UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN

FACULTY OF CHEMICAL SCIENCES

INFLUENCE OF FUNCTIONAL GROUPS OF ACTIVATED CARBON IN THE ANCHORING OF IRON PARTICLES BY FORCED HYDROLYSIS AND ITS USE TO REMOVE HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS

By

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As partial requirement to obtain the Degree of
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INFLUENCE OF FUNCTIONAL GROUPS OF ACTIVATED CARBON IN THE ANCHORING OF IRON PARTICLES BY FORCED HYDROLYSIS AND ITS USE TO REMOVE HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS

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I dedicate this thesis to the most important engine of my life, ***my family*** that have allowed me to grow up together with them living unforgettable moments, and because in one way or another they have contributed to reach this achievement.

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ABSTRACT

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Dissertation title: INFLUENCE OF FUNCTIONAL GROUPS OF ACTIVATED CARBON IN THE ANCHORING OF IRON PARTICLES BY FORCED HYDROLYSIS AND ITS USE TO REMOVE HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS

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Study area: Sustainable Processes.

Purpose and method of study: Heavy metals are a serious health problem, because when they are ingested can cause allergies, kidney or neuronal damage, cancer and death in some cases; therefore, they should be removed from the effluent before discharging to the environment. Conventional methods for removing heavy metals, such as chemical precipitation, coagulation-flocculation and ultrafiltration, among others become inefficient for solutions with concentrations less than 100 mg/l. In this work, the adsorption of Cr (VI) by modified activated carbon with anchored iron particles by forced hydrolysis was studied at different concentrations between 10 and 500 mg/l, pH 6 and 25^{o}C as an alternative instead of the traditional methods.

Contribution and Conclusions: Surface chemistry of the activated carbon had an important effect on the anchoring of iron particles by forced hydrolysis, showing the higher quantity of iron over activated carbon surface the adsorbents that were modified by an oxidation with nitric acid, and the lower quantity of iron particles those adsorbents who were treated thermally. However, forced hydrolysis treatment caused an important improvement in the hexavalent chromium adsorption capacity of modified activated carbons at concentrations lower than 150 mg/l. Heat-treated activated carbons and modified with forced hydrolysis showed the best Cr(VI) uptake (57 mg/g) and also the faster adsorption kinetic of the studied adsorbents. A 98% of Cr(VI) desorption from the best adsorbent was achieved with a 0.1 N NaOH-NaCl solution, suggesting an anionic adsorption mechanism.

ADVISOR SIGNATURE: ____
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LIST OF SYMBOLS

Symbol	**Significance**
AC	Activated carbon
C_f	Final concentration
C_o	Initial concentration
et al.	And co-workers
G	Gram
GFO	Granular Ferric Oxides
K	Freundlich constant
K_e	Equilibrium constant
L	Liter
M	Mass
Mg	Milligram
°C	Celsius degrees
ppm	Parts per million
q	Adsorption capacity
q_{max}	Maximum adsorption capacity
rpm	Revolutions per minute
T	Temperature
V	Volume

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CHAPTER 1

Introduction: Water in the environment

> **“It isn't that they can't see the solution.**
> **It is that they can't see the problem.”**
> *G.K. Chesterton*

1. INTRODUCTION

Water is essential for supporting life and it´s also considered as natural resource. Because this liquid covers around 72% of earth, its pollution is an important topic about the main environment conflicts in the world.

Due to the extensive formation of hydrogen bonds, water has high melting and boiling points as well as large heat capacity. Additionally, water has an exceptional ability to dissolve a wide variety of ionic and polar covalent substances because of its high polar character [Brown (2004)]. However, taking into account that water is a universal solvent, this property allows its use in a wide number of applications, for this reason the use of water must be done in a sustainable way to satisfy the social and economical development as well as its preservation (National Council Water, 2012).

It was reported that human body contains about 65% of water by mass and this high percentage play a major role in human´s body functioning. In fact, every cell and organ functions depends on the water for their correct functioning. Among all usages of the water, it is also used as a lubricant in digestion and almost all the other body processes; for example, water lubricates joints and cartilage in human body. In addition, water is capable of removing toxins and it helps to control body temperature and it can transport valuable nutrients to the organism.

It is important to mention that human body not only depends on water to subsist, this resource is also essential for biosphere, flora, and fauna. In general, water is required for living organisms and contributes in nutrient flows to keep the ecosystems.

Water is a renewable resource, it could be contaminated by human activities which in turn make water to be useless or harmful. For this reason clean water is an essential resource for the operation and development of a stable and prosperous society (UNESCO, 2003).

Many researchers have reported that water quality has been affected by factors or agents that causes its pollution such as pathogens, inorganic and organic substances, biodegradable wastes that require oxygen to be oxidized, sediments or suspended material, radioactive substances and heat. Also wastewater may contain nutrients, that can stimulate the growth of aquatics plants, and it could also contain toxic compounds with high mutagenic or carcinogenic potential.

For these reasons, the immediate removal of pollutants from wastewater sources (through its specialized treatment, reuse, or disposal in the ambient) is necessary for the protection of human health and, at the same time the environment (Metcalf & Eddy, 2004). Prevention of water pollution plays a major role to improve water quality and to reduce the requirement of expensive water or wastewater treatments.

1.1 Water pollution with heavy metals

The presence of heavy metal in aqueous effluents is of great concern due to its toxicity and carcinogenic effects on human health and aquatic organism (Prabhakaran *et al.,* 2009). Heavy metals are released into the environment through natural sources from volcanic eruptions and anthropogenic sources such as wastewater discharges from industrial sources, these pollutants are not easily removed without an advanced or specialized treatment (Leyva *et al.,* 2008).

Heavy metals are hazardous because of its toxic nature; furthermore they are not biodegradables and they can also be bioaccumulated in organisms. In other words, because of their persistence in the nature, metals can be dispersed in water, accumulated in plants and animals, and finally to be added in human beings throughout the food chain or by drinking polluted water, causing several health problems (García & Rangel, 2010).

Metal ions like chromium, mercury, cadmium, nickel, arsenic, lead, etc., have an adverse effect on the human physiology and other important biological systems; for example, the presence of heavy metals in water bodies have important toxic effects in animals and at higher trophic levels. Because of the wide amount of processed material the removal of metal ions from aqueous solutions (especially in low concentrations) from industrial effluents of high interest (Liu *et al.,* 2007). The source and toxicity of certain metal ions are listed in Table 1.

Table 1. Source and toxicity of heavy metals on human health (Farooq *et al.,* 2010).

Metal	Source	Toxic effects	Reference
Lead	Electroplating, production of batteries, pigments, ammunitions.	Anemia, brain damage, anorexia, loss of appetite.	Gaballah & Kibertus, 1998; Low *et al.,* 2000; Volesky, 1993.
Cadmium	Electroplating, enamel, pigments production, plastics, mining, refinery.	Carcinogenic, kidney damage, boney injury, hypertension, loss of appetite.	Sharma, 1995; Chen & Chao, 1998; Godt *et al.,* 2006; Singh *et al.,* 2006.
Mercury	Mercury wear areas, volcanic eruptions, Forrest fires from nature causes, battery production, burning fossil fuels, mining and metallurgy.	Renal and neurological damage, spoilage to the lung function, corrosive to eyes, skin and muscles, dermatitis, liver damage.	Morel *et al.,* 1998; Boening, 2000; Manohar *et al.,* 2002.
Chromium (VI)	Electroplating, leather tanning, textiles, metallurgy, wood preservation, paints and pigments.	Carcinogenic, mutagenic, teratogenic, epigastric pain, nausea, vomiting, severe diarrhea, lung tumors.	Dupont & Guillon, 2003; Kobya, 2004; Granados & Serrano, 2009; Singh *et al.,* 2009.
Arsenic	Enamels, mining, energy production from fossil fuels, sediment rocks.	Gastrointestinal symptoms, damage to cardiovascular and nervous system, melanosis in bones, hemolysis, polyneuropathy, encephalopathy, liver tumor.	Chilvers & Peterson, 1987; Dudka & Market, 1992; Robertson, 1989.
Copper	Electronics coating, galvanizing, paints production, printing, wood preservation.	Develops acute toxicity, neurotoxicity, sleep, and diarrhea.	Yu *et al.,* 2000; Chuah *et al.,* 2005; Papandreou *et al.*, 2007.
Nickel	Non-ferrous materials, mineral processing, formulation of paints, electroplating, coated porcelain, thermoelectric.	Chronic bronchitis, reduced lung function, lung cancer.	Akhtar *et al.,* 2004; Ozturk, 2007.

In recent years, the levels of toxic metals in surface waters have been increasing due to pollution caused by wastewater discharges from industrial sources (Leyva *et al.,* 2008). Untreated effluents from industries such as metallurgy, electronics, leather tanning, plating and cooling water systems among others, can pollute water bodies with heavy metals (García et al., 2009).

Table 2 shows the most common industrial processes that discharge aqueous effluents with high content of heavy metals to the environment or water bodies, and the wide use of chromium in many industries.

Table 2. Main industrial sources that discharge heavy metals (Mohan *et al.,* 2006).

Industrial Source	**Zn**	**As**	**Cr**	**Pb**	**Ni**	**Cu**	**Fe**	**Hg**	**Cd**	**Sn**
Automobiles	X		X	X	X		X		X	X
Petroleum refining	X	X	X	X	X	X	X			
Pulp and paper	X		X	X	X	X		X		
Textile			X							
Steel	X	X	X	X	X		X		X	X
Organic chemicals	X	X	X	X			X	X	X	
Inorganic chemicals	X	X	X	X			X	X	X	
Leather tanning			X							
Mining	X		X			X			X	
Glass		X								

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CHAPTER 2

Background: Chromium (VI) uptake by activated carbon

> **“The man who has ceased to learn ought not to be allowed to wander around loose in these dangerous days”**
>
> *M.M. Coady*

2.1 Chromium

Chromium (Cr) is a naturally occurring element found in rocks, plants, soil, animals as well as in smoke and volcanic gases; it is the sixth most abundant transition metal in the Earth´s crust, where it is found like oxide (Cr_2O_3) and, combined with iron and oxygen in the mineral chromite. Chromium was discovered in 1797 by the French chemist Lois Vauquelin in lead chromate ($PbCrO_4$), which is the rare mineral crocoite; its name comes from the Greek *"chromos"* meaning "color" and it is due to the different colors found in their compounds (Mohan *et al.*, 2006).

Chromium, with an atomic number of 24 and atomic weight of 51.996, is a heavy metal of the first series of transition metals (Group VI B). Chromium has important chemical and biochemical properties, among those include several oxidation states; some chromium compounds are paramagnetic and most of them are colorful, therefore some mineral and precious stones attribute their color to chromium (Zayed *et al.*, 2003).

Chromium oxidation states are -2, 0, +2, +3, and +6, but the only compounds of biological importance are derived from the oxidation states of +3 and +6; the first group belong the chromic oxide (Cr_2O_3) and chromic salts such as chromic chloride ($CrCl_3$) or chromite anion ($Cr(OH)_4^-$), and the second group, the chromium trioxide (CrO_3), chromate $(CrO_4)^{2-}$, and dichromate $(Cr_2O_7)^{2-}$ (ATSDR, 2008).

The most important mineral form of chromium is called chromite ore or ferrochromite ($FeCr_2O_4$) derived from chromium (III).

On the other hand, metallic chromium (Cr^0) is not free in nature due to its high reactivity, it is white silver bluish tint, exhibiting the property of being heat resistant and easily coated with a thin layer of oxide protecting it from further chemical reaction. Metallic chromium is higher resistant to oxidation, even at high temperatures. This property, combined with its colors, is the reason of being used as coat of different metal objects in order to protect against corrosion, processes known as chrome plating (Mohan *et al.*, 2006; Klassen *et al.,* 2008).

Compounds derived from chromium (III) are usually prevailing in the environment because they are the most stables derivate from this metallic element. The most important compound from trivalent chromium is chromic oxide (Cr_2O_3) that is extremely stable, resistant to acids and also high melting point. It is used such a pigment called “chrome green”.

In contrast, chromium (VI) derivatives are fundamentally chromates and dichromates. Both species are oxidizing agents in acidic media, and they are reduced to Cr(III) by electron donors (Kuo *et al.,* 2008). Potassium dichromate is frequently used in industry and chemical operations. Sodium dichromate is used in leather tanning since an insoluble compound is produced with skin proteins. Often, lead dichromate is used as pigment with the name “chrome yellow”.

Chromium is mainly used in three industries: metallurgic, chemical and refractory materials. In the metallurgical industry is an essential compound of stainless steel and other metal alloys.

Frequent uses in refractory materials include brick manufacturing based on a mixture of magnesite-chromium for metallurgic furnace and the use of granular chromite for many other applications requiring heat resistant materials.

Regarding applications in chemical industries, it is used in operations of chromium plating, manufacture of pigments and dyes, leather tanning and wood treatments. Minor amounts of these chromium compounds are used as corrosion inhibitors, water treatment, photographic materials, magnetic tapes, etc. (Mohan *et al.,* 2006; Klassen *et al.,* 2008; Leyva *et al.,* 2008).

2.1.1 Chromium chemistry

Chemical speciation analysis of chromium, and other elements, provides information about individual concentration of this particular element in the different forms in which it is present in biosphere. This analysis not only allows distinguish among oxidation states, also between simple and coordinate ions, cationic, neutral and anionic forms, ionized and not ionized species as well as the degree of homogeneity and heterogeneity with natural constituents (Kotás & Stasicka, 2000).

Among the chromium oxidation states, only two of these, trivalent and hexavalent chromium, are enough stable to be in the environment. However, these forms are drastically different in charge, physicochemical properties as well as in chemical and biochemical reactivity.

Moreover, chromium in its divalent form, Cr(II), is quickly oxidized to Cr(III), and it remains stable as Cr(II) only in the absence of any oxidizing agent (i.e. under anaerobic conditions). The species Cr(IV) and Cr(V) form unstable intermediates in the reactions with the oxidation states of trivalent and hexavalent chromium and oxidizing and reducing agents, respectively (Palmer, 1994; Mohan *et al.*, 2006; Kotás & Stasicka, 2000).

Pourbaix diagram illustrated in Figure 1 shows the pH and potential conditions where each chromium species is thermodynamically stable in dilute aqueous solutions, in the presence of air and absence of any complex agent that are not H_2O or OH^-.

