbon waterproof while still permitting it to absorb undesirable components.

- Applications of activated carbon:

Activated carbon is basically used for removing unwanted colour and odour in liquid substances and used extensively in food processing and chemical industries, particularly, in edible oil, sugar, glucose, starch making and pharmaceuticals. Phase carbons have a wide range of applications in gasoline vapour emissions canisters in automobiles, in air conditioning to remove industrial odour and irritants, cooking odour from building air, in nuclear reactors in emergency exhaust systems, in cigarette filter to absorb harmful components of tobacco and as a catalyst in phosgene manufacturing. They are also applied in many environmental applications, as universal adsorbents in liquid and gas phases, in heterogeneous catalytic processes as direct catalysts or as catalytic support [37], in wastewater treatment due its high adsorption capacity determined by the porous structure and the chemical nature of the surface [38-41].

They are commonly used as an adsorbent to treat phenols and are frequently employed as water or wastewater post-treatment [10]. They have an extremely high adsorption capacity and an unusual chemical stability [42], but are limited by their difficult regeneration. One study is on the interactions of phenol, aniline and

p-nitrophenol, adsorbed from aqueous solutions, with the surface of two activated carbons (with and without oxygen surface groups). When oxygen surface groups were introduced on the carbon surface, there was a sudden change in the adsorption/desorption behaviour and phenol chemisorption was inhibited and aniline and nitrophenol started to decompose [42].

In literature it´s referred that the combination of $H_2O_2$ and activated carbon into a single process could offer an attractive process treatment [43-45]. The activated carbon has a double performance, therefore being an adsorbent and a catalyst at the same time. A disadvantage of this process is the risk of saturation and/or deactivation of the catalyst, being necessary to regenerate or replace it, causing more costs.

An important factor of the activated carbon is the carbon particle size and according to a study referred in literature a particle size between 0.1 and 0.3 mm was selected, in order to reduce internal mass transfer resistances. Another factor referred by the same font is the agitation level used that has to be sufficient enough to maintain the system perfectly mixed without external mass transfer resistances [46].

### 1.5.2 Activated Carbon Fibre

Activated carbon fibre (ACF) has extremely high adsorption capacity and chemical stability. For this reason it has been intensively used to remove organic pollutants, including various phenols. Studies related in literature mention that ACF is used, because of its remarkable properties. For instance as the support for the metallophtalocyanines [42].

### 1.5.3 Carbon Xerogels

Carbon xerogels are mesostructured carbon materials that can be prepared from carbonization of organic xerogels which can be obtained by resorcinol-formaldehyde aqueous polymerization. These carbon xerogels are highly porous materials possessing several exceptional and even unique physical properties that are of great interest for many applications, including, electric double-layer capacitors, thermal insulators, chromatographic packing, adsorbents and catalyst supports. However, more recently it has been investigated as an application in adsorption, catalysis or electrochemistry which requires taking advantage of the surface area. We can find several references of studies using xerogels in literature [47]. The same font also refers another carbon, Vulcan XC-72R carbon which is another form of carbon.

A Spanish public research organization developed a new method for producing carbon xerogels by means of microwave technology. It refers that precise control of the temperature and microwave power permits to synthesize organic gel in a single step saving more than 95% of the time vs. conventional heating [48].

### 1.5.4 Carbon Nanotubes

A Carbon nanotube is a cylindrical carbon molecule, such as the one represented on figure 3. Carbon nanotubes are potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, as well as being efficient thermal conductors. Nanotubes are members of the fullerene structural family.

We can find several references in the literature related with studies done using carbon nanotubes. For example, an investigation was done using platinum nanoparticles on carbon nanotubes as supports for cathode catalyst in direct methanol fuel cells [49].

### 1.5.5 Glycerol Based Carbon Materials

#### 1.5.5.1 Glycerol

Today, the name glycerol refers to the pure chemical substance that is commercially known as glycerine. Liquid glycerol has a high boiling temperature of 290° C and is produced as a by-product in the manufacture of biodiesel and soap, from the hydrolysis of fats and oils and is also produced from a hydrocarbon called propylene (synthetic glycerol). Due to its outstanding properties such as an emollient, demulcent and humectants, glycerol is extensively used throughout the industry. Some of its applications include the use as a solvent in the preparation of tinctures in the pharmaceutical industry and in the preparation of elixirs like Theophylline which is used to treat respiratory conditions (asthma and bronchitis), as humectant to keep ointments and creams moisture (without drying), and as a levigating agent to reduce the particle size of a drug powder as well as a plasticizer coating tablets.

It´s also used in the manufacture of sealing and antifreeze compounds [50] ( the minimum freezing point temperature is at about -36 °F / -37.8 °C).

#### 1.5.5.2 Carbon Materials

Glycerol based carbon materials are prepared from raw material glycerol which is a relatively cheap material.

There is some research on these carbon materials, but it´s still a relatively recent area of investigation. One work referred in literature reports the synthesis of a carbon catalyst with a high density of sulphonic acid groups (-$SO_3H$) that is based on raw material glycerol. The glycerol-based carbon catalyst was obtained by in situ partial carbonization and sulfonation of glycerol with sulphuric acid. The resultant catalyst showed to have active sites, which are very important in the performance of catalysed reactions, and also proved to be insoluble in water and organic solvents [51]. It is also referred that the catalyst obtained is a partially crystalline material that consists of polycyclic aromatic carbons with –$SO_3H$ groups, similar to what has been proposed for sugar (glucose) catalysts. Glycerol based carbon materials will be prepared in this work.

### 1.5.6 Applications in CWPO

Activated Carbons have outstanding properties, high surface area, well-developed porous structure and variable surface composition which determine important differences in their reactivity, being used in wastewater treatments such as CWPO [37].

The research in this area is still very recent, but shows to be very promising. Amongst the little information found in literature we can find a study on the role of the activated carbon surface in CWPO at mild conditions (atmospheric pressure and 323 K), using phenol and three different activated carbons. The purpose was to learn more about the potential application of activated carbon catalysts in CWPO by investigating the decomposition of $H_2O_2$, the evolution of phenol, as well as total organic carbon (TOC) and oxidation intermediates. Some carbon samples were obtained upon heat treatment in $N_2$ atmosphere and treatment with HCl solution and were dried overnight. Various types of analysis were performed: elemental, semi quantitative chemical, thermal gravimetric and differential temperature analysis. Values of specific surface area were obtained from nitrogen adsorption and values of micropore volume and external surface area were calculated from the adsorption data. CWPO runs were done using theoretical stoichiometric amounts to completely oxidize phenol to $CO_2$ and $H_2O$ [37].

Considering now the morphology, the same study refers that, in general, the average structure of activated carbons consists of aromatic sheets and strips, often bent and resembling a mixture of wood shavings and crumpled paper, with variable

gaps of molecular dimensions between them, the micropores [37]. It also mentions that the random ordering of imperfect aromatic sheets results in incompletely saturated valences and unpaired electrons that will influence the reactivity and adsorption behaviour of these materials. An important factor of the carbons is the quantity of active sites. The same study refers that the carbon showing the most disorganized structure can be expected to have the most active sites which are associated to higher densities of unpaired electrons that could favour or catalyse chemical reactions, like $H_2O_2$ decomposition or certain AOP of important interest. The carbon that presents the most developed porous structure is considered the best candidate to be used as catalytic support for liquid-phase applications [37]. Another important factor is the amount and nature of oxygen surface groups which is the most significant factor that affects the surface characteristics and final behaviour of activated carbon materials in chemical reactions. The assessment of surface oxygen groups was performed to literature criteria [39, 40, 52].

In another study, also treating phenol, different carbon-supported materials were prepared and tested in CWPO. Three activated carbons and two iron precursors, iron nitrate and iron pentacarbonyl, were used. Analysing the results obtained, the catalysts that presented a more uniform distribution of Fe showed a higher oxidation activity than the ones with an internal (egg-yolk type) or external (egg-shell type) distribution. These last showed the poorest oxidation activity since it promoted a faster decomposition of $H_2O_2$ mainly to non-reactive $O_2$. Complete conversion of phenol and almost 80% mineralization were obtained in less than 2h with the best catalyst. The residual by-products were considered without significance in terms of toxicity. Fe leaching was observed in all cases, but was mainly due to the presence of oxalic acid as oxidation by-product [53].

## 1.6 Objectives

The objectives of this work are the preparation of different forms of carbon materials, including activated carbons, and the assessment of their catalytic efficiency in the CWPO of the azo dye Chromotrope 2R. The comparison of the results obtained with these materials and Fe base catalysts will permit to conclude about future directions of research in this area.

## 2. Experimental Part

This chapter describes the experimental techniques and procedures used for the preparation, modification and characterization of the catalysts tested in this work, namely activated carbon (AC - Norit Rox 0.8), carbon xerogel (CX) and glycerol based carbon material (GBCM) as well as these same materials treated with sulphuric acid to define whether or not the sulphonic acid groups introduce notable characteristics to the material for the removal of the pollutant. As referred in the literature, the sulphuric acid treatment applied to the carbon materials confers them special properties for adsorption of certain compounds and to improve their role as catalysts [36]. The catalysts prepared are tested for the removal of the azo dye Chromotrope 2R (C2R). We also tried to test their efficiency for the degradation of aniline, but it wasn´t possible with the available experimental conditions to set-up a proper analysis technique.