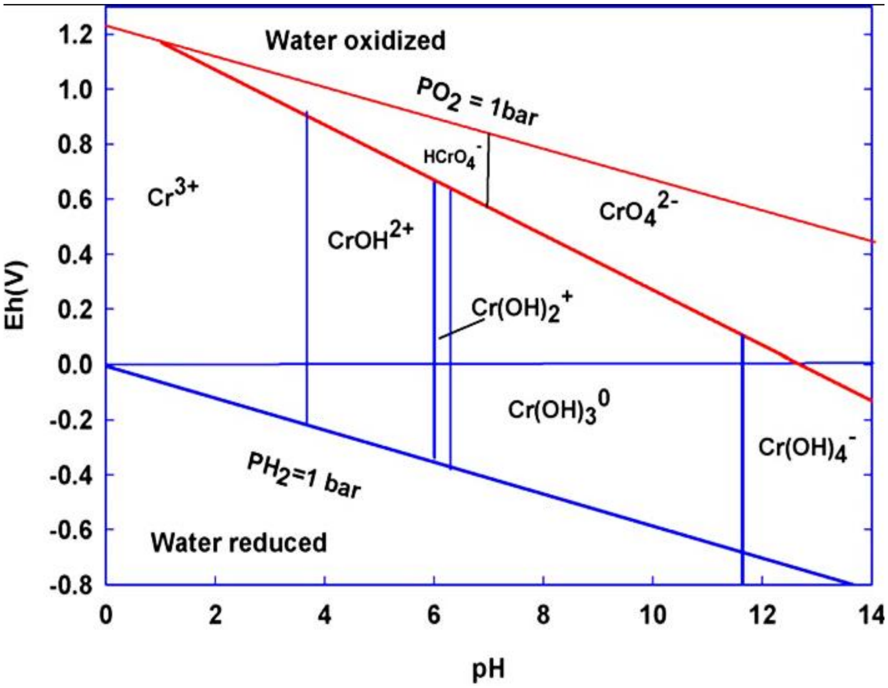

Figure 1. Pourbaix diagram for chromium species (Palmer *et al.,* 1994).

A general summary of chromium species (0 – VI) and the presence of some compounds of them in the nature are shown in the Table 3.

Table 3. Chemical chromium species in the environment (Zayed *et al.,* 2003).

Chemical specie	**Oxidation state**	**Compounds**	**Observations**
Elemental chromium	Cr(0)		It is not naturally present in the environment.
Divalent chromium	Cr(II)	$CrBr_2$, $CrCl_2$, CrF_2, $CrSe$, Cr_2Si	Relatively unstable and easily oxidized to trivalent state.
Trivalent chromium	Cr(III)	CrB, CrB_2, $CrBr_3$, $CrCl_3.6H_2O$, $CrCl_3$, CrF_3, CrN	Form stable compounds and are present in nature in the minerals as ferrochromite ($FeCr_2O_4$).
Tetravalent chromium	Cr(IV)	CrO_2, CrF_4	It is not present in nature and it is an important intermediate which affects the rate of reduction of Cr(VI). Compounds of Cr(IV) are less common. The Cr(IV) ions and their compounds are not very stables due to their short half-lives, forming intermediates en the reactions of the species of Cr(VI) and Cr(III).
Pentavalent chromium	Cr(V)	CrO_4^{3-}, potassium percromate	It is not present in nature and it is an important intermediate which affects the rate of reduction of Cr(VI). Species of Cr(V) are derivate from CrO_4^{3-} anion.
Hexavalent chromium	Cr(VI)	$(NH_4)_2CrO_4$, $BaCrO_4$,$CaCrO_4$, K_2CrO_4 , $K_2Cr_2O_7$	Second most stable state of chromium oxidation. However, the Cr(VI) is difficult to be in nature, but it is produced by anthropogenic sources. Nevertheless, it is present in the atmosphere in the rare mineral crocoite ($PbCrO_4$).

2.1.1.1 Trivalent Chromium: Cr(III)

Trivalent chromium species in the environment depends on the different chemical and physical processes, such as hydrolysis, complex formation, redox reactions and adsorption. Oxidation state of Cr(III) is the most stable and requires a substantial amount of energy to be converted to a state of lower o higher oxidation.

Hydrolysis of Cr(III) produce a mononuclear species $CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_4^{-}$, neutral species $Cr(OH)_3$ and polynuclear species $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$. All these trivalent chromium species that prevail in aqueous solutions and its dependence on pH value are shown in Figure 2.

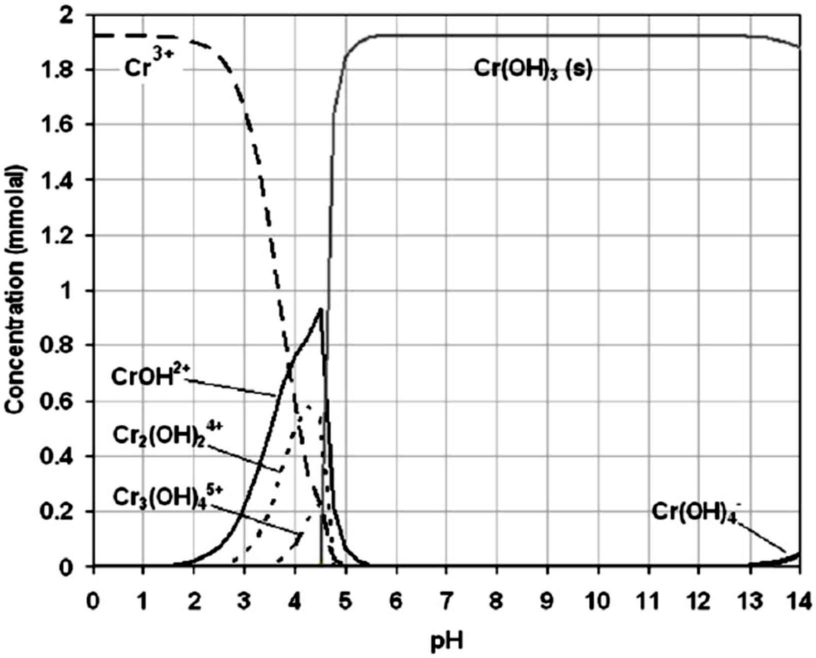

Figure 2. Species of chromium (III) in aqueous solution (García *et al.*, 2009).

Hydroxo complexes ($CrOH^{2+}$ y $Cr(OH)_3$) are the major species of Cr(III) in the aquatic environment. However, the $Cr(OH)_3$ exhibit amphoteric behavior and at high pH values can be easily transformed into a complex tetrahydroxoion ($Cr(OH)_4^-$) (Rai *et al*., 1987).

The Cr(III) is a strong acid which has a high tendency to form six-coordinated octahedral complexes with a wide variety of ligands such as water, ammonia, urea, ethylamine, and other organic compounds containing oxygen, nitrogen or sulfur.

Trivalent chromium complexation with ligands as OH^- increases its solubility when the ligands are in the form of discrete molecules or ions. Because the redox potential between Cr(VI) and Cr((III) is sufficiently high, just a few naturally occurring oxidants are able to oxidize Cr(III) to Cr(VI). Schroeder & Lee (1975) reported that oxidation of Cr(III) by dissolved oxygen in aqueous solutions is not possible. However, Saleh *et.al.* 1989 reported that through manganese oxides, an effective oxidation could be achieved in environmental systems.

2.1.1.2 Hexavalent Chromium: Cr(VI)

Hexavalent chromium in aqueous solutions forms a number of species and the relative proportions of these species depends on both pH and concentration of Cr(VI). The influence of the pH on Cr(VI) speciation is shown below in Figure 3. Hydrolysis of Cr(VI) produces only neutral and anionic species, predominantly H_2CrO_4,CrO_4^{2-}, $HCrO_4^{2-}$ and $Cr_2O_7^{2-}$ (Mohan *et al.,* 2006; Dionex, 1996).

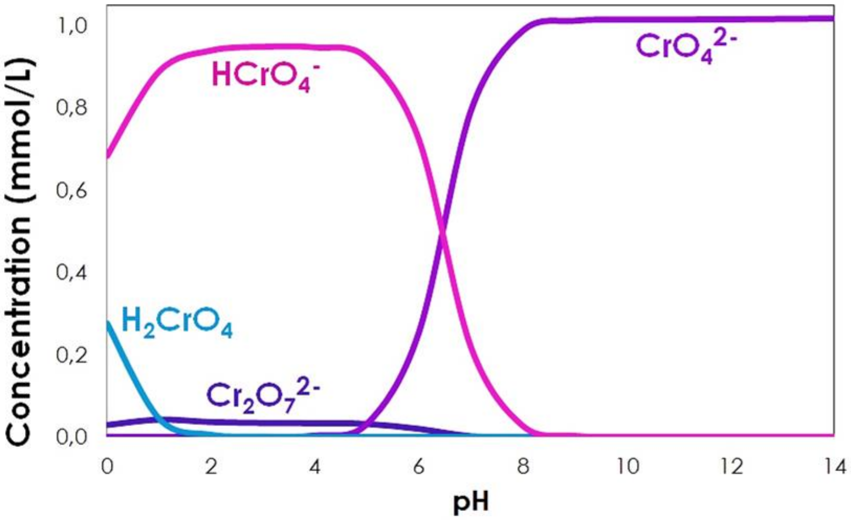

Figure 3. Chromium (VI) species in aqueous solution (García *et al.,* 2009).

Chromic acid (H_2CrO_4), the neutral specie of Cr(VI), undergoes two deprotonating steps according to equations (1.1 to 1.3) forming the $HCrO_4^-$ ion (pH between 1 y 6) and the CrO_4^{2-} ion (pH greater than 7).

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \qquad K = 10^{-0.75} \tag{1.1}$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \qquad K = 10^{-6.45} \tag{1.2}$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad K = 10^{2.2} \tag{1.3}$$

Most of Cr(VI) species are highly soluble anions and for this reason, Cr(VI) species can be transported through the soils and water. Nonetheless, the oxyanions of Cr(VI) are easily reduced to Cr(III) by electron-donors atoms or molecules like organic materials or inorganic reduced species that could be present in air, water and soils (Pyrzynska, 2012).

The hexavalent chromium in acid solutions shows a high positive redox potential (E^o between 1.33 – 1.38 V, Figure 4), which denotes that it is strongly oxidizing and unstable in presence of electron donors (Mohan *et al.,* 2006; Kotás & Stasicka, 2000).

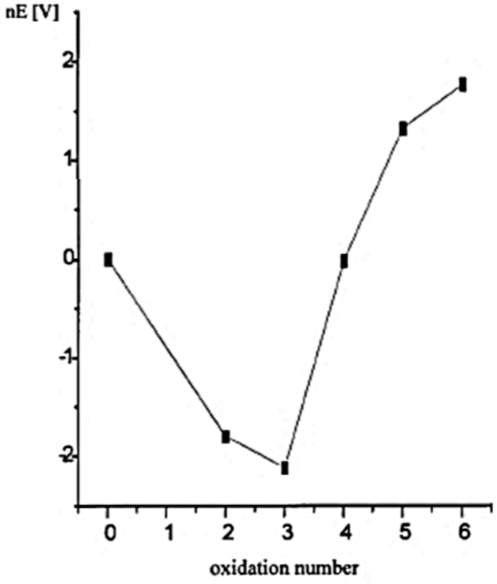

Figure 4. Frost diagram for chromium species in acid solutions (Kotás & Stasicka, 2000).

2.1.2 Toxic effects

2.1.2.1 Absorption

Chromium can enter in the human organism by inhalation, ingestion and, in lesser quantities, by absorption through the skin. Furthermore, it may be absorbed through the respiratory tract when inhaled air containing this metallic element and it takes place in the lungs through cell membranes of the alveoli.

Chromium absorption occurs via the digestive tract as a result of the ingestion of food or water containing any derivative from this metal, and exhibits significant effects when it is in contact with gastric juice. In the gastrointestinal tract of human and animals, Cr(III) is absorbed less than 1% while Cr(VI) around 10% (Klassen *et al.,* 2008).

Trivalent chromium present in food can bind to other compounds that facilitate its absorption in the stomach and intestines. Zhitkovich in 2005 conducted studies on Cr(VI) absorption, and reported that once absorbed, Cr(VI) enters the cells and it is intracellular reduced to Cr(III) as effect of red blood cells essentially cause by glutathione, ascorbic acid, and cysteine (ATSDR, 2008; USA EPA).

2.1.2.2 Distribution and warehousing

Chromium fraction absorbed in the intestine is transported into the blood, where it is distributed to the different organs. Once it has been absorbed, chromium (III) does not easily pass into cell membranes, but binds to transferrin (plasma protein which transport iron).

In contrast, after Cr(VI) absorption, it travel quickly to erythrocytes where it is converted to Cr(III). Protein complexes of trivalent chromium are deposited mainly in the bone marrow, lungs, lymph nodes, spleen, kidney, and liver (USA EPA).

2.1.2.3 Excretion

Inhaled particles containing elemental chromium can be retained in the lungs several years. Chromium excretion occurs mainly through the urine. In humans, kidney excretes approximately 60% of absorbed Cr(VI). Sedman *et.al* 2006, reported that the half-life for the excretion of potassium dichromate is about 35-40 hours. It is estimated that 10% of the absorbed dose of chromium is removed by biliary excretion and lower quantities are removed through hair, nails, milk, and sweat. As soon as the chromium was ingested with water and food, most Cr is eliminated with feces.

2.1.3 Adverse effects

The effects of chromium on human health mainly depend on the valence state at the time of exposure as well as its solubility. The most important toxicological forms are chromium (VI) and chromium (III) (Pyrzynska, 2012). Hexavalent chromium compounds, strong oxidizing agents, tend to be corrosive and irritating pollutants. In addition, Cr(VI) species are considerably more toxic than chromium (III) compounds, if doses and solubility are similar. It is postulated that this different may be related to the easy manner that the hexavalent chromium cross through cell membranes and subsequent intracellular reduction to reactive intermediates (ATSDR, 2000; Klassen *et al.,* 2008).

2.1.3.1 Chromium (III)

Trivalent chromium is an essential nutrient for the metabolism of sugar and fats, and enhances insulin action as part of the glucose tolerance factor. Chromium deficiency in the human body is not frequent, most cases are seen in undernourished or diabetic people. Chromium deficiency is characterized by glucose intolerance, hypercholestoremia, reduced longevity, reduced sperm count, fertility disorders, weight loss, reduced growth and nervous system dysfunction (García & Rangel, 2010; Miretzky *et al.,* 2010).

However, prolonged exposure to excessive quantities of chromium (III) can cause health risks, among them, human body can develop a higher sensibility to chromium causing skin redness and injuries (USA EPA).

2.1.3.1 Chromium (VI)

As above-mentioned, the most important toxic effects of chromium are mainly attributed to the hexavalent state. Chronical exposure of eyes to hexavalent chromium species is observed as conjunctivitis, tearing and pain. On the other hand, chromic acid and its salts are corrosive to skin and mucous membranes which can cause severe damage such as chronic ulceration and perforation of the nasal septum. The characteristic injury caused by a random dermal exposure to hexavalent chromium compounds is a sharp and deep ulcer that not ooze and its recovering is slow (ATSDR, 2000; WHO, 1996).

In addition, exposure to hexavalent chromium compounds can cause allergic reactions characterized by severe redness and edema of skin. On the other hand, long occupational exposure of the respiratory system to high levels of Cr(VI) in inhaled air (more than 2 mg/m^3) may cause irritation of nose, bleeding, ulcers, etc. (Klassen *et al.*, 2008).

Inhalation for short periods of small quantities of chromium (VI) into the air, does not cause adverse effects in most people, however, in allergic people to this metal, exposure to high concentration of chromium in air can trigger asthma attacks and other diseases like rhinitis, laryngitis, nosebleeds, nasal pain, pulmonary fibrosis, etc. (ATSDR, 2008).

Ingestion of small quantities of hexavalent chromium has no adverse effects on the gastrointestinal tract. However, the accidental or intentional ingestion of large quantities of Cr(VI) causes an acute gastrointestinal pain with bloody vomiting, diarrhea, blood in the feces and can cause cardiovascular collapse. If the intoxicate person survives, subsequent effects may be liver and kidney necrosis and, perhaps death (Klassen *et al.,* 2008; Demiral *et al.,* 2008).