### 2.1 Preparation of the Catalysts

The activated carbon used (Norit Rox 0.8) was a commercial material which had already been previously treated with sulphuric acid. The carbon xerogels and glycerol based carbon materials were synthesized in the present work following existing procedures [54, 55].

#### 2.1.1 Carbon Xerogel (CX)

The carbon xerogel was prepared following an existing procedure [54] which consists in the policondensation of resorcinol with formaldehyde (1:2). An amount of 9.91 g of resorcinol (Aldrich, 99%) was dissolved in 18.8 ml of deionised water in a glass container. Then, 13.5 mL of formaldehyde was also added (Sigma, 37 wt. % in water, stabilized with 15 wt. % methanol). According to the procedure used, a pH of 6.1 was pertinent to develop the mesoporous character of the carbon xerogel. This parameter was set to the required pH (6.1) adding sodium hydroxide solutions (1 M and 0.02 M). From here on the material developed due to polymerization reactions. The obtained gel was heated in an oven at 85 ºC during 3 days, gaining a dark red colour and a solid texture. Afterwards the material was ground into small particles (0.106-0.25 mm) being then dried thoroughly during several days increasing gradually the temperature from 60ºC to 150ºC (20ºC each day then 10ºC last day). The materials prepared were further calcined in a nitrogen flow (100 mL/min $N_2$) at 120ºC, 400ºC and 600ºC during 60 minutes at each temperature and then at 800ºC for 240 minutes, defining a heating ramp of 2ºC/min.

### 2.1.2 Carbon Xerogel treated with Sulphuric Acid (CXSA)

The synthesized carbon xerogel was also treated with sulphuric acid to introduce sulphonic acid functional groups by placing the material in contact with concentrated sulphuric acid (40 mL) at 353 K during 3 hours following an existing procedure [56]. After functionalization, it was carefully washed with distilled water until the rinsing waters became neutral and then dried overnight in an oven at 120ºC.

### 2.1.3 Glycerol Based Carbon Material (GBCM)

The glycerol based carbon material was also produced following an existing procedure [55]: a mixture of glycerol (10 g) and concentrated sulphuric acid was gently heated to 180ºC then left at that temperature for 20 minutes to allow the in situ partial carbonization and sulfonation. During the heating the liquid gradually got darker and at 145ºC the mixture started to foam intensely and quickly thickened and gained density resulting in a black porous solid which was then cooled, washed and filtered in warm water until the drained water presented a neutral pH value. The in situ partial carbonization consists in a polymerization reaction where the bonds of the initial glycerol molecules are broken and reconnected until the final product (GBCM) is produced.

The molecule Glycerol has three hydroxyl groups as can be observed on figure 5. The hydroxyl groups form a cyclic structure with three internal hydrogen bond lengths and provide the starting geometry for the mechanism of the reaction of polymerization that occurs (figure 5) [57].

So being it´s a highly flexible molecule forming both intra and intermolecular hydrogen bonds which permits the polymerization of the molecule to form the new product (GBCM).

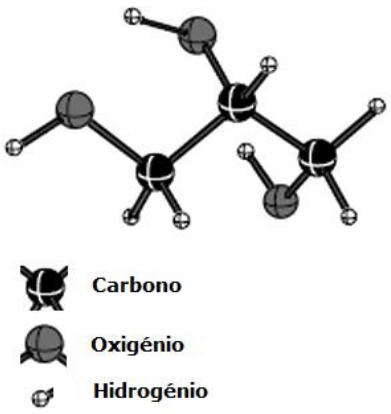


**Figure 5 -** Glycerol´s structure in its lowest energy conformer in the liquid phase determined by DFT methods.

The resultant partially crystalline product was placed in a glass flask (figure 6) and dried in an oven overnight and weighed the following day. A mass of 5 g was obtained, corresponding to 50% of the mass of glycerol used in the reaction (10 g), which was quite good considering the conversion referred in the literature [55]. The presence of sulphuric acid during the polymerization of glycerol acts as a catalyst and permits the synthesis of a material functionalized with sulphonic acid groups.
Afterwards the material was ground into small particles (0.106-0.25 mm measured with appropriate sieves) as shown on figure 7.
The materials prepared were further calcined using the procedure described in section 2.1.1.


**Figure 6** – Glycerol carbon based material before drying.


**Figure 7** – Grinding of the GBCM.

### 2.1.4 Iron Supported on Activated Carbon and on Glycerol Based Carbon Material

The carbon materials prepared in this work were compared with iron supported catalysts. Hence, two iron supported activated carbon and glycerol based carbon material catalysts were prepared and tested following a procedure referred in the literature [58], involving incipient impregnation (4 wt.% Fe) at room temperature over AC and GBCM, using iron nitrate as precursor. The samples were carefully

contacted at room temperature for 7 hours, dried at 60ºC overnight and lastly heat-treated at 200ºC during 4 hours. Fe/AC and Fe/GBCM were thus obtained.

## 2.2 Characterization of the Catalysts

Different techniques were used to characterize the catalysts, namely point of zero charge, acid-base titrations, TPD (Temperature Programmed Desorption) and also $N_2$ adsorption isotherms.

### 2.2.1 Determination of the Point of Zero Charge

A surface charge is at its point of zero charge when the surface charge density is zero or, in other words, the point of zero charge ($pH_{pzc}$) means the pH at which the total number of positive and negative charges on its surface becomes zero. It´s a value of the negative logarithm of the activity in the bulk of the charge-determining ions [59].

PZC was experimentally determined preparing 5 solutions, each one with 50 mL of NaCl (0.01 M), used as electrolyte, and with different values of pH between 1.5 and 10, using HCl and NaOH (0.02 M and 1M) to adjust them to more acid or more basic. The carbon materials (0.15 g) were added and the solutions were stirred during 24 h (figure 9). Afterwards, the equilibrium pH of the solution was measured and the initial pH values (Y) plotted versus the final pH values (X). The value of PZC was obtained where the regression line intercepted the Y = X line, as shown in figure 8 for PZC of AC.

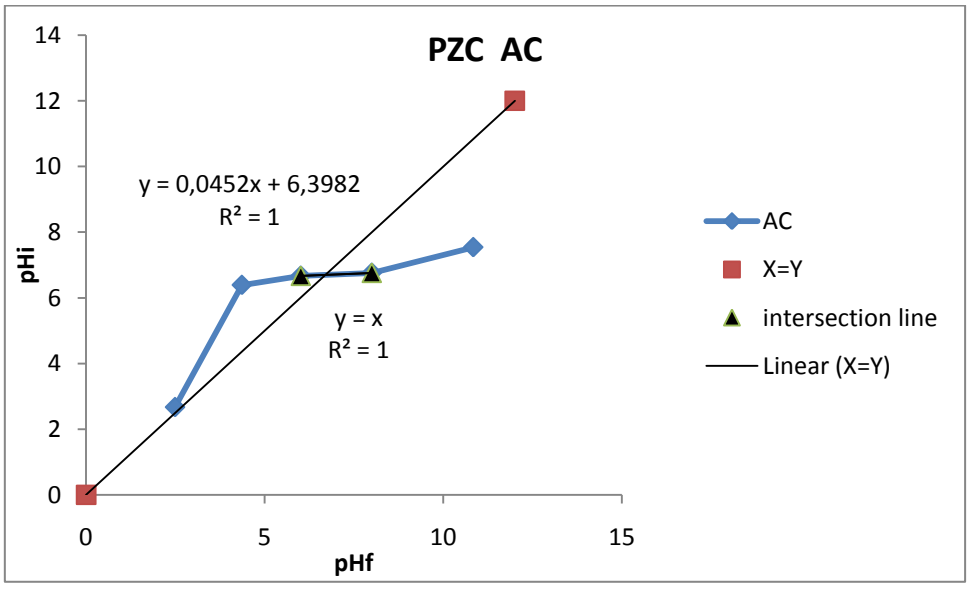


**Figure 8** – Graphic representation for the determination of PZC of AC

The PZC permits to evaluate the character of the material, acid or basic, a low PZC signifying that the material is acidic and a high PZC that the material´s more basic.

**Figure 9 –** Five solutions prepared with different pH values being stirred.

### 2.2.2 Acid-base Titrations

Acid-base titrations are based on the neutralization reaction. They are sometimes called alkalimetric titrations and the general name of the method is alkalimetry, although these are not used as often as just "acid-base titration".

Acid-base titrations can be used to determine most acids and bases, strong and weak, monoprotic and polyprotic. For example, we can use acid-base titration to determine concentration of hydrochloric acid, sulphuric acid, acetic acid, as well as bases - like sodium hydroxide, ammonia and so on. During this work it was used to determine the acidity or basicity of the synthesized materials to help understand certain properties and whether or not these influenced the results obtained. Most commonly used reagents are hydrochloric acid and sodium hydroxide.

This method determined surface functional groups by standard neutralization-titration with HCl and NaOH following this procedure:

- Acid titrations: 25 mL HCl (0.02 M) and 0.20 g carbon material were placed into a glass flask and stirred during 48 h. Afterwards the solution was filtered and 20 mL was titrated with NaOH (0.02 M) using phenolphthalein as indicator.
- Basic Titrations: 25 mL NaOH (0.02 M) and 0.20 g carbon material were placed into a glass flask and stirred during 48 h. Afterwards 20 mL of the solution was titrated with HCl (0.02 M) using phenolphthalein as indicator.

The concentration of the acid and basic groups was calculated using equations (21), (22) and (23).

$$C_{H^+} * V_{HCl} = C_{OH^-} * 20E^{-3} \qquad (21)$$

$$[Active\ acid\ centres] = \frac{(C_{NaOH} - C_{OH^-}) * 25E^{-3}}{m_{cat}} \qquad (22)$$

$$[Active\ basic\ centres] = \frac{(C_{HCl} - C_{H^+}) * 25E^{-3}}{m_{cat}} \qquad (23)$$

### 2.2.3 Temperature Programmed Desorption (TPD)

This analysis technique consists in heating the material being analysed so that molecules are desorbed due to energetic bonds that are broken. The temperature at this occurs is designated as the desorption temperature. Thus TPD shows information on the superficial groups of materials and their binding energy.

This analysis was performed by an AMI-200 machine (Altamira Instruments) in the Laboratory of Catalysis and Materials - Porto University - to evaluate the nature of superficial groups existent on the different carbon materials prepared.

Usually, 0.10 g of material in analysis is placed in the reactor and heated at 5 K/min with a constant flow of helium gas at 25 $cm^3$/min and monitoring the masses 28, 44, 48 and 64 by mass spectrometry.

The functional groups are identified by the temperatures at which the $CO/CO_2$ and $SO/SO_2$ gases are released since every functional group decomposes/releases at a certain temperature.

### 2.2.4 $N_2$ Adsorption Isotherms at 77 K

To analyse texturally the materials used their $N_2$ adsorption isotherms were examined at 77 K. A Quantochrome NOVA 4200e instrument was used at the Laboratory of Catalysis and Materials in Porto University.

The procedure consists in introducing around 0.15 g of the material in a glass cell which is degasified at 473 K during 6 hours to remove chemical species from the surface followed by the adsorption analysis using $N_2$ at 77 K.

## 2.3 Adsorption/Reaction Runs

As referred before, carbon materials are used as adsorbents and as catalysts in peroxidation reactions so both contributions were evaluated in the different materials to conclude in which the best results were obtained.

### 2.3.1 Adsorption Experiments

The efficiency of the synthesized carbon materials as adsorbents in the removal of the azo dye Chromotrope 2R (initial concentration of 100 mg/L) was performed at a controlled temperature of 50ºC, during 2.5 hours, pH = 3 (acidic) and a concentration of adsorbent of 0.5 g/L. The experimental set-up is shown in figure 10.

Each adsorption run was performed using 250 mL of the azo dye solution heated to 50ºC. After reaching this temperature a pH of 3 was adjusted with a pH measurer adding a few drops of sulphuric acid 1 M and then the carbon material was added. Periodically, 5 mL samples were taken from the reactor, diluted 4 times and analysed by UV-VIS (spectrophotometer). Initially, an experimental run performed only with the azo dye was done concluding about the inexistence of degradation of pollutant due to heating.


**Figure 10** – Experimental set-up used for the adsorption and reaction runs.

### 2.3.2 Peroxidation Reactions

In order to test the activity of the prepared materials in peroxidation reactions, they were used as catalysts in the removal of the azo dye with hydrogen peroxide. These reactions were carried out with 100 mg/L C2R solution at 50ºC, pH adjusted to 3 with a couple of drops of sulphuric acid, 5 mL of hydrogen peroxide 6 % and

0.5 g/L of carbon material. Several samples (5 mL) were removed from the reactor during 2.5 hours to evaluate the evolution of the dye removal by analysis with UV-VIS (spectrophotometer). These were diluted 4 times into a volume of 20 ml before being analysed.

At the end of the reaction 0.25 g of manganese oxide was added and the pH adjusted to 10 to stop the reaction. The solution was stirred during 15 minutes, filtered and stored in amber glassware to later on analyse the COD (chemical oxygen demand).

## 2.4 Reaction Analysis Methods

As mentioned above the degradation of the azo dye Chromotrope 2R was followed using an UV-VIS spectrophotometer. This technique is explicitly described in the following text.

### 2.4.1 UV-VIS

UV-VIS was used to analyse the samples obtained from the adsorption and reaction runs. UV is a spectrometric method based on electromagnetic radiation, which consists of several forms being the most recognizable light and radiant heat. The analytical signal detected is known as absorbance and is represented in function of the concentration. The UV detector is often used to indicate and record the presence of eluted analytes in liquid chromatography. Spectrometric methods are a large group of analytical methods that are based on atomic and molecular spectroscopy (spectroscopy is a part of science that deals with the interactions of several types of radiation with matter). The units used for frequency and wavelength are the reciprocal second ($s^{-1}$) or Hertz (Hz) and nanometre ($nm=1*10^{-9}m$). In ultraviolet visible absorption the usual wavelength range is 180-780 nm, the wavenumber range $5*10^4$ to $1.3*10^4$ and the type of Quantum transition bonding electrons.

In each adsorption and reaction run, from the absorbance obtained and applying the equation the calibration curve that was previously constructed (figure 11) the concentration was calculated. The maximum absorbance value of C2R is 510 nm as can be seen on figure 12 and 13. This is the wavelength used to monitor the concentration of C2R.

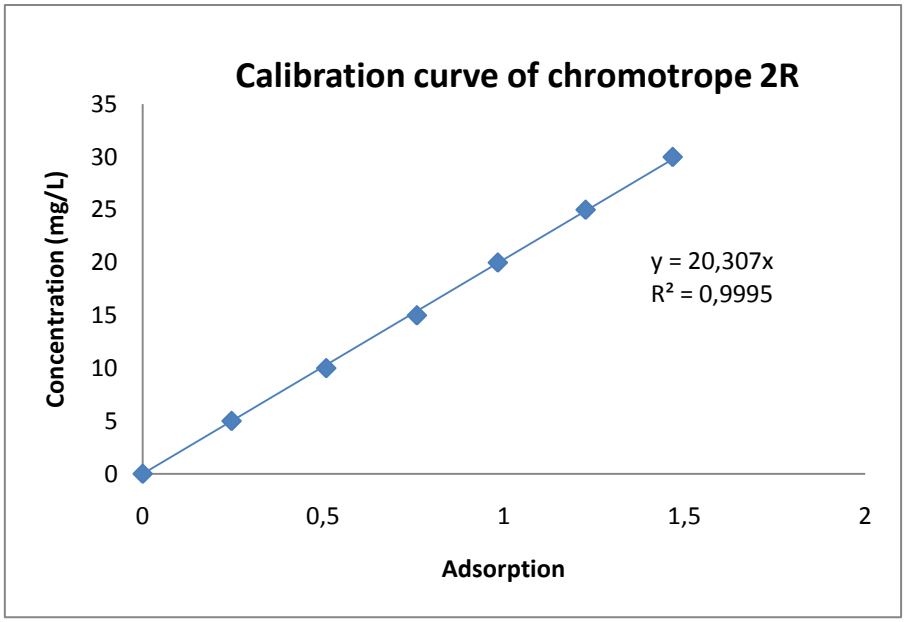


**Figure 11 –** Calibration curve obtained from the preparation of different concentrations of C2R.

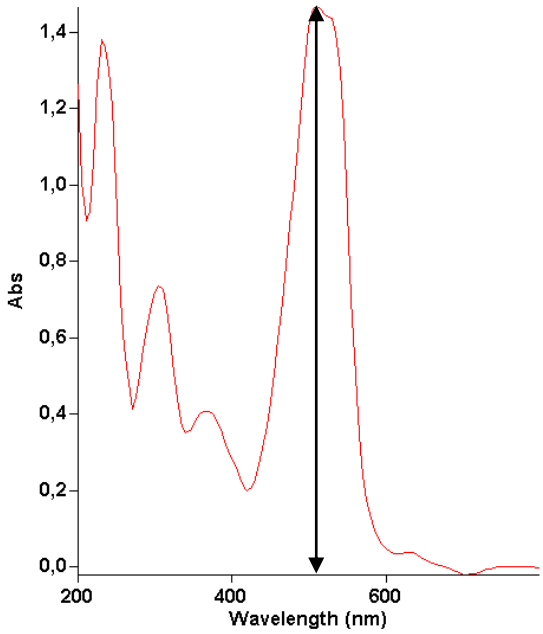


**Figure 12** – UV-Vis spectrum of C2R.

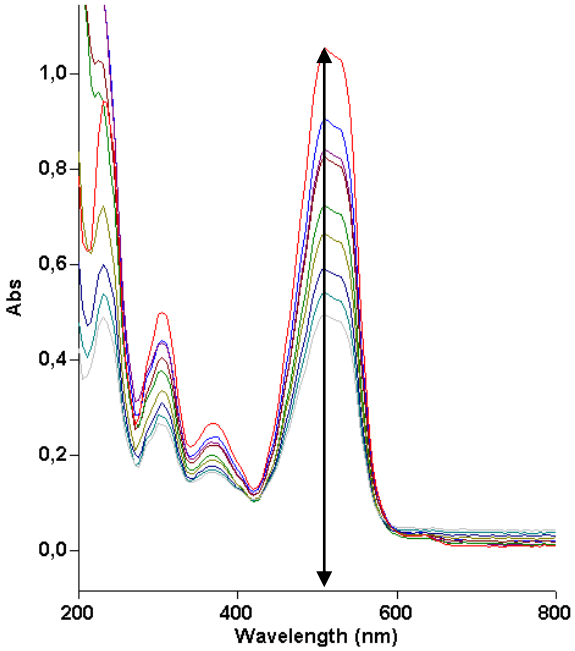


**Figure 13** – Spectrum obtained from the reaction using AC

### 2.4.2 COD (Chemical Oxygen Demand)

The organic matter found in water can be estimated from the chemical oxygen demand (COD), the oxygen absorbed permanganate value (PV) or from the total organic content (TOC). These tests are indirect measures of the total organic carbon by determining it`s oxidisability. In this work, the organic content was measured by COD using the closed reflux titrimetric method. Chemical oxygen demand is defined as the amount of a specific oxidant ($Cr_2O_7^{2-}$) that reacts with the sample under controlled conditions and is reduced to chromic ion. The oxidant consumed is expressed in terms of its oxygen equivalence.