Currently, occupational exposure to hexavalent chromium compounds, especially in the production of chromium and pigments industries, are associated with an increased risk of lung cancer, given that is considered as cancergenic and genotoxic compound (Miretzky *et al.* 2010; Saha *et al.,* 2010).

Once hexavalent chromium enters to cells, it is reduced by various intracellular agents to give reactive species as trivalent chromium. During this reduction process, different genetic damages can be produced like damage to DNA structures. Reduction of Cr(VI) can also generate oxygen radicals, inhibits protein synthesis and stop DNA replication (WHO, 1996).

O´Brien *et al.* (2003) reported that all these effects could play an integral function in the chromium carcinogenicity. Inhaled compounds of Cr(VI) can penetrate many body tissues and, therefore they have the potential to cause lung or cancer at different sites. Costa and Klein in 2006 indicated that could be a close relationship among Cr(VI) and cancer of prostate, stomach, kidney, urinary system, and bones cancer. Similarly, Seedman *et al.* 2006 reported that there is a relationship between stomach cancer and hexavalent chromium present in drinking water (Klassen *et al.*, 2008).

2.1.4 Permissible limits: Water

Because of the toxic effects of chromium, it is important to regulate the discharge of this pollutant in receiving water bodies. There are different agencies worldwide (namely WHO, EPA, SEMARNAT) responsible for establishing and enforcing environmental regulations. Mexican regulations establish that industrial waste effluents containing chromium are considered hazardous and must be disposed of or treated appropriately according to the norm NOM-052-SEMARNAT-2005.

The table 4 shows the maximum permissible levels for chromium in effluent discharges into diverse water bodies according to the actual regulations.

Table 4. Maximum permissible levels of chromium in water established by different regulations.

Environmental regulation	Maximum permissible limit (mg/L)	Description
NOM-001-SEMARNAT-1996	0.50 - 1.00	Sets the maximum permissible levels of pollutants in discharges in sewage waters and national properties.
NOM-002-SEMARNAT-1996	0.50	Sets the maximum permissible levels of pollutants in discharges of wastewater to urban or municipal sewage systems.
NOM-127-SSA1-1994	0.05	Establishes the maximum permissible levels for drinking water and treatments that must be applied for such purpose water purification.
WHO	0.05	Guidelines for drinking-water quality.
EPA	0.10	U.S EPA 40 CFR Parts 141, 142 and 143, National Primary Drinking Water Regulations.

2.1.5 Technologies developed for removing chromium from water

Different treatment technologies have been developed for the removal of chromium from wastewater, in order to comply with the maximum permissible limits according to the applicable regulation and to reduce the toxicological effects of chromium after effluent discharge in water bodies.

The most common methods of treating wastewater contaminated with heavy metals include chemical precipitation, ionic exchange, membrane separation, electrocoagulation, chemical reduction and/or oxidation, reverse osmosis, evaporation recovery processes as well as the adsorption processes, among others (Blázquez *et al.,* 2009; Singha *et al.,* 2011; Ertugay *et al.,* 2008). Table 5 shows a comparative study of conventional methods used for the removal of heavy metals from wastewater.

Table 5. Methods for removing metal ions from wastewater (Farroq *et al.,* 2010).

Method	Advantages	Disadvantages
Chemical precipitation	• Simple • Inexpensive • Most metals can be removed	• Large amounts of sludge is generated • Waste disposal problems
Chemical coagulation	▪ Sludge sedimentation ▪ Dehydration	▪ High cost ▪ High consumption of chemical reagents
Ionic exchange	• Excellent regeneration of materials • Selective	• Fewer ions removed • High capital costs
Adsorption		
By activated carbon	▪ Most of metals can be adsorbed ▪ High efficiency (>99%)	▪ Cost of activated carbon ▪ Dependence on the type of adsorbent
By zeolites	• Most of cationic metals can be adsorbed • Relatively less cost of materials	• Low efficiency
Ultrafiltration y Membrane processes	▪ Lower production of solid waste ▪ Lower consumption of chemical reagents ▪ High efficiency (>95% for a single metal)	▪ High initial capital and operating costs ▪ Low flow rates ▪ Percentage of removal decreases with the presence of other metals

The most frequently used method for control of discharges of Cr(VI), after a reduction processes, is the chemical precipitation method, but have disadvantages such as poor selectivity, continuous consumption of chemicals and sludge production increasing the total cost of disposal of solid waste (Kumar *et al.* 2011).

In general, these treatment processes have considerable limitations such as incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent and energy requirements, and generation of toxic sludge or other waste product requiring final disposal (Ertugay *et al.,* 2008).

Furthermore, the ion exchange is a better way for the treatment of heavy metals containing effluents; however, ion exchange is not economically viable due to high cost of the polymeric resins compared to adsorption processes, in which the price of activated carbon in less than polymeric resins (Jung *et al.,* 2013; Leyva, 2007).

2.2 Adsorption processes

The adsorption phenomenon is a mass transfer operation that allows the selective removal of a pollutant (adsorbate) present in a fluid (aqueous o gas) on a solid surface (adsorbent) that has a high affinity for the adsorbate (Metcalf & Eddy, 2004).

A number of adsorbent materials have been tried for metal ions removal including activated carbon, zeolites, activated alumina, synthetic polymers and silica gel among others, but the last three adsorbents are less common used in adsorption processes because of their high cost (Metcalf & Eddy, 2004).

Moreover, the adsorption is defined as the concentration or accumulation of a solute on the surface of a solid, caused by disequilibrium of the surface forces. On the other hand, adsorption can be defined as a process where atoms in a solid surface, attract or retain molecules of other compounds by electrostatic forces as depicted in Figure 5; these attraction forces are known as Van der Waals forces (Crittenden *et al.,* 2005).

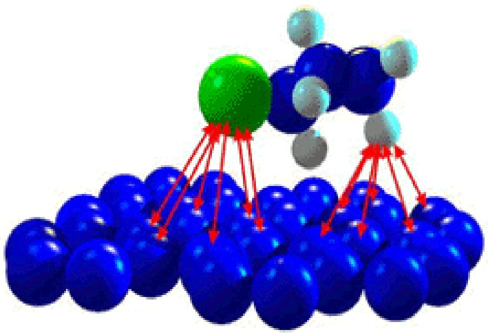

Figure 5. Scheme of adsorption process by electrical forces.

Taking into account that adsorption phenomenon occurs on the surface of the adsorbent, high surface area would enable the better performance of the adsorbent. Nevertheless, the adsorption process is also strongly influenced by the functional groups present in the adsorbent surface.

Other forces involved in the adsorption process are dipole-dipole and dipole-cuadropole interactions, London or van der Waals dispersion forces, covalent bonding and hydrogen bond formation as shown in Table 6 (Coneey, 1998; Critteden *et al.,* 2005).

Table 6. Active forces in the three interfaces involved in the adsorption processes.

Force	**Approximate Energy of Interaction, kJ/mole**	**Interface**		
		Adsorbate/ adsorbent	**Adsorbate/ Water**	**Water/ adsorbent**
Coulombic repulsion	>42	Yes	No	No
Coulombic attraction	>42	Yes	No	No
Ionic species - neutral species attraction		Yes	No	No
Covalent bonding	>42	Yes	No	No
Dipole – Ion species attraction	<8	Yes	Yes	Yes
Dipole –dipole attraction	<8	Yes	Yes	Yes
Dipole – Induced dipole attraction	<8	Yes	Yes	Yes
Hydrogen bonding	8 – 42	Yes	Yes	Yes
Van der Waal´s attraction	8 – 42	Yes	Yes	Yes

Adsorption is classified depending on chemical or physical interaction type between the adsorbate and adsorbent surface. Physical adsorption is a reversible phenomenon which results from intermolecular forces of weak electrostatic attraction between complexes from solid surface and molecules of the adsorbate. The molecules do not adsorb on a specific site on the surface and they can move freely in the interfase.

This kind of adsorption occurs at low temperatures and is characterized by an exothermic heat very similar to condensation heat (Leyva, 2007; Bottaniand *et al.,* 2008). Chemical adsorption is due to a chemical interaction between the specific surface complexes of the adsorbent and adsorbate molecules, typically occurs at high temperatures (> 200^{o}C) and a high activation energy (10-100 Kcal/gmole); involves formation of chemical bonds and, generally, it is irreversible. Additionally, the adsorption heat is very high and similar to the heat of chemical reaction (Leyva, 2007; Cooney, 1998).

Adsorption in liquid phase is caused by interactions between solute in solution and functional groups on the surface of the solid adsorbent. The main factors affecting adsorption are the following (Leyva, 2007; Metcalf & Eddy, 2004; Crittenden *et al.,* 2005; Cooney, 1998):

a) Texture properties of the adsorbent such as specific surface area, average pore diameter and pore volume, physical and chemical properties of the adsorbent such as surface charge distribution, which depends on the type and the quantity of functional groups on the adsorbent surface; and the chemical composition of the adsorbent, among others.
b) The chemical and physical characteristics of the adsorbate, for example: molecule size, polarity, solubility, chemical composition and concentration of adsorbate in solution.
c) The characteristics of the liquid phase, such as pH, temperature, ionic strength and polarity.

Adsorption has evolved as a cost effective method for removing chromium. Among the most commonly used adsorbents for removing chromium from aqueous solutions are activated carbon and polymeric resins.

Activated carbon and polymer resins have a high capacity for removing metal ions from aqueous solution, and activated carbon present a superior chemical stability than other adsorbents materials (zeolites, metal oxides and biosorbentes such as chitin, chitosan, seaweed, etc.) (Fang *et al.,* 2007). Special characteristics of activated carbon like high surface area, pore structure, high adsorption capacity, functional groups and high chemical stability make it a versatile adsorbent. In addition, saturated activated carbon can be regenerated and reused once again and the recovered pollutant can be return to the process where it was generated.

Otherwise, it has been reported the use of metal oxides to remove Cr(VI) from aqueous effluents and they have shown to be highly efficient; however, this adsorbent cannot be used in continuous systems because of the high pressure drop in packed bed columns and, additionally, separation of metal oxide adsorbents used in batch systems is not easy due to the small particle size (Arrigo *et al.,* (2010).

More recent applications of metal oxides as adsorbents include anchorage of metal oxide particles in porous materials by different impregnation techniques, for example: chemical precipitation (Vitela *et al.,* 2013), incipient wet impregnation (Kuo & Bembenek, 2008), synthesis processes *in-situ* and *ex-situ* (Cannon *et al.,* 2008) as well as forced hydrolysis processes (Sarkar *et al.* 2012).

2.2.1 Activated alumina

Activated alumina is a semi-crystalline inorganic porous material constituted essentially by aluminum oxide. It is a compound that present a high surface area, mechanical strength and amphoteric character, aluminum oxides are found in several crystalline forms. The principal phase of the activated alumina used as adsorbent is the gamma alumina ($\gamma - \mathrm{Al_2O_3}$).

Activated alumina is prepared from aluminum salts (Table 7) through many processes. It is very important to properly control the process of preparation and activation since the products of the reaction can be multiple in term of crystalline structure and adsorption capacity (Singha *et al.,* 2011).

Table 7. Salt of aluminum for the production of activated alumina (Naiya *et al.,* 2009).

Mineral name	Chemical composition	Crystallographic Designation
Gibbsite	Aluminum trihydroxide	γ- Al(OH)$_3$
Bayerite	Aluminum trihydroxide	α- Al(OH)$_3$
Nordstrandite	Aluminum trihydroxide	Al(OH)$_3$
Boehmite	Aluminum hydro(oxide)	γ-AlOOH
Diaspore	Aluminum hydro(oxide)	α- AlOOH
Pseudoboehmite	Aluminum hydro(oxide)	$Al_2O_3(1.3\text{-}1.5)H_2O$
Corundum	Aluminum oxide	α - Al_2O_3

Activated alumina can be prepared by two methods: i) thermal dehydrolixation of aluminum hydroxides and ii) thermolysis at elevated temperatures of hydrated aluminum salts. Hydroxides and oxyhydroxides of aluminum are generally precursor substances to prepare activated alumina with a great adsorption capacity (Leyva, 2007). The basic method of preparation of $\gamma - \mathrm{Al_2O_3}$ consist of a dehydration of hydrated aluminum oxides at relatively low temperatures (300 to 700^{o}C).

The values of specific area and diameter of pores of the activated alumina area are from 150 to 500 m^2/g and from 3 to 12 nm, respectively, and these depend on the preparation method. An elemental analysis of the activated alumina reveals that is constituted basically by aluminum oxide (Al_2O_3), and it can contain impurities like Na_2O, Fe_2O_3 and SiO_2 (Leyva, 2007).

Activated alumina have a wide variety of industrial applications such as gas desiccant, catalysts support and catalyst in different chemical reactions (hydrodesulfuration, cracking, reforming and isomerization of hydrocarbons of petroleum, among others). In addition, activated alumina is a very effective adsorbent to remove certain trace elements present in gases and liquids. Due to the pH_{pzc} of the activated alumina around 6.2 to 8.9, it is mainly employed for the removal of anions (arsenate [$HAsO_4^{-2}$], fluoride [F^-], phosphate [PO_4^{-3}], and selenate [SeO_4^{-2}]) present in aqueous solutions. The main applications of activated alumina are the removal of arsenate and fluoride anions from drinking water for human consumption (Swarupa *et al.,* 2006; Tingzhi *et al.* 2008).

2.2.2 Polymeric resins

Many macroreticular commercial polymers are based on synthetic polymers such as styrene and acrylic ester, among others. These polymeric matrices are characterized by the presence of functional groups that contain O, N, S and P (Figure 6) which are able to form complexes with metal ions. This special characteristic gives the polymeric resins properties of being used as ion exchangers (Pilsniak *et al.,* 2007). Ion exchange resins are used for water treatment since they can be easily regenerated and the adsorbed chemical pollutants can be recovered. In some industrial fields, the polymeric resins are used because they can be designed for specific separations (Annesini *et al.,* 2007).

Particularly, ion exchange resins contain selective functional groups which are very useful to ion separation of noble metals from aqueous solutions (Pilniak *et al.,* 2007). Currently, there is a raising interest in polymeric porous resins as especial adsorbent for the removal of volatile organic compounds from contaminated gas streams (Liu *et al.,* 2009; Long *et al.,* 2013). Table 8 shows a comparison of the main adsorbents used to remove Cr(VI) from aqueous solutions.

Table 8. Analysis of the main adsorbents used in the hexavalent chromium removal.