Reagents were prepared beforehand (standard potassium dichromate digestion solution 0.01667 M, sulphuric acid reagent and standard ferrous ammonium sulphate titrant – FAS 0.10 M).

Culture tubes with caps are used and are previously washed with $H_2SO_4$ to prevent contamination. Inside the culture tubes is added the following: four glass marbles, a volume of sample (5, 4 and 3 mL were used in different occasions) (previously filtered), 3 mL of standard potassium dichromate digestion solution and 7 mL of sulphuric acid reagent. The tubes need to be gently swirled and mixed and the caps can´t be too tight on the tubes to allow some pressure to be released from within with the increase of the temperature to avoid any hazard. The tubes are placed in

the block heater and left for 2 and ½ hours at 150ºC. During this time the $K_2Cr_2O_7$ is reduced (consumed). The tubes are cooled at air temperature for an hour and then transferred to a support and left for ½ hour. Afterwards these are put in erlenmeyer's and a couple of drops of ferroin indicator are added. The solution that consists of the remaining unreduced $K_2Cr_2O_7$ is then titrated to determine the $K_2Cr_2O_7$ consumed and afterwards to calculate the oxidizable matter using the FAS. The end point is detected when the solution changes from blue-green to a brownish-orange colour. A blank sample should also be done. The concentration of organic matter (mg $O_2$/L) is calculated using equation (21).

$$COD = \frac{(A-B)*M*8000}{V_a} \quad (21)$$

*A* – Volume of FAS used to titrate the blank sample
*B* – Volume of FAS used to titrate the sample
*M* – Molarity of FAS
$V_a$- Sample volume

COD is limited when using hydrogen peroxide, because values of COD are usually greater than normal [60].

# 3. Results and Discussion

## 3.1 Characterization Results

### 3.1.1 PZC and Acid-base Titrations

The PZC and the acidity and basicity values of the materials prepared are given in table 2.

**Table 2 –** Results of PZC, acidity and basicity of the carbon materials used.

| Carbon materials | PZC | Acidity (mmol/g) | Basicity (mmol/g) |
|---|---|---|---|
| **AC** | 6.7 | 1 | 0.4 |
| **ACSA** | 2.7 | 1.3 | 0.3 |
| **CX** | * | 0.8 | 0 |
| **CXSA** | 1.5 | * | 0 |
| **GBCM** | 1.3 | (a) | 0 |

* Analysis not done due to insufficient material.

(a) GBCM was an unstable material under basic conditions and partially decomposed.

AC is a slight acidic material, because there are more acid groups than basic groups. ACSA is the most acidic material having a high concentration of acid groups (1.3) and few basic groups (0.3), this is also confirmed by the results of PZC (2.7).

ACSA is more acid than AC, due to the introduction of sulphuric containing groups upon treatment of AC with sulphuric acid which introduced acid groups on the surface of the resulting ACSA.

Taken into consideration the very low PZC values of GBCM and CXSA, and also the absence of detectable basic groups, these materials are extremely acid.

### 3.1.2 TPD

TPD gives information about the functional groups containing oxygen on the surface of the carbon materials, which while are heated decompose releasing CO, $CO_2$ and $SO_2$ as decomposition products and analytical signals are reported as observed on Figures 14, 15 and 16, due to energetic bonds which are broken at the desorption temperature as referred before.

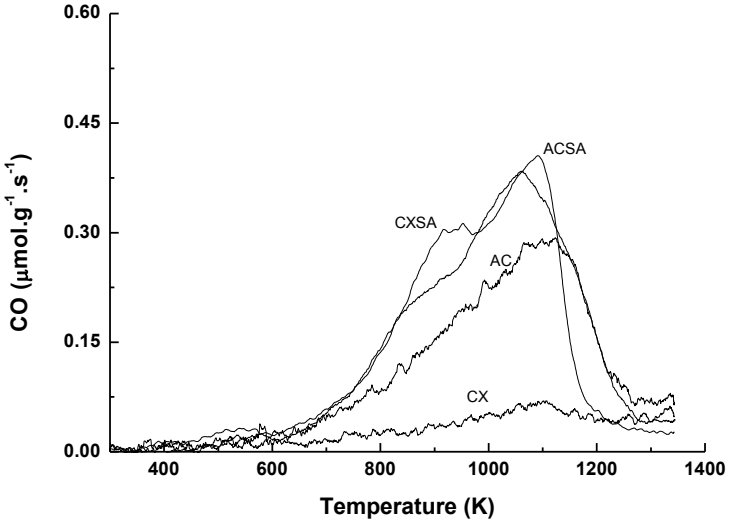


**Figure 14** – TPD spectres of 4 different carbon materials releasing CO.

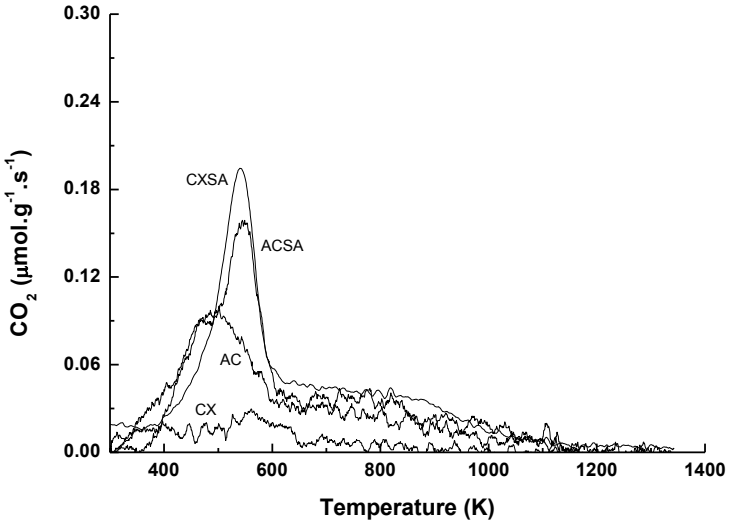


**Figure 15** – TPD spectres of different carbon materials releasing $CO_2$

Analysing figures 14 and 15 it is observed that the materials treated with sulphuric acid (ACSA and CXSA) are those releasing the most CO and $CO_2$ followed by AC then CX. The materials treated with sulphuric acid are significantly more acid materials when compared to AC and CX due to the sulphuric groups introduced to the surface when it was functionalized with sulphuric acid. Regarding $SO_2$ spectra (figure 16), ACSA releases the most $SO_2$ groups, around 7 times more than AC which releases some groups, but much less than ACSA. CX releases a few and GBCM practically none. Table 3 resumes the values obtained (concentrations).

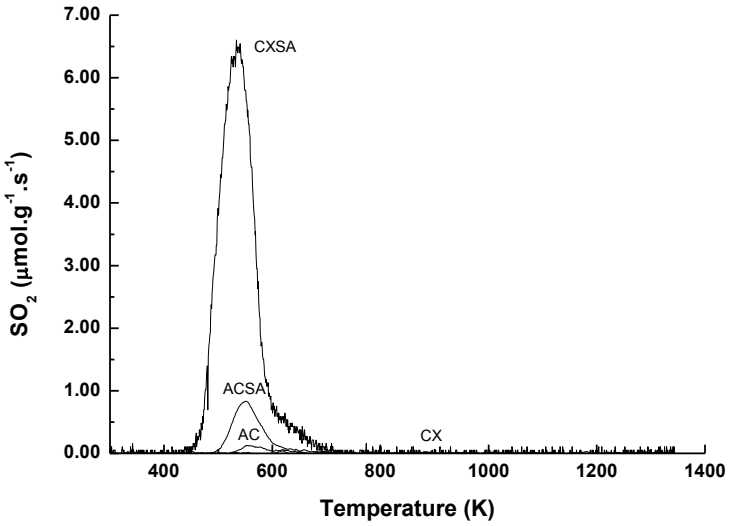


**Figure 16** - TPD spectres of different carbon materials releasing $SO_2$

**Table 3 –** Concentrations of CO, $CO_2$ and $SO_2$ released during the TPD of 4 different carbon materials

| Catalyst | CO (± 20 μmol.g$^{-1}$) | $CO_2$ (± 20 μmol.g$^{-1}$) | $SO_2$ (± 20 μmol.g$^{-1}$) |
|---|---|---|---|
| AC | 1240 | 360 | 120 |
| ACSA | 1700 | 420 | 680 |
| CX | 240 | 100 | 0 |
| CXSA | 1540 | 440 | 6360 |

Analysing table 3, CX has more reduced concentrations of CO, $CO_2$ and $SO_2$ than the other carbon materials. ACSA presents the largest concentration of CO, over 7 times more than CX. CXSA presents the largest concentration of $CO_2$ releasing groups, over 4 times more than CX. Relatively to the concentration of $SO_2$, CXSA has an enormous concentration compared to the other materials which is also observed on figure 16, while CX practically none.