Adsorbent	pH	% Removal	Q (mg/g)	Reference
Activated alumina	2	97.44	-	Bishnoi *et al.,* 2004
Granular activated alumina	4	99.00	7.44	Mor *et al.,* 2007
IRN77 resins	2.75	95.00	35.38	Rengeraj *et al.,* 2001
Amberlite resin	6.9	-	52	Bhatti *et al.*, 2013
Activated rice husk carbon	2	93.28	-	Bishnoi *et al.* (2004)
Activated charcoal	2	99.00	12.87	Mor *et al.* (2007)

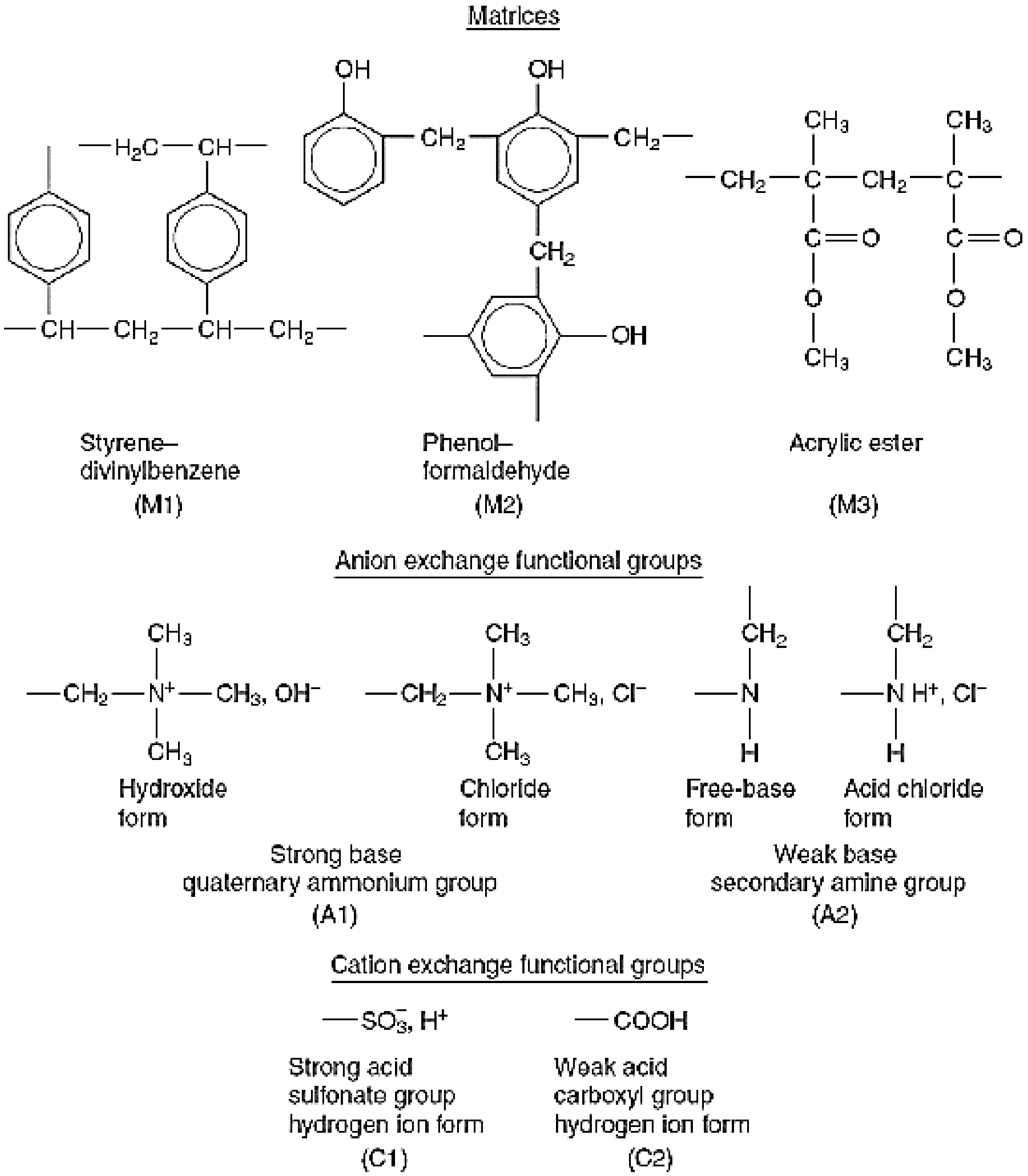

Figure 6. Polymeric matrices and functional groups of ion exchange resins [García *et al.* (2009)].

2.2.3 Activated carbon

Activated carbon (AC) is a material having a lattice crystal structure similar to graphite. It has a highly porous surface with small amounts of heteroatoms of oxygen, hydrogen and nitrogen which are chemically bonded. Carbon is the principal constituent of activated carbon making up between 85% and 95% in weight of the adsorbent material. Also, AC exhibits a wide range of pore sizes, classified as shown in Table 9, from visible cracks until openings of molecular dimension cracks [Bottaniand & Tascón (2008)].

Table 9. Classification of pores size according to the IUPAC [Schultz *et al.* (1999)].

Type of pore	Pore diameter, *d* (nm)
Macropores	$d > 50$
Mesoporos	$2 \leq d \leq 50$
Micropores	$d < 2$
Ultramicropores	$d < 0.7$
Supermicropores	$0.7 \leq d_o \leq 2$

Note: d_o is the pore width, for pore type slot; ***d*** is the diameter of pore, for cylindrical pores.

Activated carbon is known as an effective adsorbent due to its high developed porosity, high surface area (up to 3000 m^2/g), variable characteristics of chemical surface and a high degree of surface reactivity [Elizondo (2009)]. Currently, activated carbon is widely used as catalyst, catalytic support and adsorbent. Activated carbon as adsorbent can be used for the removal of a wide variety of species like organic substances, metal ions, and other pollutants in liquid or gaseous phase as well as it is used in purification and recovery of chemical species [Elizondo (2009), Dias *et al.* (2007)].

Activated carbon presents some advantages compared with other adsorbents such as silica, zeolites and porous polymers. Generally, activated carbons are cheap, heat and radiation resistant, stable in acid and basic solutions; they show good mechanical resistance, not expand or contract by effects of changes in pH and AC adsorbents are economically effective from the point of view that can be regenerated, while the silica are degraded at high pH values whereas zeolites are dissolved at acidic pH values and they are usually rather efficient and expensive in terms of regeneration because of its small size of pore structure. In addition, porous polymers structures show contractions or expansion by pH variation and the cost of these adsorbents is higher than activated carbons [Yang *et al.* (2007), Yue *et al.* (2009)].

Adsorption in aqueous phase of organic and inorganic compounds has been one of the most important applications of the activated carbon. Rivera-Utrilla *et al.* (2001) reported that about 80% of total produced activated carbon is used in liquid phase applications. When activated carbon is contacted with an aqueous solution, an electric charge is released. This charge is result of the dissociation of functional groups attached to the surface of activated carbon or by ions adsorption from solution, and the electric charge strongly depends on pH of solution and adsorbent surface characteristic [Li *et al.* (2002)].

The central topic of ions adsorption in aqueous medium is the understanding of the mechanism by which ionic species begin to adhere onto carbon surface. There are three different mechanisms by which metal ions (or other ions) are removed from aqueous solutions [Dias *et al.* (2007)].

The first mechanism is based on electrostatic interactions between adsorbate and adsorbent being totally dependent on the existence of functional groups on carbon surface, especially oxygenated surface complexes (ion exchange process). The second mechanism suggests an improvement in the potential for adsorption, as what happened due to the narrowness of microposority which can be strongly sufficient to adsorb and retain ions. The third mechanism is based on the concept of acid and bases, strong and weak, consequence of the amphoteric nature of the carbon surface [Elizondo (2009), Dias *et al.* (2007)].

Natural and synthetic precursors have been used for manufacturing activated carbon. Carbonaceous natural precursors consist of wood, coal, lignite, peat, coconut shells, rice husks, bones, sawdust, etc., while synthetic precursors include polymeric materials such as nylon, rayon, cellulose, phenolic resins, polyacrylonitrile resins, etc. [García *et al.* (2009)].

Activated carbon manufacturing begins with pyrolityc carbonization of raw precursor materials. During carbonization step many of the non-carbon elements (such as oxygen, hydrogen and nitrogen) are eliminated as volatile products in the pyrolitic decomposition of the precursor and the remaining residues promote the formation of graphite. Residual atoms of carbon are staked in a system of flat sheets of aromatic rings that are united randomly [Leyva (2007), Elizondo (2009)].

This arrangement of sheets is irregular and therefore leave interstitial spaces between them. Pores are formed from these interstitial spaces. In the carbonization step, these spaces can be filled with tarred materials or products of pyrolysis and they can be blocked by free carbon atoms. At the same time or after carbonization, an activation step is required to develop a highly porous structure [Leyva (2007)].

Activation of carbon may be physical or chemical. Physical activation, is also called thermal activation, involves the carbonization at 500-600 °C to eliminate most of the volatile matter followed by a partial gasification between 800 °C and 1000 °C in the presence of an oxidizing gas (steam, carbon dioxide, air or a mixture of gases) to develop porosity and to increase surface area [Yang *et al.* (2007)].

Chemical activation involves the incorporation of inorganic additives, metal chlorides such as chloride of zinc or phosphoric acid in the precursor before carbonization, this process is performed generally at lower temperatures (400-600 °C) than physical activation. Chemical agents helping to develop porosity in activated carbons, mainly from dehydration and degradation of carbon surface [García *et al.* (2009)]. The best advantages of chemical activation are high performance, low activation temperature (less energy costs), less activation time, usually, develops a higher porosity, nonetheless has some disadvantages as additional cost for activate agents and an additional washing step is also necessary for removing residual chemical agents [Elizondo (2009)].

Characteristic of activated carbon depend strongly on both the precursor material as well as activation method (activation conditions and temperature employed), among other factors. Figure 7 depicts a scheme of chemical surface of activated carbon.

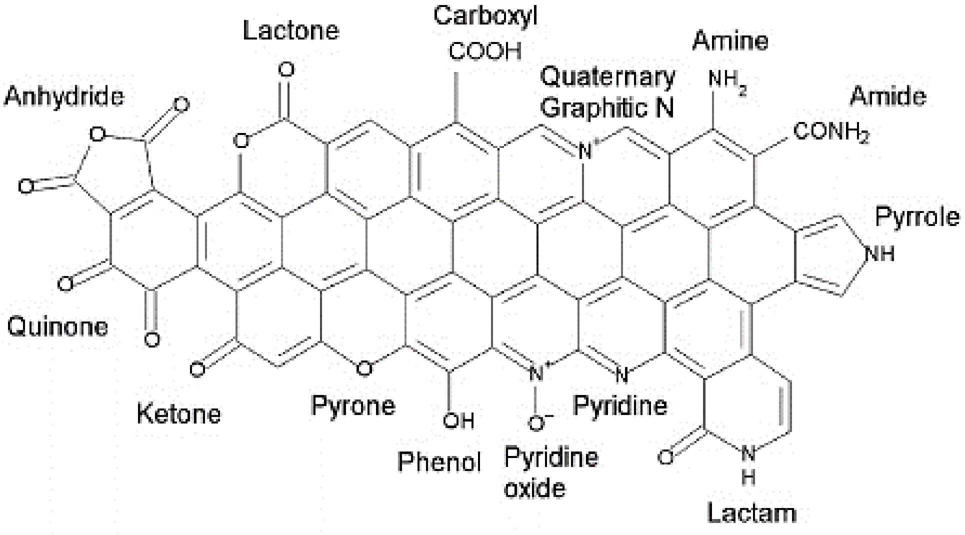

Figure 7. Scheme of chemical surface of activated carbon [Arrigo *et al.* (2010)]

On the surface of carbonaceous material, particular carbon atoms of the edge of the basal planes, can be found predominantly combined in greater or lesser proportion with others atoms different from carbon (heteroatoms), giving place to different surface groups. These activated carbon present functional groups that can be acid or basic depending on its behavior in solution. Most of them are oxygenated groups, due to the tendency of the carbons to be oxidized even at room temperature. Delocalized electrons of π orbitals play an important role in the surface chemistry of activated carbons [Sevilla (2012)].

The surface of activated carbon is mainly non-polar, but its surface presents the interesting and advantageous feature to be easily modified by heteroatoms (oxygen, nitrogen, hydrogen, phosphorus, sulfur, etc.) [Mohd *et al.* (2010)].

Oxygen is the most important heteroatom which forms covalent bonds with carbon; however, carbon-oxygen bonds are less stables than carbon-hydrogen bonds. Chemisorbed groups that contain oxygen in the edges of the graphene layers (see Figure 8), give acid properties to activated carbon and allow the property of cation exchange.

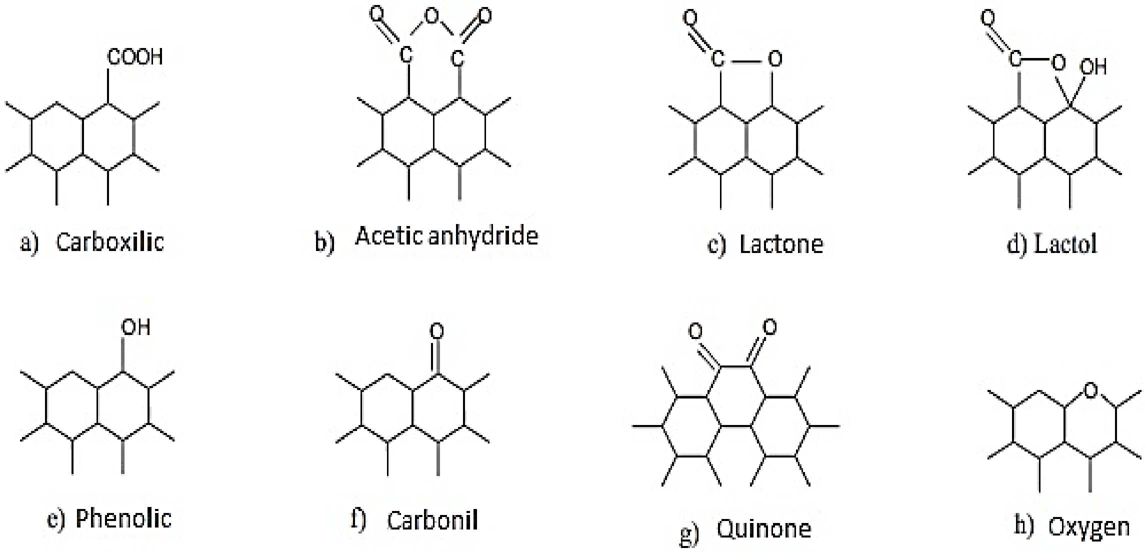

Figure 8. Chemisorbed acid groups on the edges of the layer of graphene [Leyva (2007)].

Surface groups which carbon-oxygen bonds are quite important and have great influence on surface properties such as: wettability, polarity and acidity besides physicochemical properties such as catalytic, electrical and chemical reactivity.

It has been reported that carboxylic groups increase by chemical oxidation of activated carbon with nitric acid or activation of AC by air at high temperature. In both cases, oxidized AC improved the adsorption capacity of metal cations from aqueous solutions [Jaramillo *et al.* (2010)]. Nevertheless, an increment in the content of oxygenated functional groups can modify the porous carbon texture because they can block some of the micropores decreasing accessibility to porous network, while thermal treatment at high temperature eliminate surface functional groups and cause a collapse of the porous texture diminishing the volume of pores [Sevilla (2012)].

Dissociation of acidic functional groups such as carboxylic, lactone and phenolic provoke a negative charge on the adsorbent surface as shown in Figure 9 [Yang *et al.* (2007)]. These ionized functional groups could adsorb positive charged metal cations or dyes from aqueous solutions.