### 3.1.3 $N_2$ Adsorption Isotherms at 77 K

The $N_2$ adsorption isotherms at 77 K are represented on figure 17. It is observed that AC and ACSA are very different from the CX samples (sizes lower than 0.106 mm and between 0.106-0.25 mm) and from GBCM. The textural parameters calculated from the adsorption isotherms are gathered in table 4. It is observed that GBCM show the lowest specific surface area ($S_{BET}$ = 10 $m^2/g$). GBCM has hardly no specific area nor any volume of micro pores ($V_{mic}$ = 0) which justifies the material to be a bad adsorbent and catalyst as will be discussed further on. AC and ACSA have the largest specific surface area, due to the presence of a large amount of micro pores. CX samples are mainly characterized by large mesoporous areas. A larger specific surface area usually implies a better adsorbent material due to a great quantity of sites for adsorption.

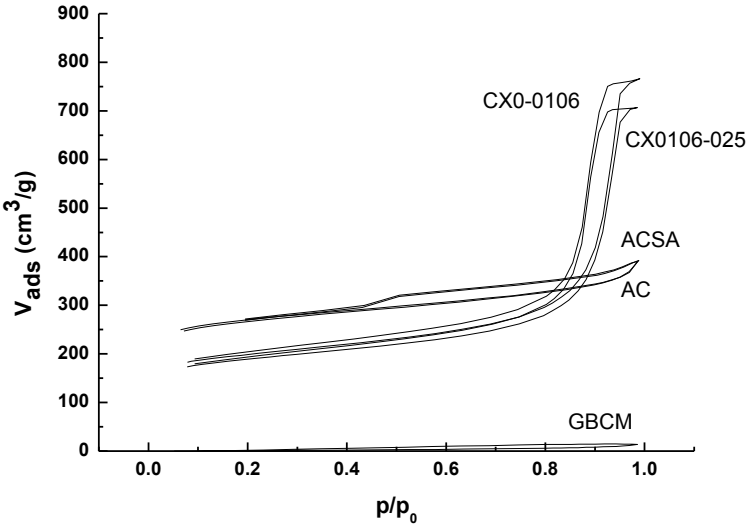


**Figure 17** - $N_2$ adsorption isotherms of different carbon materials

**Table 4** – Specific surface areas of AC/ACSA/CX/GBCM obtained by the analysis of the $N_2$ adsorption isotherms at 77K

| Catalyst | $S_{BET}$ ($\pm$ 10 $m^2.g^{-1}$) | $S_{MES}$ ($\pm$ 10 $m^2.g^{-1}$) | $V_{MIC}$ ($\pm$ 0.01 $cm^3.g^{-1}$) |
|---|---|---|---|
| AC | 850 | 190 | 0.33 |
| ACSA | 870 | 190 | 0.34 |
| CX0-0106 | 640 | 260 | 0.20 |
| CX0106-025 | 610 | 240 | 0.19 |
| GBCM | 10 | 10 | 0 |

As referred before, carbon materials are used as adsorbents and as catalysts in peroxidation reactions so the contribution of both mechanisms in the total removal of C2R was evaluated for the different materials.

### 3.2 Adsorption Experiments

Adsorption can be described as a mass transfer phenomena of a solute present in a liquid to the porous surface of a solid. Adsorption by activated carbons is a well known process and is being explored for the removal of organic polutants in which the superficial chemical properties are gaining considerable importance.

The results obtained using the different prepared carbon materials as adsorbents of the azo dye are represented on figure 18, as relative C2R removal plotted versus time.

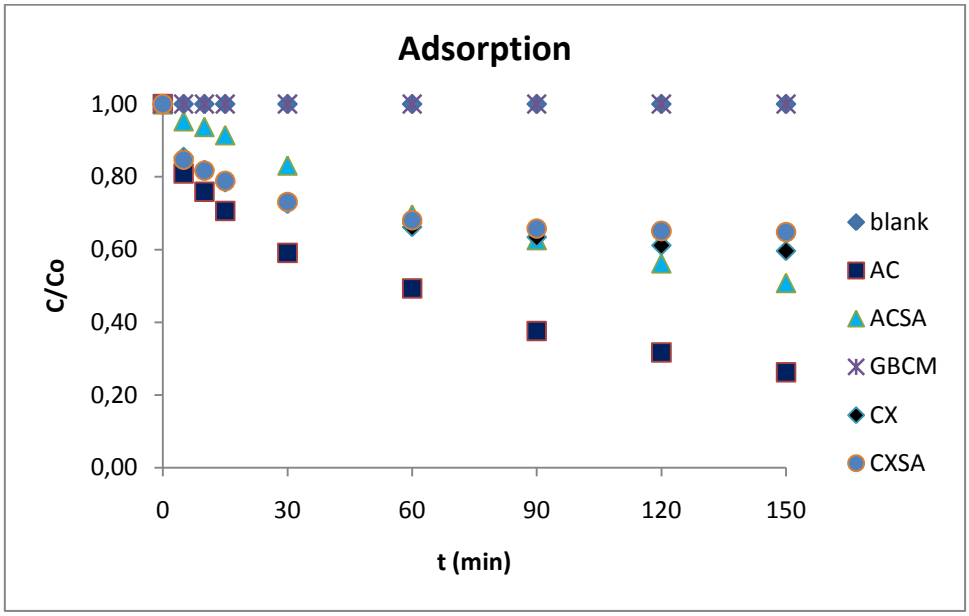


**Figure 18** – Removal of the azo dye Chromotrope 2R using the prepared carbon materials. [azo dye] = 100 mg/L, [catalyst] = 0.5 g/L, pH = 3 and T = 50ºC.

Observing the results obtained it´s concluded that the materials have the following decreasing order of adsorption capacity: activated carbon, activated carbon treated with sulphuric acid, carbon xerogel, carbon xerogel treated with sulphuric acid and lastly glycerol based carbon material, which practically doesn´t present any adsorption of the azo dye Chromotrope 2R.

Relative to CX and CXSA, AC/ACSA are better adsorbents, which is due to the larger superficial area of these materials (Table 4: $S_{BET}$ AC/ACSA > $S_{BET}$ CX/CXSA). However, comparing the materials treated with sulphuric acid with their original materials without treatment (activated carbon materials and carbon xerogel materials), the materials treated with sulphuric acid have inferior results when compared with the original material (without treatment with sulphuric acid). The treatment with sulphuric acid inhibits them to adsorb the azo dye. This is explained

by the surface chemistry and PZC of the materials and the pH in which the experiments were performed. CXSA is less efficient removing C2R due to the lower PZC (1.5) compared to the pH of the solution of the runs performed (pH = 3) . The carbon materials surface is thus negatively charged while the C2R is in anionic form, which causes repulsion.

AC has a PZC of 6.7, higher than the pH of the solution, thus the surface will be positively charged, favouring the adsorption of the anionic dye, which justifies why it's the best carbon material to remove C2R as observed on figure 18. The adsorption is also favoured by the specific area of the material (Table 4), AC and ACSA have larger areas removing more C2R than the other carbon materials. GBCM has practically no specific area, so no C2R is adsorbed.

In conclusion, the highest adsorption removal of AC is due to the large specific surface area of this material and to the lower concentration of sulphur containing groups, which in this system, inhibits C2R adsorption.

### 3.3 Peroxidation Reactions

The results obtained with the prepared carbon materials in the peroxidation reactions are shown in figure 19. A blank run with the azo dye Chromotrope 2R and hydrogen peroxide was done for comparison.