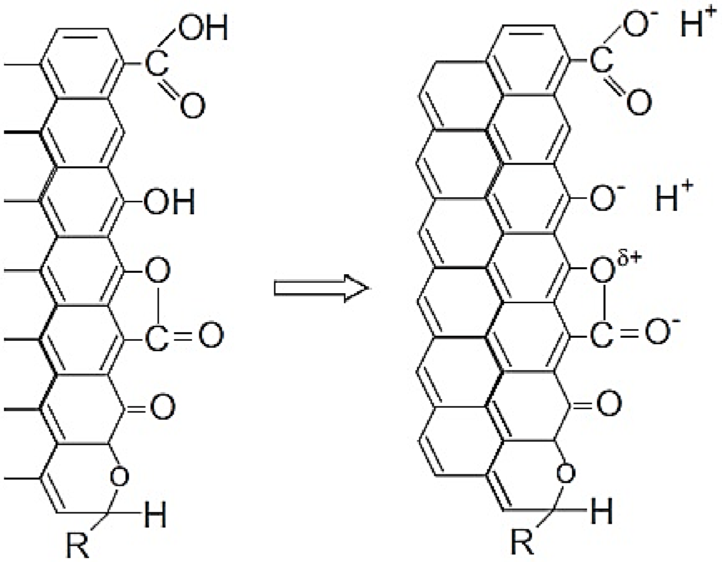

Figure 9. Dissociation of acidic functional groups on activated carbon [Leyva (2007)].

Basic behavior of the activated carbon surface is usually caused by certain functional groups containing oxygen atoms such as pyrone, superoxide ions (O_2^-) and also groups containing nitrogen including pyridine, quaternary ammonium, nitrogen oxides, nitriles, amines, amides, etc. [Mohd & Hossein (2010)]

Some other oxygen containing groups like chromene and diketone (Figure 10) have been reported to contribute to the basic character of the activated carbon. On the other hand, non-polar surface of the activated carbon has basic properties originated from π electrons of carbon rings.

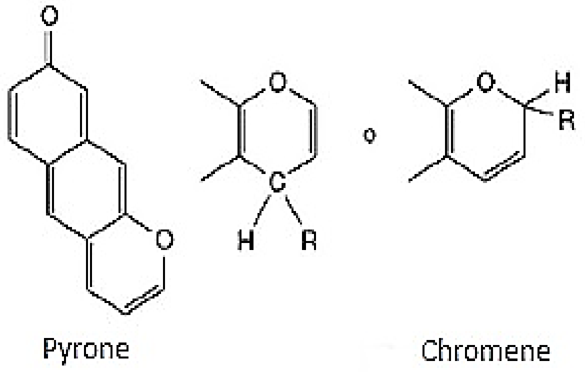

Figure 10. Possible basic groups in activated carbon [García *et al.* (2009)].

Nitrogen groups that are covalently bound to the activated carbon surface (Figure 11) remain at the AC surface after a thermal treatment at elevated temperatures (lower than 1200K).

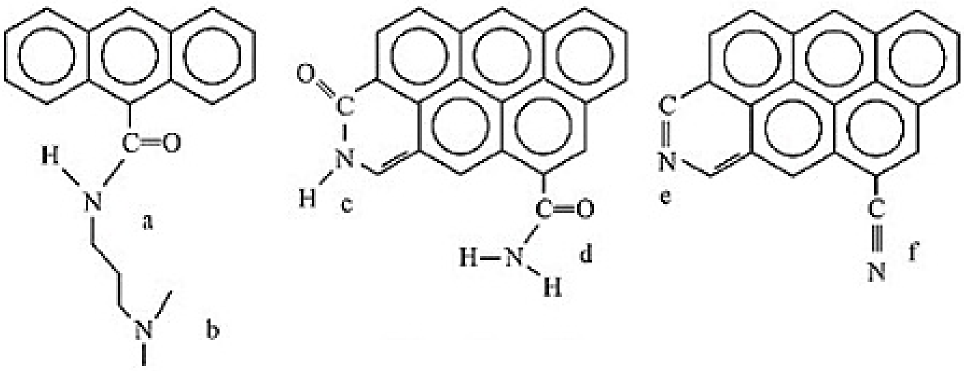

Figure 11. Types of nitrogen groups (a) and (d) amide groups, (b) tertiary amines, (c) lactams, (e) type pyridine – pyrrole, (f) nitriles [Mohd *et al.* (2010)].

Some basic groups (Brönsted-Lowry bases) tend to attract protons when they are found in an acid medium. The behavior of basic groups can be used as adsorption sites of anionic species. Surface charge of an adsorbent depends on the quantity of acid and basic functional groups. The pH at the point of zero charge (pH_{PZC}) from an adsorbent is acid when the concentration of acid sites is greater than that of the basic sites and viceversa [Leyva (2007)].

When activated carbon acquires negative net surface charge, the cation species adsorption will be preferred, but anion pollutants adsorption is enhanced on positively-charged activated carbon. Taking into account that effluent pH values is not always an easy task and implies an increment in the total cost of water treatment, it is preferred to modify the surface chemistry of activated carbon to increase the pollutants adsorption [García *et al.* (2009)]. For these reasons, sometimes may be necessary to optimize the porous texture and/or incorporate functional groups on activated carbon surface retaining particles of interest [Yang *et al.* (2007)].

2.2.1.1 Activated carbon treatments

Activated carbon is modified by several treatments to incorporate or eliminate functional groups, and to modify its chemical surface. When the surface of an adsorbent is modified, new functional groups are created on the AC surface and they change the physical and chemical properties of the adsorbent. In addition, these modifications provide thermal stability, and reactivity of the AC. It is important to mention that AC new features depend on the nature of the modified or attached surface groups [Zhao *et al.* (2005); Mohd *et al.* (2010)].

Oxidation process is mainly used to incorporate functional groups containing oxygen on the activated carbon surface. It is believed that oxidation reactions probably occur in the aliphatic chains of the activated carbon surface or in peripheral carbon atoms because these sites are highly susceptible to be oxidized. Generally, oxidation increases the acid groups and decrease basic groups. However, Sayed *et al.* (2004) have been reported, as a strange case, a slight increment in basic functional groups as well as acid functional groups by chemical oxidation of AC with nitric acid because of incorporation of nitrogen and oxygen on the adsorbent surface.

Oxidation of the activated carbon may be categorized into two methods: dry and wet oxidation. In Dry oxidation, the adsorbent is in contact with oxidizing gases such as steam, carbon dioxide, oxygen, ozone and usually takes place at elevated temperatures (greater that 970 K). In wet oxidation, activated carbon reacts with a solution of oxidizing agents such as nitric, sulfuric or a mixture of acids, under moderate concentration and temperature conditions [Mohd *et al.* (2010), Rivera *et al.* (2011)].

Oxidation of activated carbon with air or oxygen can increase the ketone and phenolic groups, or hydroxyl and carbonyl groups. Similarly, it was reported that oxidation of AC by ozone keeps the adsorbent texture, but oxidation creates large quantities of carboxylic groups on AC surface. Nonetheless, ozonation treatment decreases the surface area and pore volume of activated carbon [Mohd *et al.* (2010), Valdés *et al.* (2011)].

Nitrogenation is another common treatment applied to the activated carbon to protect the environment by the removal of sulfur compounds, nitrogen oxides and carbon dioxide; in catalysis applications as catalyst or catalytic support; and in electrochemistry for the electrodes manufacturing, cells and batteries [Rivera *et al.* (2011)]. Nitrogenation of activated carbon increases its basicity which is strictly required in adsorption and catalytic processes. This treatment significantly increases the surface polarity and therefore, specific interactions with polar adsorbates are possible [Saleh *et al.* (2011)].

Ammonia have been used to incorporate nitrogen atoms in activated carbon, before or after oxidation with nitric acid (amination) or a mixture of gases of air – NH_3 (ammoxidation). In addition, HCN, HNO_3, urea, diocyanoamine, melanin, polyaniline have been used for nitrogenation of activated carbon. Depending on the used reagent, the nitrogenation treatment can be performed in gas (ammonia, cyanuric acid, amines) or liquid phase (nitric acid, urea) [Rivera *et al.* (2011), Saleh *et al.* (2011)]

Generally, nitrogenation process consist of one or two consecutive stages in which the activated carbon is oxidized first in liquid phase and later nitrogen is added to AC in liquid or gas phase [Rivera *et al.* (2011)]. It has reported ammonia treatment develops surface area and microporosity of AC. As a consequence of this treatment, nitrogen containing functional groups are covalently bound to the activated carbon surface. Moreover as a consequence of the nitrogenation gets forming nitrogenized functional groups on the activated carbon surface. Table 10 shows several treatments for binding specific functional groups on activated carbon.

Table 10. Treatments applied to modify activated carbon chemistry surface.

Treatment	Modification	Reference
Oxidation		
HNO_3	Increase of acid and basic groups.	Sayed *et.al.* (2004)
H_2O_2	Increased surface area and surface oxygenated groups.	Domingo *et.al.* (2000)
Air	Increase in phenolic and ketone groups.	Figuereido *et.al.* (2000)
Ozone	Increase of carboxylic groups, decreases surface area and pore volume.	Jaramillo *et.al.* (2002)
Heating under hydrogen atmosphere	Decomposition of oxygenated groups, increase in basicity.	Agulai *et.al.* (2003) Bandosz *et.al.* (2006) Ríos *et.al.* (2007)
Nitrogenation		
NH_3	Increase of amine, nitriles, pyridines, and amines, lactams, and imides groups.	Vinke *et.al.* (1994) Biniak *et.al.* (1997) Abe *et.al.* (2000) Przepiórski *et.al.* (2004) Przepiórski *et.al.* (2006)
HCN	Increase of amine and nitrile groups.	Stöhr *et.al.* (1991) Jansen & Bekkam (1994)
Urea	Increase of pyridine, pyrroles, N quaternary.	Bashkova *et.al.* (2003) Stavropoulos *et.al.* (2008)

Table 10. Treatments applied to modify activated carbon chemistry surface (continued).

Treatment	Modification	Reference
Sulfuration		
H_2S	Increase of the content of sulfur, slight decrease in pore volume.	Feng *et.al.* (2006)
SO_2	Decrease in surface area (BET), increase in the average diameter of pore, formation of bonds C=S.	Tajar *et.al.* (2009)
Na_2S	Decreases the surface area, increase the content of sulfur about 7.3% in weight, formation of bonds C=S, S=O, S-S.	Valenzuela *et.al.* (1990)

2.3 Forced Hydrolysis

Metal oxides and hydroxides (e.g. iron, zirconium, titanium, manganese, aluminum, etc.) have been tried as adsorbents and researchers have reported high efficiencies towards anionic species from aqueous solutions [Beker at al. (2010), Nieto *et al.* (2012)].

Due to the high adsorption capacity, availability and low cost, iron hydro (oxide) have been widely used. Some researchers have synthetized with success granular ferric oxides (GFO) with surfaces around 250 m^2/g; however, there are some disadvantages for its applications adsorbent, for instance: the mechanical resistance of GFO must be improved; high pressure drops are reached when GFO are packed in columns and loss of adsorbent is possible in continuous operation. On the other hand, if GFO are used in batch operations, the adsorbent recovering is not an easy task [Music *et al.* (2004), Arcibar *et al.* (2012)].

An interesting option to overcome these shortcomings is the anchorage of metal hydro (oxides) on the activated carbon surface. Methodologies used for anchoring metal oxides particles on activated carbon include evaporation of iron salt in presence of the support, incipient wetness impregnation at room temperature using aqueous or organic solutions; iron precipitation with alkali solutions as well as forced hydrolysis processes of ferric salts.

Iron particles impregnation techniques allow the formation of iron hydro(oxides) nanocrystals on the activated carbons and these anchored particles increased the adsorption capacity of anion species such as hexavalent chromium [Nieto *et al.* (2012), Arcibar *et al.* (2012)].

Synthesis of iron oxides nanoparticles is widely described in literature. However, most of these techniques require voluminous chemical products such as tensoactives, chelating agents, and organometallic compounds which have a low level of diffusion in the pores of the activated carbon. Nevertheless, among the other options, forced hydrolysis (also called thermal hydrolysis) is a simple route that allows the synthesis of iron hydro(oxide) nanoparticles inside the pores of the activated carbon without the use of additional chemical products [Shultz *et al.* (1999), Music *et al.* (2004), Wang *et al.* (2008), Muñiz *et al.* (2009)].

In forced hydrolysis a metal cation in solution is heated promoting the metal ions agglomeration until the formation of a solid phase on the support. Depending on the experimental conditions for forced hydrolysis (temperature, metal concentration, time of hydrolysis, pH, mass/volume ratio, etc.), crystalline phases and the particle size are formed on the porous support material (Figure 12). If the iron hydrolysis is carried out in the external surface of the activated carbon, it is expected that certain quantity of the iron hydro (oxides) particles will link to the activated carbon surface [Shultz *et al.* (1999), Wang *et al.* (2008)].

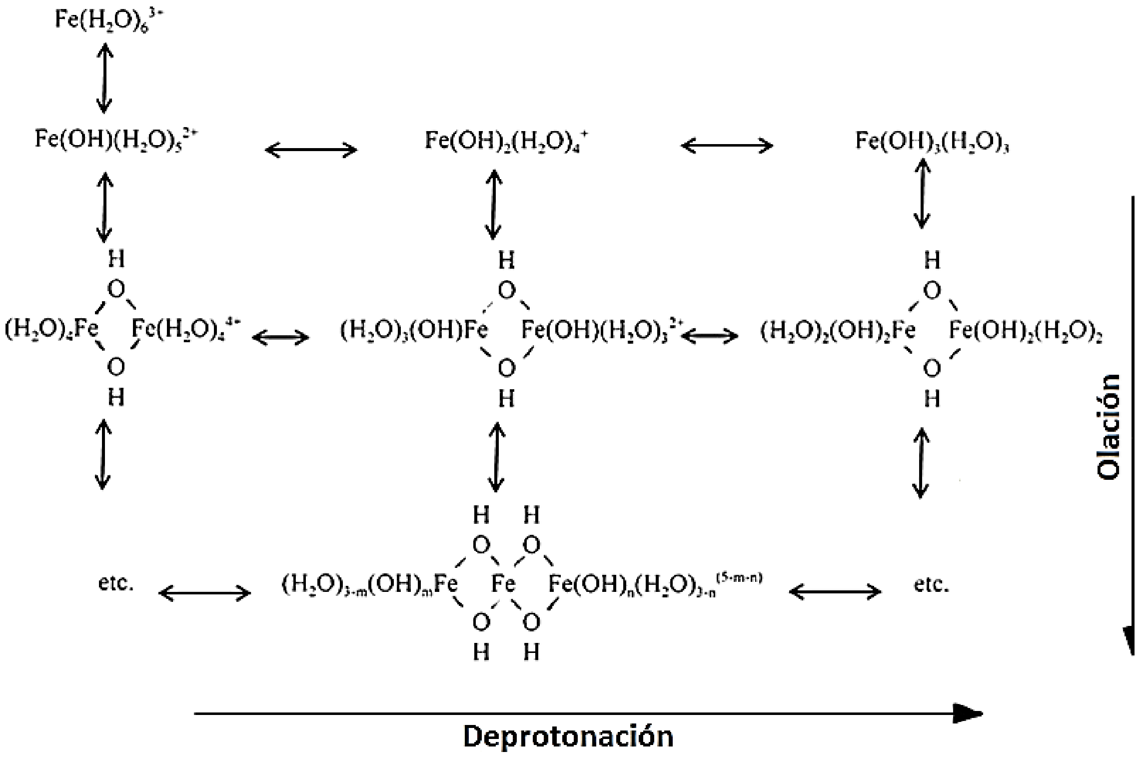

Figure 12. Pathway for the synthesis of iron hydro (oxides) nanoparticles by forced hydrolysis [Shultz *et al.* (1999)]

Recent studies have used the method of forced hydrolysis to bind iron oxides particles on the activated carbon surface; however, the influence of functional groups of the activated carbon to anchoring iron oxides nanoparticles by forced hydrolysis have not been studied as well as its potential use as adsorbent for the removal of hexavalent chromium from aqueous solutions.