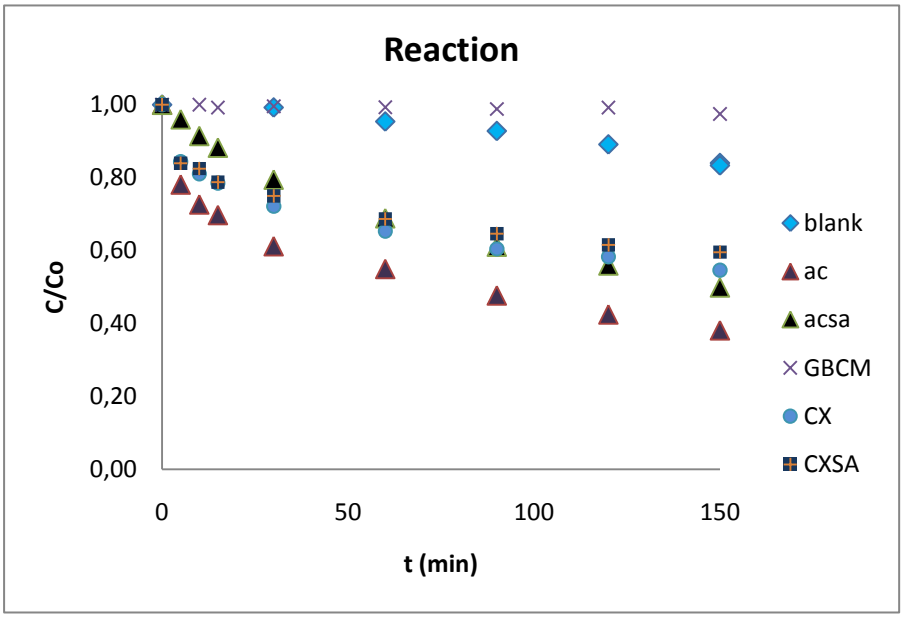


**Figure 19** – Evolution of concentration of Chromotrope during reaction with the different carbon materials.

Using hydrogen peroxide as oxidant it´s observed that the azo dye is slightly removed without any catalyst and that the removal increases when the prepared carbon materials are used, except for the GBCM which inhibits the removal of the azo dye with hydrogen peroxide, probably due to a selective interaction between hydrogen peroxide and GBCM, leaving less hydrogen peroxide molecules in solution to react with C2R.

The following figures compare the removal of Chromotrope 2R obtained in the adsorption and reaction runs with the different prepared materials.

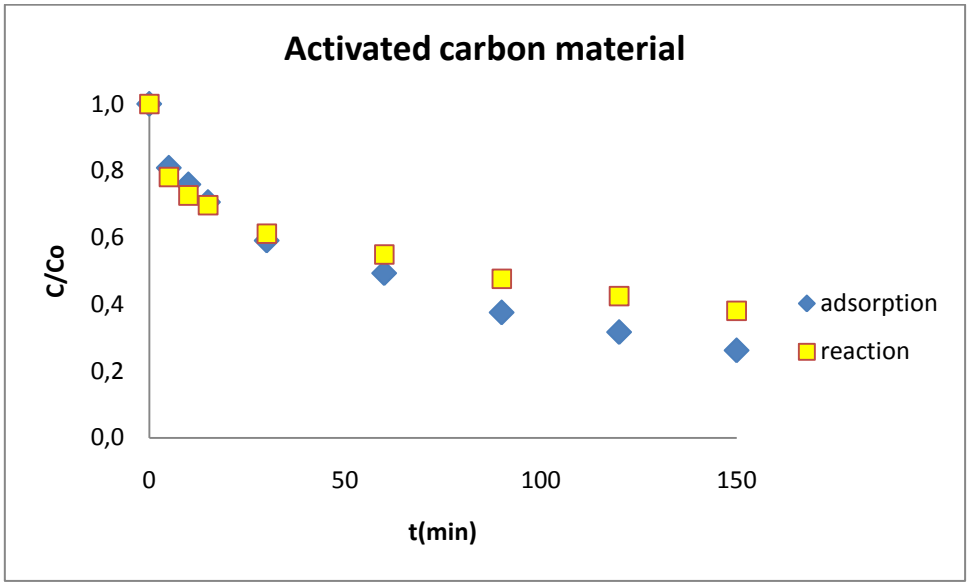


**Figure 20** - Adsorption and reaction results obtained with the activated carbon material (AC)

As observed on figure 20 the simultaneous presence of AC catalyst and hydrogen peroxide doesn´t improve the removal of the azo dye compared to the results obtained through adsorption. In this case adsorption is more efficient than reaction. This may be due to a selective interaction between hydrogen peroxide and AC, leaving less adsorption sites on the surface of AC to adsorb C2R.

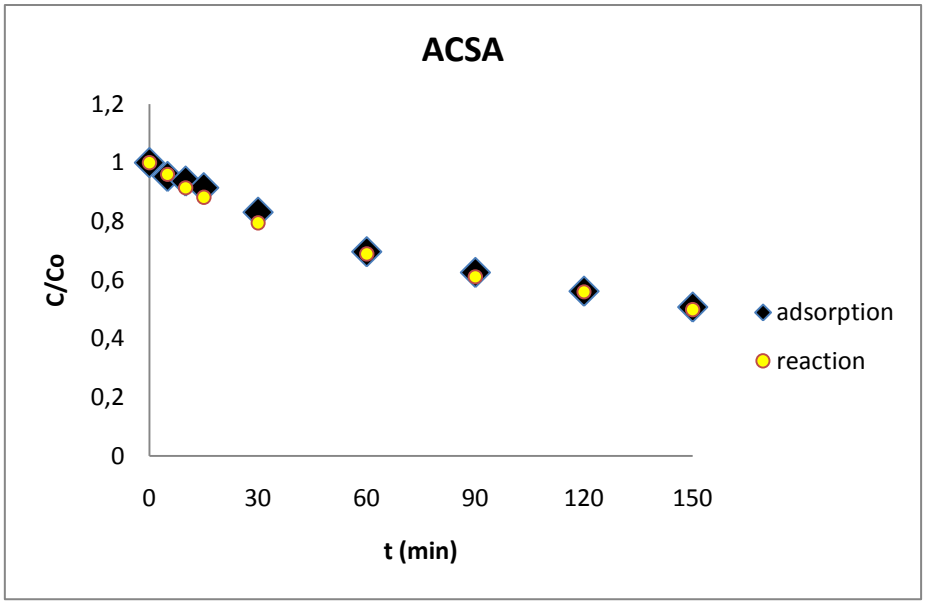


**Figure 21** - Adsorption and reaction results obtained with the activated carbon treated with sulphuric acid (ACSA)

With the activated carbon material treated with sulphuric acid there are no differences between the adsorption and the reaction so we can conclude that adding hydrogen peroxide doesn´t affect the removal behaviour.

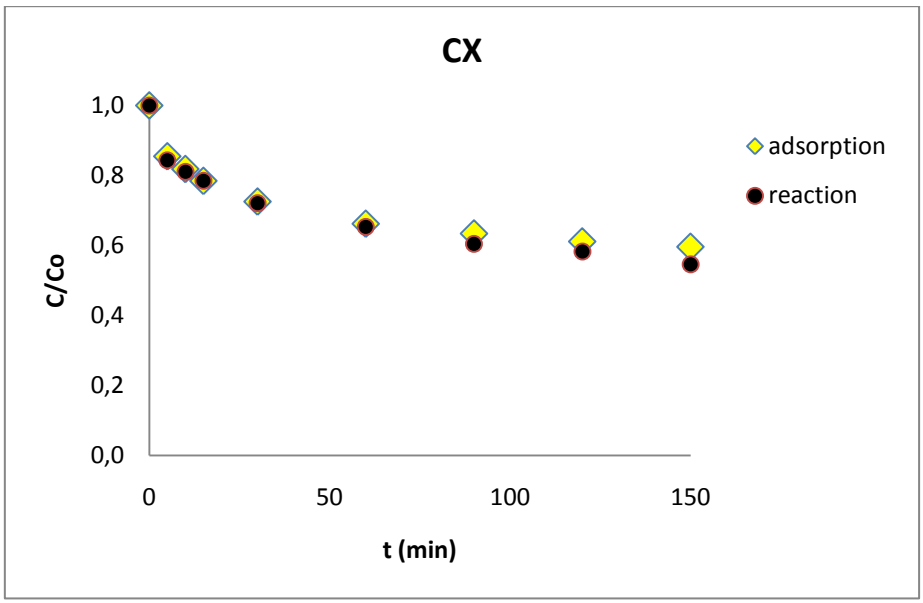


**Figure 22** - Adsorption and reaction results obtained with the carbon xerogel (CX)

Using the carbon xerogel as catalyst with hydrogen peroxide there is a slight improvement of the removal of the azo dye.

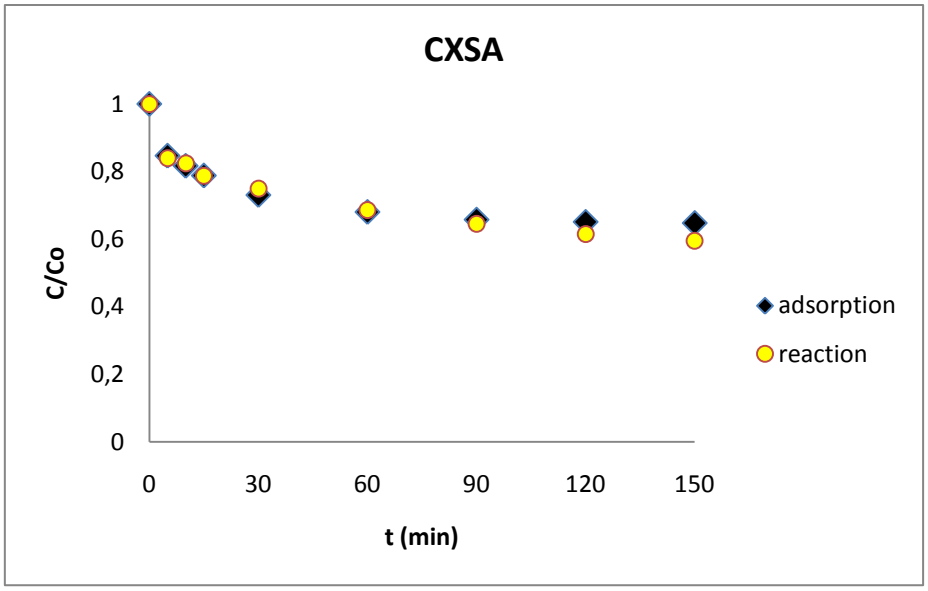


**Figure 23** - Adsorption and reaction results obtained with the carbon xerogel treated with sulphuric acid.

There is also only a very slight improvement between the adsorption and reaction of this material.

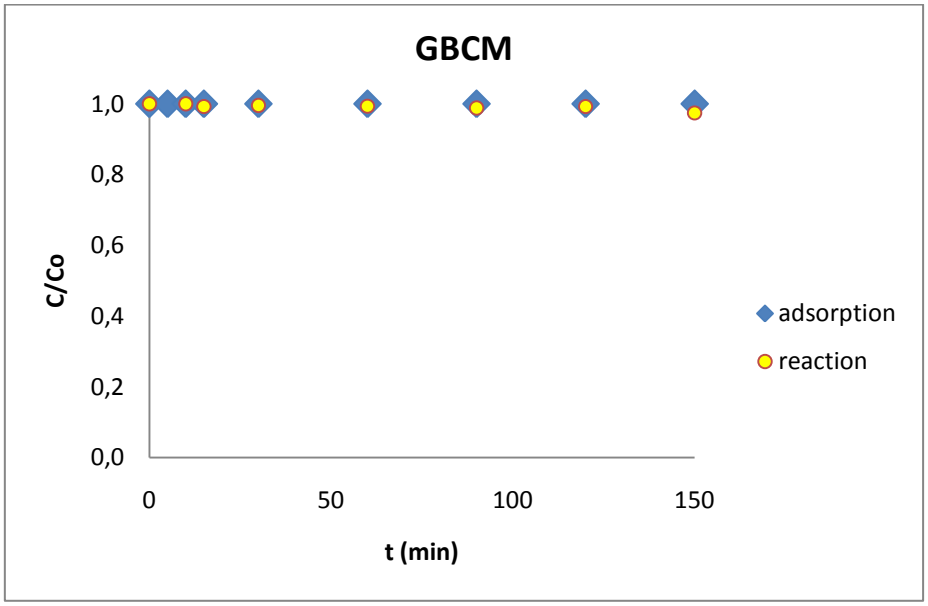


**Figure 24** - Adsorption and reaction results obtained with the glycerol based carbon material (GBCM)

The GBCM only improves slightly using the hydrogen peroxide and shows to be a poor material for the removal of the colouring by this process.

Introducing hydrogen peroxide doesn´t significantly increase the removal of the azo dye C2R and in some cases even decreases the removal. This can be due to a saturation created by adsorption of C2R that occurs at the same time as reaction. There is a transfer of mass (C2R) by 2 methods, adsorption and reaction, into the carbon material and these enter into conflict diminishing the removal of C2R.
The C2R removal percentages obtained after 150 min through adsorption and reaction runs are compiled in table 5 to easier compare the different materials.

**Table 5 –** Removal of C2R by different carbon materials in adsorption and reaction experiments after 150 min.

| Carbon Materials | Adsorption (%) | Reaction (%) |
|---|---|---|
| AC | 74 | 64 |
| ACSA | 58 | 58 |
| GBCM | 1 | 8 |
| CX | 43 | 48 |

### 3.4 Reaction Runs with Fe Supported on Carbon Materials

Since the tested carbon materials did not increase appreciably the removal of C2R in peroxidation reaction, when compared to adsorption removal, the AC and GBCM materials were used as support for Fe based catalysts, to assess the influence of this active metal in the overall C2R removal efficiency. The results obtained are shown in Figures 25 and 26, for Fe/AC and Fe/GBCM, respectively.

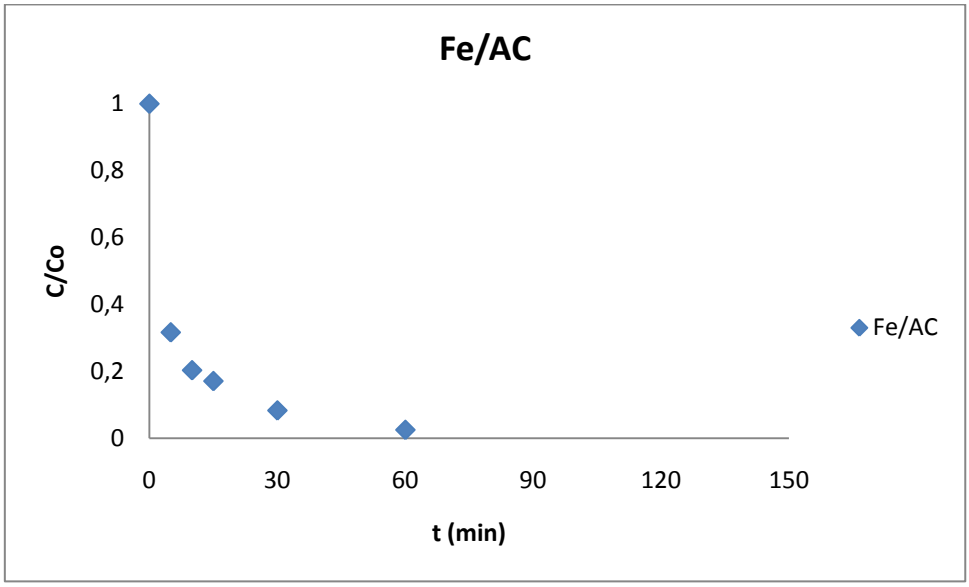


**Figure 25** – Adsorption and reaction results obtained with the iron supported carbon material (Fe/AC)

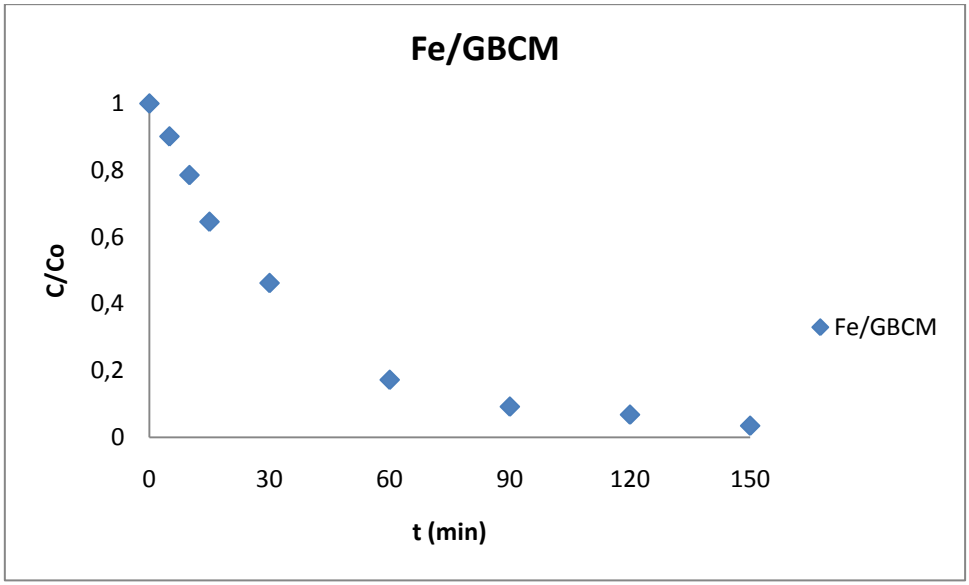


**Figure 26** – Adsorption and reaction results obtained with the iron carbon supported material (Fe/GBCM)

Observing the results obtained it is concluded that the incorporation of iron in the carbon materials increases radically their catalytic behaviour, with 100 % removal being attained after 150 min of reaction. Ac/Fe is the best carbon material without doubt being C2R removed completely after an hour of reaction. C2R is removed at an extraordinary fast rate as observed on figure 25, being 80 % C2R removed after only 10 minutes of reaction. This justifies why iron based carbon materials are preferred to other treated carbon materials. GBCM/Fe is also efficient, although not as efficient as AC/Fe.

Incorporating Iron into the carbon materials improved immensely the removal of C2R. This is explained in literature [58] as resultant of the iron active centres that can be considered responsible of promoting oxidation of the aromatic compounds (C2R) in the so called Fenton-heterogeneous process.

There was more precipitated iron in the solution of the reaction with Fe/GBCM as catalyst than in the Fe/AC material. This was due to the properties of the materials. Since GBCM is not porous, the impregnated iron remained on the material only as a coating and was easily removed during the reaction run. In the opposite, as AC possesses a well defined porous structure, it establishes stronger bonds with the iron, so less iron leached into solution. The resultant solution from the reaction with the Fe/AC material was colourless while the solution resultant from the Fe/GBCM was yellowy-brown coloured. The leaching of iron into the treated water is the main problem associated with iron based carbon materials. Iron in the water distribution system leads to the growth of microorganisms and also slime layers that reduce the pipelines capacities to higher chlorine dosages. There exists legislation on the iron limits in water. The USEPA has established a secondary maximum contaminant level (SMCL) at 0.3 mg/L [61]. Thus, it is important to develop iron based catalyst with high activity associated to high stability.