2.4 Motivation of this research

The use of activated carbon as adsorbent of metal cation pollutants in water is the preferred method when these pollutants are present at trace concentrations levels. On the other hand, metals oxides have a high adsorption capacity of anionic species, but they are used only once and they are not totally recovered from the treated effluent limiting its application in real systems because of the increment in operation cost of the process.

According to the above-mentioned reason, to immobilize iron nanoparticles onto activated carbon is of great interest because it will allow regenerating the saturated adsorbent, to reuse the regenerated adsorbent and to recover the adsorbate to perform the adsorption process as an attractive economically alternative. Additionally, it is possible to reduce the environmental impact of pollutants into receiving aquatic streams and, at the same time complying with the federal regulations about the maximum permissible levels of pollutants.

2.5 Hypothesis

The activated carbon functional groups allow anchoring iron hydro(oxides) particles in the adsorbent surface by forced hydrolysis and dispersed particles increases the Cr(VI) adsorption capacity greater than commercial activated carbon.

2.6 Objectives

2.6.1 General Objective

To evaluate the effect of activated carbon functional groups on the anchoring of iron hydro(oxides) particles by forced hydrolysis and to determine its potential use for the removal of hexavalent chromium from aqueous solutions.

2.6.2 Specific objectives

- To modify the activated carbon functional groups by chemical and thermal treatments.
- To anchoring iron hydro(oxides) particles on raw and modified activated carbon by forced hydrolysis.
- To characterize the raw, modified and impregnated activated carbons by instrumental (FTIR, SEM, XRD, N_2 physisorption) and conventional (Boehm titrations) techniques.
- To conduct adsorption-desorption experiments of Cr (VI) in batch systems using the raw, modified, and impregnated activated carbons.
- To carry out experiments adsorption kinetics of Cr(VI) in batch system with the selected adsorbents.

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CHAPTER 3

Materials & Methodology

> **“I have learned that success is to be measured not so much by the position that one has reached in life as by the obstacles which he has had to overcome while trying to succeed”**
>
> *Bokker T. Washinton*

3.1 Techniques used to characterize the activated carbon

3.1.1 Boehm titration method

Traditionally called “Boehm titration” have been used as chemical method to identify oxygenated surface groups on carbon materials. Boehm titration acts over the principle which the oxygenated groups of the activated carbon surface have different acidity and they can be neutralized with different bases. Sodium hydroxide (NaOH) is the strongest base generally used, and it is used to neutralize all Brönsted acids (including phenols, lactone and carboxylic acid groups), whereas the use of sodium carbonate (Na_2CO_3) neutralize lactone and carboxylic groups (lactol and lactone rings), and sodium bicarbonate ($NaHCO_3$) solution neutralizes carboxylic acids groups. The difference among the neutralization of the bases may be used to identify and quantify the types of oxygenated surface groups present in the sample of activated carbon.

For applying the Boehm method, some factors have to be taken into account, for example: the mass of carbon and reaction base ratio, stirring time, CO_2 expulsion method from solutions, and titration method for the determination of the equivalence point [Boehm (2002)].

It was reported that CO_2 expulsion is conducted through boiling (or reflux), degasification with N_2 during the reaction and titration, complete titration under a N_2 atmosphere, or by subtracting the value obtained from the titration of a blank (without carbon) of the sample results [Kim *et al.* (2009), Kalijadis *et al.* (2011)].

In determining the equivalence point, several methods can be used, for instance: indicators such as phenolphthalein, methyl red and blue methylene or pH measurements of "one point" (titration is performed until the value of pH 7 is reached). Most of the experimental works have reported the use of a blank in titrations. This issue removes dissimilarities which can be achieved due to differences in the functional groups of the activated carbon as well as properties as wettability or origin of itself [Goertzen *et al.* (2010)].

3.1.1.1 Boehm titration procedure

The general titration procedure is based on the method described by Boehm. A mass of 100 mg of activated carbon was added to 25 mL of one of the three bases of reaction with concentration 0.1 N: $NaHCO_3$, Na_2CO_3, and NaOH. The samples were stirred for a week at 25^oC and after stirring the samples were filtrated to remove the activated carbon. Finally, aliquots of 10 mL from were withdrawn the filtrated samples, and they were titrated directly with 0.1 N HCl [Goertzen *et al.* (2010)].

A similar procedure was performed to determine total basic groups, but an activated carbon mass (100 mg) was added to 25 mL of 0.1 N HCl. The samples were shaken for a week at 25^oC, filtered to separate the activated carbon and subsequently the filtrate aliquots were titrated with 0.1N NaOH [Bagreev *et al.* (2004)].

3.1.1.2 Determining the quantity of surface functional groups

The equations used to determine the quantity of surface functional groups depend on the titration method: back-titration or direct titration. For a back-titration, the quantity of acid functional groups is estimated:

$$[\mathrm{HCl}]\mathrm{V}_{\mathrm{HCl}} = [\mathrm{NaOH}]\mathrm{V}_{\mathrm{NaOH}} + \left(\frac{n_{HCl}}{n_B}[\mathrm{B}]\mathrm{V}_{\mathrm{B}} - n_{\mathrm{CFS}}\right)\frac{\mathrm{V}_{\mathrm{a}}}{\mathrm{V}_{\mathrm{B}}} \tag{3.1}$$

$$n_{CSF} = \frac{n_{HCl}}{n_B}[\mathrm{B}]\mathrm{V}_{\mathrm{B}} - ([\mathrm{HCl}]\mathrm{V}_{\mathrm{HCl}} - [\mathrm{NaOH}]\mathrm{V}_{\mathrm{NaOH}})\frac{\mathrm{V}_{\mathrm{B}}}{\mathrm{V}_{\mathrm{a}}} \tag{3.2}$$

Where [B] and V_B are the concentration and volume of base of reaction mixed with the activated carbon, and n_{HCl} , n_B indicate the moles available of acid and base in the neutralization reaction, respectively. These data allow to obtain the number of moles of the base of reaction which were available to react with the functional groups of the activated carbon. The parameter n_{CSF} indicates the moles of functional groups of activated carbon that reacted with the base during the stirred stage. V_a is the volume of the aliquot which was taken from V_B, [HCl] and V_{HCl} are the concentration and volume of acid added to the aliquot of the original sample.

This parameter (n_{CSF}) provides the numbers of equivalents added to the aliquot, and available to react with the remaining base. The moles of the remaining acid are then determine by titration using a certain volume (V_{NaOH}) of known concentration ([NaOH]). In this way, through the knowledge of the remaining moles of the acid, and according to the difference of the used bases of reaction, the acid groups of the activated carbon can be quantified [Hu *et al.* (2001), Wang *et al.* (2009)].

When NaOH is used in Boehm titration and directly titrated with HCl, the following equation is used:

$$n_{\mathrm{CSF}} = [\mathrm{B}]\mathrm{V_B} - [\mathrm{HCl}]\mathrm{V_{HCl}}\frac{\mathrm{V_B}}{\mathrm{V_a}} \tag{3.3}$$

The amount of different possible surface groups (phenols, lactones, carboxylic) are quantified by the difference in the estimated quantity of the reacted equivalents from the different bases (n_{CSF}). Equivalents of NaOH reacts with all surface acid groups; therefore, the value n_{CSF} will include all surface acid groups. Because the solutions of Na_2CO_3 reacts with carboxylic and lactones groups, the difference between the values n_{CSF} from NaOH and n_{CSF} from Na_2CO_3 is equivalent to the quantity of phenolic functional groups on the activated carbon surface.

Similarly, $NaHCO_3$ solution reacts only with carboxylic groups (for this reason, it provides a direct measurement of carboxylic groups) and the difference between Na_2CO_3 and $NaHCO_3$ is the number of lactone functional groups on activated carbon. For blank solutions (without activated carbon) n_{CSF} must be equal to zero, because there are not adsorbent particles present in the solution and, therefore, no functional groups which react with the base equivalents [Kim *et al.* (2009)].

3.1.2 Elemental Analysis

Elemental composition (carbon, hydrogen, nitrogen, and sulfur) for the synthetized adsorbent materials was conducted in an elemental analyzer equipment (Permin Elmer 2400) and Thermogravimetric analysis (TA Instrument, Model SDT2960) in oxidizing atmosphere for determining the ash content for a complete characterization of the activated carbon. Oxygen percentage was obtained by difference of initial mass sample and the sum of the all determinated elements plus ash content.

3.1.3 Fourier Transform Infrared Spectrometry (FT-IR)

Infrared spectrometry is a very versatile tool that is applied for qualitative determination of molecular species. The applications of the infrared spectrometry are divided in three categories: near, middle, and far infrared. The most commonly used region is by far the mid-infrared categories which are extended from about 650 to 4,000 cm^{-1}, being the main tool for the determination of organic and biochemical species [Silverstein *et al.* (2005)].

The use of the Fourier transform for the processing of the obtained data from infrared spectrometry has been widely used, because it offers a signal/noise ratio which exceeds that of the dispersive instruments in more than one order of magnitude, also it is characterized by high resolutions (<0.1 cm^{-1}), and highly accuracy and reproducibility for the determination of the frequencies [Skoog (2001)].

Infrared analysis was performed in agreement after drying and pulverizing activated carbon samples at 100°C during 24 h. The FT-IR spectra of the samples were recorded over an interval of 400 a 4000 cm^{-1} with a total of 50 measurements (Spectrum-one Perkin Elmer).

3.1.5 Nitrogen physisorption studies

The textural properties of the activated carbon are of great relevance in order to understand if adsorbates can diffuse through the activated carbon pores. The use of nitrogen at low temperature (77.4 K) have been traditionally proposed as a probe molecule for the determination of major textural parameters such as specific surface area, micropores volume, and so on, after the application of the corresponding mathematic models [Silvestre *et al.* 2012].

To determine the specific surface area, pore volume and average diameter of porous it is required a physisorption equipment (Quantachrome Instruments, Autosorb-1). The basis of this equipment is the gas (N_2, Argon, or CO_2) adsorption method. The specific surface area analysis is obtained by the theory of Brunauer, Emmett y Teller (BET). The BET theory is based on the formation of multilayers and supposes that the adsorption heat of the monolayer is different from the rest of the other layers, which have the same adsorption heat.

To estimate the amount of the necessary adsorbed gas to the formation of a monolayer (V_m) is required the use of the following equation [Sing *et al.* (1985), Brunauer *et al.* (1938)]:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{c - 1}{V_m c}\frac{p}{p_0} \tag{3.4}$$

$$c = \exp\left\{\frac{\varepsilon_1 - \varepsilon_2}{RT}\right\} \tag{3.5}$$

Where:

P	Pressure of N_2 in equilibrium with the adsorbed gas in the adsorbent, atm.
P_0	Saturation pressure of N_2 at the experimental temperature, atm.
V	Volume of adsorbed N_2 referred at standard pressure and temperature, m^3.
V_m	Volume of adsorbed N_2 referred at standard pressure and temperature which is required to form a monolayer on the adsorbent surface, m^3.
ε_1	Adsorption heat of the first layer of N_2, cal/mole.
ε_2	Condensation heat of N_2, cal/mole.
R	Ideal gas constant, cm^3-atm/mole-K
T	Absolute temperature, K.

The specific surface area (S) of the material (BET area) is obtained once the volume of the adsorbed gas on the monolayer (V_m) is known, as the following equation [Brunauer *et al.* (1938)]:

(3.6)

$$S = \left(\frac{P_s V_m c}{RT_0}\right) N S_{N_2}$$

Where:

N	Avogadro´s number, 6.023 x 10^{23} molecules/mole.
P_s	Standard pressure, 1 atm.
S	Specific area of the adsorbent, nm^2.
S_{N2}	Projected area which occupy a molecule of N_2, 16 nm^2/molecule.
T_0	Standard temperature, 273.15 K.

The pores size distribution is performed in accordance with the method developed by Barret, Joyner and Halena (BJH method), 1951. Most specifically, the method of Dubinin-Radushkevich (DR) allows to obtain the value of micropores volume [Nguyen & Do (2001)]:

$$W = W_0 \exp\left(-\frac{K}{\beta^2 \left(RT\ln(P/P_0)\right)^2}\right) \tag{3.7}$$

Where:

W	Adsorbed volume to each relative pressure
W_0	Volume of pores
K	Constant dependent on the structure
Β	Affinity coefficient

Experimental N_2 physisorption data were obtained as follows: the sample holder of the equipment is closed with a filter seal, this holder is placed in the degasification port, and vacuum is applied until obtaining a pressure less than 100 µm Hg. Subsequently, sample holder was removed, weighed and activated carbon sample (approximately 120 mg) was placed at the sample holder.

After that, the sample holder was weighed and placed in the degassing port. The sample was degassed at 105°C until reach a vacuum less than 100 µm de Hg. Next, the sample holder containing the activated carbon was removed from the degassing port, it was weighted and the weight of the sample was calculated by difference. Finally, the sample holder was placed at the test port of the equipment and the analysis was carried out automatically.

3.2 Techniques to determine metal species

3.2.1 Hexavalent chromium determination

The determination of Cr(VI) was performed as described in the Mexican Norm NMX-AA-044-SCFI-2001, which is based primarily on a qualitative technique at one the principles of colorimetry, followed by UV-visible spectroscopy at 540 nm.

3.2.1.1 Colorimetry

The colorimetric method is useful for the determination of hexavalent chromium in natural or treated water in a concentration range of 100 to 1000 µg/L. The principle of this method is based on a oxidation-reduction reaction, where the hexavalent chromium (Cr^{6+}) reacts with 1,5-diphenylcarbazide in acid solutions to give Cr^{3+} and 1,5-diphenylcarbazone according to the following reaction [Clesceri *et al.* (1995), Dionex (1996)]

$$2CrO_4^{2-} + 3H_4L + 8H^+ \rightarrow Cr^{3+}(HL)_2 + Cr^{3+} + H_2L + 8H_2O \tag{3.8}$$

Where:

H_4L = 1,5-diphenylcarbazide

H_2L = 1,5-diphenylcarbazone

This reaction seems to be the simultaneous oxidation of the dipheylcarbazide to diphenylcarbazone, reduction of Cr(VI) to Cr(III), and the chelation of Cr(III) by diphenylcarbazone.

The actual chelate structure is unknown, but it is identified by visible absorbance using a photometric detector. To determine initial and final hexavalent chromium from aqueous solutions, aliquots were taken according the Cr(VI) content content and the calibration curve range (0.1 – 1 mg/L).

Afterwards, aliquots were transferred to volumetric flasks, and they were filled up to 50 mL with added 0.1 N sulfuric acid. Next, one ml of diphenylcarbazide solution (5 mg/mL) was added to each flask and they were stirred vigorously for one minute. Finally, samples were allowed to stand for 10 min for developing the red-violet color completely and the sample absorbance was measured at 540 nm using a spectrophotometer.

3.2.1.2 Ultraviolet-visible spectroscopy

Absorbance measurements, at both ultraviolet and visible radiation, have a wide application for identifying and determining inorganic and organic species. The UV-Vis spectroscopy is the an adequate technique for quantifying the Cr(VI) concentration in solution. The red-violet complex, a product formed during the redox reaction between Cr(VI) and 1,5-diphenylcarbazide, can be determined in an UV-Vis spectrophotometer at a wavelength of 540 nm by using a calibration curve.

Firstly, a calibration curve was constructed by measuring at least 5 volume of stock solution (5.0 µg of Cr(VI)/mL) approximately between 2.0 mL and 20.0 mL for standards in the range of 10 µg to 100 µg of Cr(VI) or a concentration range of 0.1 to 1 mg/L of Cr(VI).

Next, the procedure for color development of sample was followed. Aliquots of each standard were transferred to absorption cells of 1 cm and their absorbance was measured at 540 nm in a spectrophotometer (GENESYS 10s UV-Vis Spectrophotometer).

Calibration solutions were measured starting with the lowest concentration. Finally, a calibration curve was constructed by plotting the read absorbance vs mg/L de Cr(VI).

Before sample analysis, sample must be as clear as possible, and the colorimetric procedure of diphenylcarbazide is performed. Then, the spectrophotometer was adjusted with a blank (water with diphenylcarbazide) to zero and the sample absorbance was measured at 540 nm. Finally, absorbance measurements were recorded and the mg/L of Cr(VI) present in the sample were determined directly from the calibration curve as follows:

$$\mathrm{X} = \frac{\mathrm{Y} - \mathrm{b}}{\mathrm{m}} \tag{3.9}$$

Where:

m	Slope of the calibration fitting curve
b	Y intercept of the calibration fitting curve
Y	Absorbance of sample at 540 nm
X	Sample concentration of Cr(VI), mg/L.

The concentration of the analyzed samples (in mg of Cr(VI/ L) was calculated with the following equation:

$$\mathrm{mg\ Cr/L} = \frac{\mathrm{mg/L\ Cr(obtained\ from\ the\ calibration\ curve)}}{\mathrm{A\ (mL\ of\ original\ sample)}} * DF \tag{3.10}$$

Where DF represent the dilution factor used to analyze the hexavalent chromium.

3.2.2 Total Chromium determination

3.2.2.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) constitutes a sensible test for the quantitative determination of more than 60 metal or metalloid elements. The method to determine metals in natural, drinking and wastewaters by AAS is based on the generation of atoms in the basal state and measurement of the amount of absorbed energy by them, which it is directly proportional to the concentration of that element in the analyzed sample [Beaty (1993)].

The experimental procedure for total chromium determination was developed as indicated in the Mexican Norm NMX-AA-051-SCFI-2001. In brief, five standards of chromium (25 mL) were prepared in a concentration range of 0 to 20 mg/L by using a certified standard to perform the calibration curve for subsequent samples analysis by atomic absorption spectrometer (Thermo Jarrell Ash, Model MSCAN1).

Samples of chromium in solution were aspirated and atomized into air/acetylene flame; a monochromatic electromagnetic radiation (λ = 359.3 nm) passed directly into the flame and the atomized sample, then a detector measured the amount of light absorbed by the atomized chromium. The quantity of absorbed energy is proportional to the quantity of chromium in sample and it was determined from the calibration curve.

3.2.3 Trivalent chromium determination

The quantity of trivalent chromium (Cr^{3+}) was determined by the difference between the total chromium (obtained by atomic absorption) and the hexavalent chromium (estimated by ultraviolet-visible spectroscopy) as shown in Equation 3.11. Trivalent chromium, is an important parameter to analyze and to determine if the hexavalent chromium was reduced during the adsorption process, and it helps to suggest a mechanism based on adsorption/ reduction [López *et al.* (2012)].

$$\mu\mathrm{g\ Cr^{3+}} = \mu\mathrm{g\ Cr^{0}(Atomic\ absorption)} - \mu\mathrm{g\ Cr^{6+}(Uv - vis)} \qquad (3.11)$$

3.2.4 Iron determination

3.2.4.1 Atomic absorption spectrometry (AAS)

The content of iron was determined after an acid digestion of the iron-loaded activated carbons. A sample of activated carbon (200 mg) was powdered and placed in a 50 mL plastic capped tube and 25 mL of a solution of HNO_3/H_2SO_4 or HCl/H_2SO_4 (5:1 v/v ratio) was added. Flask was capped and remained in constant stirring for 24 h. The activated carbon was separated from the solution by filtration. The iron concentration of the filtrated was obtained by atomic absorption spectrometry (Thermo Jarrell, Model MSCAN1) at a wavelength of 248.3 nm.

3.3 Modifications of commercial activated carbon

3.3.1 Oxidation Treatment

The activated carbon was modified in acid medium as follows: 5 grams of activated carbon were placed in a distillation flask with 3 necks containing 150 mL of HNO_3. The adsorbent material was oxidized with solutions of 10, 20 and 40% v/v from concentrated nitric acid (min. 68% - max. 71%). A condenser was connected to this flask in the central neck and a thermometer in the other neck. The mixture was heated to the boiling point (68 - 70^{o}C) and suspension was refluxed for 2 hour. After the oxidation period, the system was allowed at room temperature. Subsequently, the remaining acid was removed from the flask and the adsorbent material was recovered by filtration with glass filters. The oxidized activated carbon was washed several times with deionized water or 0.01 N NaOH solutions until the mixture adsorbent-water reached a neutral pH. Finally, modified activated carbon was dried in an oven at 100^{o}C for 24 hours [Andrade *et al.* (2007)].

3.3.2 Thermal Treatment

The removal of carboxylic groups on the surface of the activated carbon by a heat treatment has been widely reported, resulting in a decrease in the quantity of acid sites (essentially carboxylic and lactones groups) and an increment of basic sites cause by the formation of pyrone structures.

The procedure for carrying out this modification of the activated carbon is mentioned below: The thermal process was conducted under a nitrogen flow (60 cm^3/min) and it was started by heating, a sample of 100 mg of activated carbon, from room temperature to a selected temperature (800, 900^{o}C) at a heating rate of 10^{o}C/min. Samples were maintained at constant temperature (800, 900^{o}C) for 2 h. Afterwards, the system was cooled under nitrogen flow (60 cm^3/min) until room temperature.

3.3.3 Nitrogen treatment

The incorporation of nitrogen containing groups on the activated carbon surface was performed by a treatment with concentrated ammonium hydroxide. Activated carbon (5 mg/mL ratio) was placed in a sealed vessel with concentrated ammonium hydroxide, continuously stirred at 150 rpm for 24 h. Next, the suspension was filtered into a fume hood, and the modified activated carbon was dried at 100^{o}C for 24 h, in order to react the remaining ammonium hydroxide present in the sample [Wibowo *et al.* (2007), Mangun *et al.* (2001)].

3.3.4 Forced hydrolysis

The granular activated carbon was modified with iron hydro (oxides) particles by forced hydrolysis using $\mathrm{FeCl_3 \cdot 6\,H_2O}$ solutions as follows: A sample (1000 mg) of activated carbon was placed in a glass vessel containing 50 ml of distilled water at a temperature of 100°C for 5 min, to remove air bubbles from pores, to moisten the adsorbent material and to promote the diffusion of iron particles inside the activated carbon pores, ultimately the solution was cooled at room temperature. The wet activated carbon was placed in 200 mL of 1 mM $FeCl_3$ at pH 1 adjusted with sulfuric acid.

This suspension was heated at 60°C and 200 rpm for 1.5 hours. After heating, samples were washed with distilled water to remove all iron from the outer surface of the activated carbon. Finally the iron loaded adsorbent was dried at 100°C for 24 h.

3.4 Adsorption and desorption of chromium by activated carbon

Adsorption isotherms of the activated carbon provide important information to determine the adsorption capacity of the adsorbent material as well as to obtain models and kinetic parameters which play a key role for designing and comparison purposes. However, desorption studies are essential to regenerate the activated carbon for its subsequent use and to recover the adsorbate for final disposal, treatment or re-use.

3.4.1 Equilibrium adsorption studies

A mass of activated carbon (m = 50 mg) was added to a volume (V = 25 mL) of Cr(VI) solutions which initial concentration (C_o) varied from 10 to 500 mg/L. These suspensions were adjusted to pH 6 with 0.1 N HCl or NaOH as required, and these experiments were continuously stirred at 200 rpm for 7 days at 25°C. Once the equilibrium was achieved, the final pH was measured and the activated carbon was separated by filtration and aliquots were taken from the filtrate to determine the Cr(VI) concentration. The equilibrium concentration (C_e) was determined by the colorimetric method coupled with UV-Vis spectroscopy [Gupta *el al.* (2010), Kobya (2004); Terzyk (2001)]. The adsorption capacity at equilibrium (q_e) of the activated carbon was then determined with the following equation:

$$q_e = \frac{V(C_o - C_e)}{m} \tag{3.12}$$

Equilibrium data was used to calculate the parameters of the adsorption isotherms models and they are shown in Table 11.

Table 11. Adsorption isotherm models [Verma *et al.* (2006)].

Model	Equation
Langmuir	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$
Freundlich	$q_e = k_F C_e^{1/n}$
Dubinin – Raduskevich	$q_e = q_m \exp(-Be^2)$
Temkin	$q_e = B_1 \ln(k_T C_e)$

3.4.2 Adsorption kinetics of metals

Adsorption kinetics of hexavalent chromium provide important data that can be used for modeling of continuous flow packed bed adsorbers. The adsorption tests were performed in a basket-typed reactor at room temperature. A know mass of activated carbon (1000 mg) was added to 1L of solution with 30 ppm of Cr(VI) at pH 6. The reactor stirred at 400 rpm and the pH value of the solution was only continuously recorded and the selected interval of time, aliquots were taken for determining hexavalent and total chromium by the colorimetry method coupled to UV-Vis spectroscopy and atomic absorption spectroscopy, respectively.

3.4.3.1 Empirical models

The adsorption kinetics of several metals have been predicted by using various proposed empirical models (Table 12), such models can provide important information in agreement with the theoretical basis on which they were developed.

Table 12. Empirical models of adsorption kinetics [Mittal *et al.* (2006)].

Kinetic model	Equation
First order	$\mathrm{q_t} = \mathrm{q_e} - \exp(k_1 t)$
Pseudo-first order	$\mathrm{q_t} = \mathrm{q_e}[1 - \exp(-\mathrm{k_1 t})]$
Second order	$q_t = \dfrac{q_e}{1 + q_e k_2 t}$
Pseudo- second order	$q_t = \dfrac{k_2 q_e^2 t}{1 + k_2 q_e t}$

3.4.3.2 Diffusive models

Just a few researchers have reported studies using diffusion models predicting the adsorption kinetics of metals in lignocellulosic materials and activated carbon, some of these models are shown in Table 13. The mass transfer phenomenon is vital in the adsorption process, as a result, it cannot be omitted when analyzing the adsorption kinetics.

However, the kinetic processes are mostly controlled by the diffusion in aqueous phase or by intraparticle diffusion, being this step the limiting rate; for this reason, the models are mainly designed to describe these two diffusive processes [Kannan *et al.* (2001)].

Table 13. Diffusive adsorption kinetic models [Qiu *et al.* (2009)].

Kinetic model	Equation
Diffusion in the liquid phase	
Cooney	$\frac{\partial \bar{q}}{\partial t} = k_f S_o (C - C_i)$
Boyd	$\ln\left(1 - \frac{q_t}{q_e}\right) = -R^1 t$
	$R^1 = \frac{3D_e^1}{r_0 \Delta r_0 k'}$
Intraparticule diffusion	
Cooney	$\ln\left(1 - \frac{q}{q_0}\right) = -\frac{D_s}{R^2} t + \ln\left(\frac{6}{p}\right)$
Weber & Morris	$q_t = k_{int} t^{1/2}$
Dumwald & Wagner	$\log\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) = -\frac{K}{2.303} t$

3.4.4 Desorption studies

The possibility of adsorbent regeneration (desorption) and the metal recovery are the mainly studied topics based on the general assumption that the adsorbent promotes an economic adsorption treatment. It has been reported the desorption of Cr(VI) using as eluent alkaline solutions such as: NaOH, Na_2CO_3, or $NaHCO_3$ [Isa *et al.* (2008)].

The desorption test of hexavalent chromium from activated carbon were performed using the following procedure: After the adsorption test, activated carbon was separated from the solution of hexavalent chromium, and it was placed in a new plastic tube with 25 mL of a solution of 0.1N NaOH-NaCl, with the objective to have two exchangeable anions (OH^- , Cl^-) besides to control the solution ionic strength.

Desorption test was allowed in stirring for a week to simulate the same conditions in that the adsorption test was performed. After one week of contact, an aliquot was taken for analysis by colorimetry coupled to ultraviolet-visible and, in this way, the concentration of desorbed Cr(VI) from the adsorbent material was determined.

3.5 Residues disposal

The general disposal of residues generated during this investigation project will be according with the integral manage of residues and normative aspects from Faculty of Chemical Sciences, UANL.

UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN
FACULTY OF CHEMICAL SCIENCES
MASTER IN SCIENCE WITH ORIENTATION IN SUSTAINABLE PROCESSES

CHAPTER 4

Results & Discussion

> **“Research is to see what everybody else has seen, and to think what nobody else has thought.”**
>
> *Albert Szent-Gyorgy*

4.1 Characterization of adsorbent

4.1.1 Acid and basic sites: Boehm Method

The determination of acid (Phenolic, lactone and carboxylic) and basic sites were estimated according to the established in the methodology for the Boehm method, and the summary of results are shown in Table 14.

Table 14. Acid and basic sites of the studied activated carbon (Boehm method).

Activated carbon	Phenol group (mEq/g)	Lactone group (mEq/g)	Carboxylic group (mEq/g)	Total acid sites (mEq/g)	Total basic sites (mEq/g)
AC raw	1.00	0.75	1.00	2.75	0.38
AC Ox(10%)	4.00	0.25	0.50	4.75	2.25
AC Ox(20%)	2.25	0.50	1.00	3.75	0.38
AC Ox(40%)	1.38	0.25	0.88	2.50	1.88
AC raw FH	1.62	0.00	1.13	2.75	2.00
AC Ox(10%) FH	0.50	0.00	2.00	2.50	2.00
AC Ox(20%) FH	0.88	1.00	1.00	2.88	2.00
AC T800	0.00	0.00	0.00	0.00	2.50
AC T900	0.00	0.00	0.00	0.00	2.38
AC T800 FH	1.25	0.00	0.00	1.25	2.38
AC T900 FH	1.25	0.00	0.00	1.25	2.38
AC NT	1.25	0.00	0.00	1.25	2.00
AC NT FH	1.25	0.00	0.00	1.25	2.25

Abbreviation	Description
AC raw	Commercial activated carbon
AC Ox ( )	Oxidized Activated carbon with % HNO_3.
AC T#	Activated carbon with thermal treatment at temperature #.
AC NT	Activated carbon modified with NH_4OH.
FH	Forced hydrolysis

Analysis of the results obtained with Boehm method revealed a greatly increased in the total acidity of the surface that resulted from the increase in surface acid functional groups such as carbonyl, lactone, and phenol groups, according to found by Huang *et al.* (2009), the total acid sites (TAS) of raw adsorbent increased up to 72% with the nitric acid oxidation, reflecting an increase in phenolic groups, Nevskaia *et al*. (2003) reported a similar behavior for activated carbon oxidized with 10% HNO_3, however, the TAS decreased with the oxidation degree, in addition was shown an increase in the amount of the total basic sites (TBS) according with the increase of the oxidation of the activated carbon.