### 3.5 Results obtained from COD

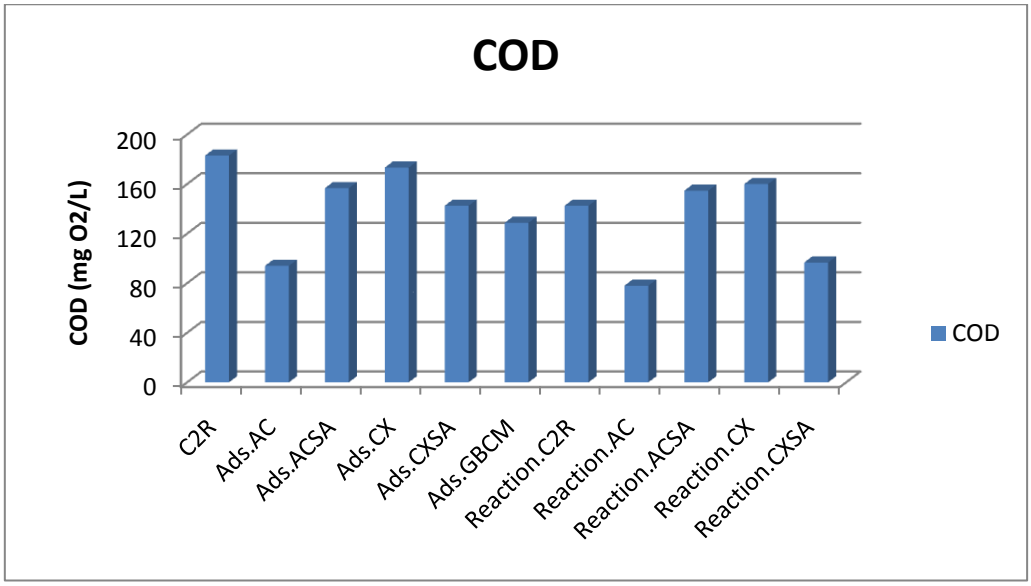


**Figure 27 - COD of the samples**

From the observation of figure 27 the following can be observed:

- Samples from the reactions have less COD than samples from the adsorption analysis (for example: COD Reaction.CXSA < COD Ads.CXSA) which means that Hydrogen peroxide reduced the organic matter.
- All samples have a COD inferior to C2R, so there was always degradation of the organic matter. The samples with the lowest COD are the ones from the adsorption analysis and reaction using AC. AC is the best material to remove organic matter.
- The results were credible, because the method used is valid for values of COD up to 400 mg $O_2$/L.

## 4. Conclusions

- From the adsorption results: adsorption is favoured by materials with large specific area (AC and ACSA) and materials with PZC higher than the pH of the solution (AC), due to the surface which is positively charged, favouring the adsorption of the anionic dye. AC was the best adsorbent, being 74 % of the azo dye removed after 150 min of the adsorption run.

- Obtained from the reactions:

  - The introduction of $H_2O_2$ doesn´t hardly improve the removal of C2R, only CX shows a little improvement and GBCM, but very insignificant. In the case of AC it even decreases the removal. This may be due to a saturation created by adsorption of C2R that occurs at the same time as reaction. There is a transfer of mass (C2R) by 2 methods, adsorption and reaction, into the carbon material and these enter into conflict diminishing the removal of C2R.
  - The best results were obtained with Activated Carbon, this material was the best catalyst, removing 64 % of C2R after 150min of the reaction run.

- In the mean time, COD shows that samples from the reactions have less organic matter than samples from the adsorption analysis, which signifies that the intermediates of the reaction continue to degrade C2R, whilst with adsorption this doesn´t happen. The sample with the lowest COD is also AC, being the COD of the solution from reaction lower than the one from the adsorption run. The COD from the reaction could even be lower, because values of COD are usually greater than normal when $H_2O_2$ is used.

- Introducing iron into the AC and GBCM improves significantly their activity, obtaining 100 % removal of C2R. Iron supported AC removed C2R in 15 min of reaction, while the Iron supported GBCM also removed C2R, but not as fast as AC. Both materials removed all of the azo dye by the end of the reaction (150 min) which wasn´t achieved with the carbon materials without iron. AC obtained better results, due to its well defined porous structure and also the stronger bonds that were established with the iron when the material was impregnated. There was less iron leaching with the iron supported AC as the

final solution was transparent, while the solution using iron supported GBCM had a yellowy-brown colour.

- Taking in consideration all the results obtained during this work, the best carbon material is AC, due to its large specific area and high PZC which favour the material to remove the azo dye Chromotrope decreasing the organic matter present in solution.
- Iron supported carbon materials are more efficient than the carbon materials prepared in this work, in the mean time there are disadvantages like the iron leaching which attributes extra costs to the treatment. Iron has to be removed, because it leads to the growth of microorganisms and slime layers in the water distribution systems, which reduce the pipelines capacities to higher chlorine dosages.
- Although the iron supported carbon materials removed more Chromotrope, AC removed a good quantity of the azo dye (74%) and without creating other problems. Using AC without iron we avoid iron leaching and further costs.

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**Appendix 1**

In Table A1 are the reactants and materials used during the work.

**Table A1** – reactants used in this work and respective purity.

| Reactants | Purity |
|---|---|
| Chromotrope 2R | - |
| Hydrogen Peroxide | 30 % (m/V) |
| Sulphuric Acid | 95 – 97 % (m/V) |
| Potassium Permanganate | 99 % (m/m) |
| AC Norit Rox 0.8 | - |
| Sodium Hydroxide | 98 % (m/m) |
| Hydrochloric acid | 37 % (m/V) |
| Sodium Chloride | - |
| Manganese Oxide | 90 % (m/m) |
| Iron(III) nitrate 9-hydrate | 98 % (m/m) |

**Appendix 2**

In Table A2 are the reactants used for the COD and respective purity.

**Table 2** – Reactants and respective purity.

| Reactants | Purity |
|---|---|
| Sulphuric acid | 95 – 97 % (m/V) |
| Potassium Dichromate | 98 % (m/m) |
| Silver Sulfate | 98 % (m/m) |
| Sodium Thiosulfate | 98 % (m/m) |
| Mercury(II) Sulfate | 98 % (m/m) |
| Standard Ferrous Ammonium Sulfate | 98 % (m/m) |

An example of the calculations done is as the following:

$$COD = \frac{(A-B)*M*8000}{V_a}$$

$\leftrightarrow COD = \frac{(2.8-0.85)*0.025*8000}{5}$ = 78 mg $O_2$/L

*A* = 2.8 mL (Volume of FAS used to titrate the blank sample)
*B* = 0.85 mL (Volume of FAS used to titrate the sample from the reaction with AC)
*M* = 0.025 M (Molarity of FAS)
$V_a$ = 5 mL (Sample volume)

The sample obtained from the reaction with AC has a concentration of the COD of 78 mg $O_2$/L.

**Appendix 3**

Examples of calculation for the active basic/acid centres for ACSA:

- **Active acid centres:**

[HCl] = 0.02M (titrant solution)
[NaOH] = 0.02M
Volume of solution containing NaOH = 20mL (solution to be titrated)
Volume of HCl used on the titration = 9.2 mL

$$C_{H^+} * V_{HCl} = C_{OH^-} * 20E^{-3}$$

$\leftrightarrow 0.02 * 9.2E^{-3} = C_{OH^-} * 20E^{-3}$

$\leftrightarrow C_{OH^-} = 0.0092\ M$

The final concentration of the ions $OH^-$ is 0.0092 M.

$$[Active\ acid\ centres] = \frac{(C_{NaOH} - C_{OH^-})*25E^{-3}}{m_{cat}}$$

$\leftrightarrow [Active\ acid\ centres] = \frac{(0.02-0.0092)*25E^{-3}}{0.2002} = 1.35\ mmol/g$

The concentration of active acid centres on the surface of ACSA is 1.35 mmol/g.

- **Active basic centres:**

[NaOH] = 0.02 M (titrant solution)
[HCl] = 0.02 M (initial concentration)
Volume of solution containing HCl = 20 mL (solution to be titrated)
Volume of NaOH used on the titration = 17.8 mL

$$C_{H^+} * V_{HCl} = C_{OH^-} * V_{NaOH}$$

$$\leftrightarrow C_{H^+} * 20E^{-3} = 0.02 * 17.8E^{-3}$$

$$\leftrightarrow C_{OH^-} = 0.0178\, M$$

The final concentration of the ions $H^+$ is 0.0178 M.

$$[Active\ basic\ centres] = \frac{(C_{HCl} - C_{H^+}) * 25E^{-3}}{m_{cat}}$$

$$[Active\ basic\ centres] = \frac{(0.02 - 0.0178) * 25E^{-3}}{0.2004} = 0.27\ mmol/g$$

The concentration of active basic centres on the surface of ACSA is 0.27 mmol/g.