Forced hydrolysis was performed to the activated carbon with lesser oxidation degree due to the AC Ox(40%) presented a decrease of 48% of TAS with respect to AC Ox(10%); Forced hydrolysis of these adsorbent materials caused changes in the structure of the acid sites of the both materials raw and oxidized, decreasing to 47% TAS of the oxidized adsorbents and increasing 5 times the amount of TBS of the commercial activated carbon.

In concerning the thermal treatment, the objective was reached with the modification of the surface of the adsorbent material, due to heat treatment causes the removal of an important part of the oxygen surface groups or oxygen surface complexes (phenol, lactone and carboxylic groups) from the activated carbon, resulting an increase of 6 times the amount of TBS regarding commercial activated carbon, Belhachemi *et al. (*2011) reported similar results with activated carbon with thermal treatment at 600°C.

Thermally treated samples have a basic character which is due to some kind of oxygen-containing groups and mainly to the electron rich oxygen-free sites located on the carbon basal planes. Nonetheless, the thermal treatment developed to 900°C showed a decrease of 5% TBS with respect to the modified carbon at 800°C, suggesting the volatilization of some oxygenated groups which acted as basic sites, analogous results were found by Attia *et al.* (2006) with activated carbon heated at 400°C and 600°C for 2h. The effect of heat treatment is summarized as follows, the same way as the treatment temperature increased, the amount of oxygenated surface functional groups decreased until their complete elimination. At the start, the decrease of carboxylic groups primarily occurred and the ketone or quinone structure began to disappear when the treatment temperature further increased, a similar behavior was reported by Shin *et al.* (1997) with activated carbon modified at 600, 1100 °C and for an hour in inert atmosphere.

On the other hand, the results of forced hydrolysis of the adsorbents thermally treated developed an increase of 1.25 mEq/g of phenolic groups compared with the heat-treated materials without hydrolysis, remaining constant the amount of TBS. The increased in the surface acidity indicates that the conditions in which the hydrolysis of the thermal-treated adsorbents were carried out permitted the formation of new structures containing oxygen above the activated carbon surface.

The effect of nitrogen treatment of the raw activated carbon (AC NT) suggested the rupture of lactone and carboxylic groups, remaining only phenolic groups in 1.25 mEq/g, also causing the enhancement of alkalinity, the objective of this modification was reached achieving an increase of 5 times the amount of TBS regarding commercial activated carbon, this increase of the total concentration of basic sites was attributed to the decrease of oxygen-containing acid groups and the formation of nitrogen-containing basic groups via acid sites reacting with the ammonia solution, this effect was also found by some authors (Yang *et al.* (2014); Cao *et al.* (2014)) in research about the amination and the nitration of activated carbon. However, Salame *et al.* (2001) reported that the increase in alkalinity was due to the introduction of nitrogen species and changes in the chemistry of the activated carbon surface. Nonetheless, forced hydrolysis of adsorbent with nitrogen treatment (AC NT FH), did not provide any effect on the amount of total acid sites of nitrogenized activated carbon; hydrolysis caused only an increase of 12% in total basic sites of this adsorbent material.

Boehm method was a technique that allowed to characterize the acid and basic sites of the different adsorbent materials in base to selective neutralizations, nevertheless, this technique did not allow to identify specific basic sites. The results obtained by this method shown the fulfilment of the planted objectives of the different treatments applied to commercial activated carbon; an increase in the TAS by an oxidation with HNO_3; a complete removal of TAS on the surface of activated carbon by a thermal treatment as well as an increase of TBS through a modification of the commercial activated carbon with NH_4OH.

4.1.2 Elemental analysis

Adsorbents were subjected to differential thermal analysis to determine the content of oxygen and ash, also was coupled to an elemental analysis for a better characterization of the adsorbent, the results obtained are shown in Table 15.

Table 15. Overview of elemental analysis of the studied adsorbents.

Activated carbon	Elemental content (wt %)					
	C	H	O	N	S	Ash
Ac raw	72.91	1.65	16.20	0.54	0.70	8.00
AC Ox(water)	76.63	0.53	13.84	0.67	0.33	8.00
AC Ox(10%)	65.12	1.50	18.65	1.19	0.54	13.00
AC Ox(20%)	65.77	1.43	31.22	1.09	0.49	0.00
AC Ox(40%)	69.06	1.24	21.92	1.30	0.48	6.00
AC raw FH	57.91	2.50	29.14	4.60	0.85	5.00
AC Ox(10%) FH	69.22	1.08	20.95	1.13	0.62	7.00
AC Ox(20%) FH	67.12	1.13	21.05	1.15	0.55	9.00
AC T800	68.52	0.41	20.10	0.72	0.25	10.00
AC T900	78.60	0.24	15.29	0.69	0.18	5.00
AC T800 FH	61.97	2.76	26.76	2.34	1.17	5.00
AC T900 FH	66.01	2.44	22.41	3.09	1.05	5.00
AC NT	64.95	4.52	24.02	4.02	0.49	2.00
AC NT FH	67.60	3.77	22.80	4.70	1.13	0.00

Abbreviation	**Description**
AC raw	Commercial activated carbon
AC Ox ( )	Oxidized Activated carbon with water or HNO_3.
AC T#	Activated carbon with thermal treatment at temperature #.
AC NT	Activated carbon modified with NH_4OH.
FH	Forced hydrolysis

Elemental analysis of the adsorbents showed an increase in the content of nitrogen and in the fixation of the acidic functional groups on the commercial activated carbon surface during the oxidation with nitric acid, the changes in activated carbon surface suggested a mechanism proposed by Wehzhong *et.al.* (2008) similar to the reaction involving the oxidation of aromatic hydrocarbons shown in Figure 13. The first step, reaction (a), suggested the formation of the dicarboxylic group on the aliphatic side of the molecule specially if consist of more than one carbon atom.

In the reaction (b), occurs the oxidation involving a methylene group which would result in the formation of a ketone. Nitrogen can be added to the carbon by a similar reaction as in the nitration of benzene, this mechanism would involve the formation of the highly reactive nitronium ion (NO_2^+), which will be ultimately the nitrated product as shown in reaction (c). However, in the case of the oxidized carbons the nitrated product would appear in small quantities due to the limited amount of the nitronium ion since its formation is favored in the presence of concentrated sulphuric acid.

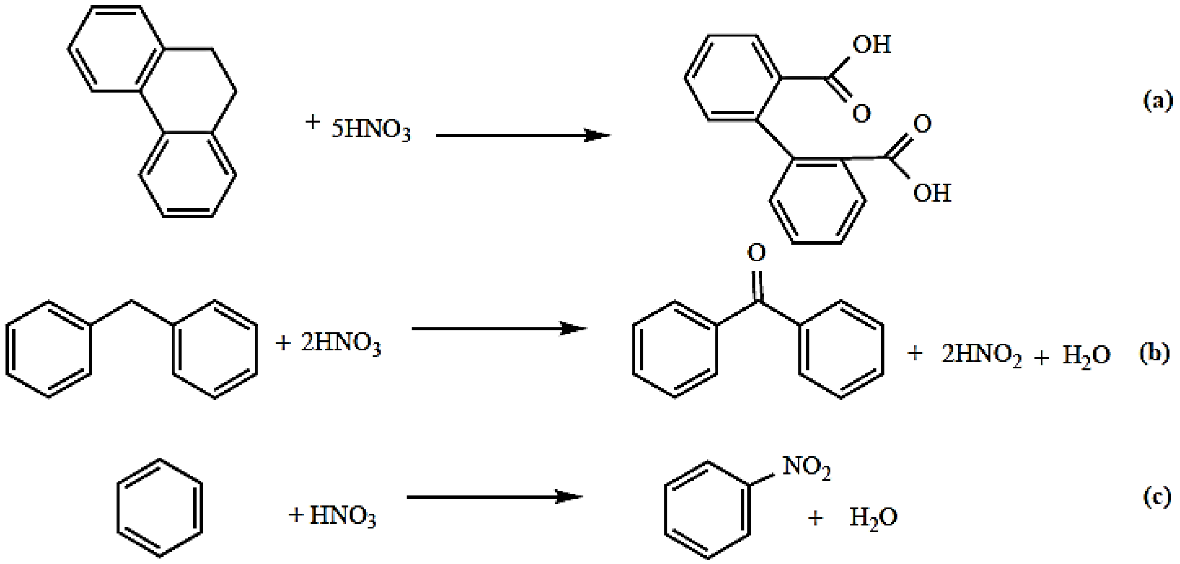

Figure 13. Mechanism of oxidation of aromatic hydrocarbons: (a) 9, 10 Dihydrophenanthrene, (b) Diphenylmethane, (c) Benzene [Wehzhong *et al.* (2008)].

On the other hand, thermal treatment can remove impurities such as hydrogen, nitrogen and oxygen as the temperature increases due to most of the acidic oxygen-containing functional groups are unstable and are subsequently removed, which also was observed by Figueiredo *et al.* (1999) and Moreno-Castilla *et al.* (2004). Elemental carbon content also increases with increasing thermal treatment temperature, Zheng *et al.* (2002) reported that is well known that thermal treatment of carbon at high temperature under an inert atmosphere brings a more or less graphitization, also enhances the basicity and the electronic conductivity of the carbon support.

Forced hydrolysis of the heat-treated activated carbons (AC T800 FH, AC T900 FH) caused an increased in the amount of sulfur compared with the adsorbents without hydrolysis, this result was obtained because of the acid solution of iron, pH of the solution was adjusted with sulphuric acid, that was used to modified the two thermal activated carbons, also was observed an lightly increased in the amount of hydrogen and oxygen which could be attributed as an effect of the acid media of the forced hydrolysis modification.

The modification of the activated carbon with an ammonia solution allowed the introduction of nitrogen-containing functional groups cause by the increase in the amount of elemental nitrogen in the adsorbent compared with the commercial activated carbon, this is consistent with the results obtained with Boehm method, also was modified the amount of amount of hydrogen and oxygen as a result of the strong solution used to modified the adsorbent. Szymanski *et al.* (2004) reported that the modification with ammonia solutions enhanced the basic properties of carbons at the expense of their acid properties, this kind of modifications allowed the incorporation of nitrogen mainly, but also they reported an increase in amount of oxygen especially when a foreign material as iron is incorporated in the adsorbent. As a result of the forced hydrolysis (AC NT FH), an increase in the amount of elemental sulfur was showed which it was a similar behavior obtained with the others adsorbents after their modification with forced hydrolysis.

4.1.3 Fourier Transform Infrared spectrometry (FT-IR)

The qualitative analysis of surface functional groups of the adsorbents was performed with the help of the infrared spectra, Figure 14, the spectrum of each adsorbent was analyzed individually, and the identified bands are shown in Table 16 and 17.

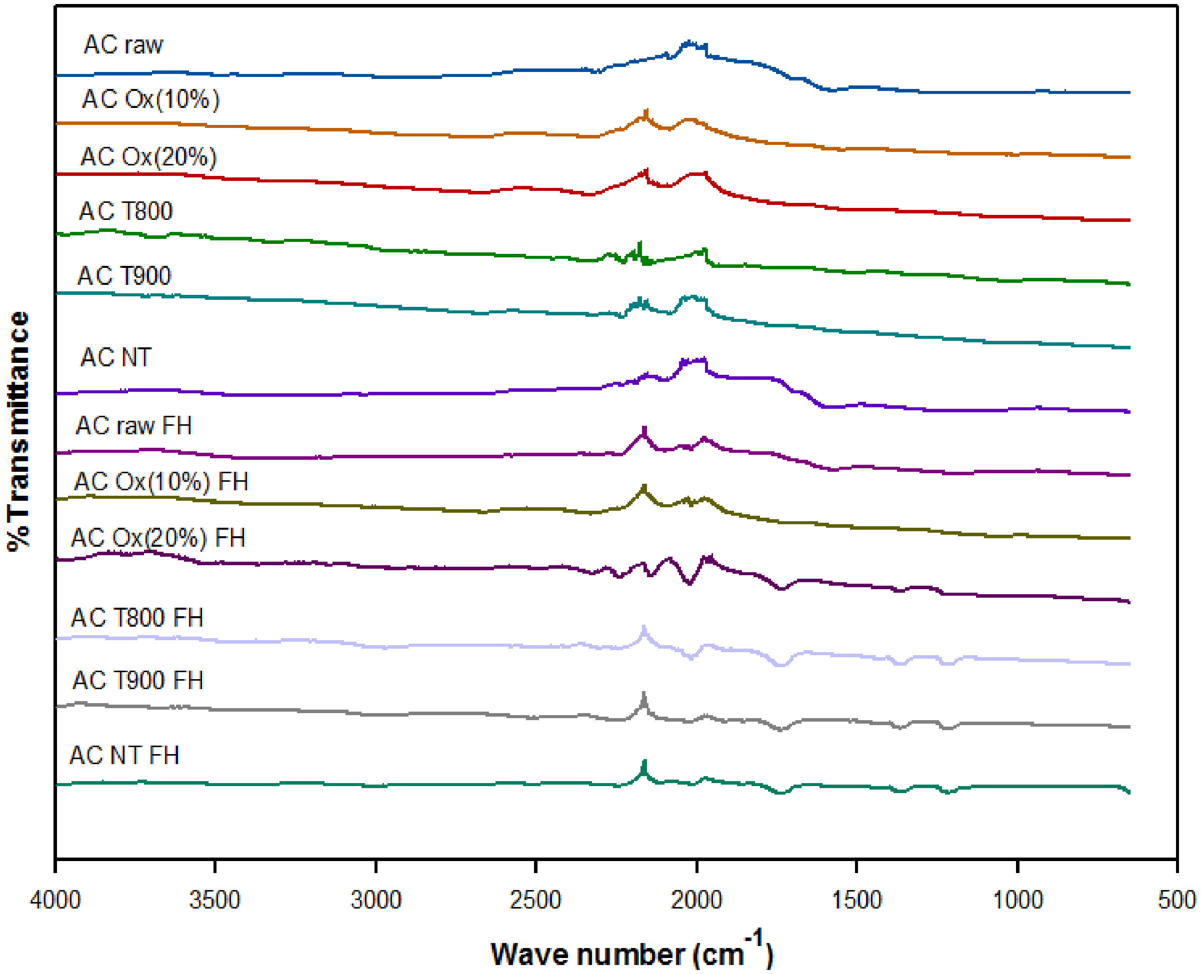

Figure 14. Representative FT-IR spectra of the untreated carbon and modified samples.

IR assignments of the possible functional groups on carbon surfaces (raw and modified) were summarized in Table 16. Commercial activated carbon presented important absorption bands at specific wave numbers related with functional groups such as quinone, carboxylic acid and lactones based on the review of the main characteristic peaks of activated carbons in infrared spectra performed by Wenzhong *et al.* (2008).

Table 16. IR Assignments of functional groups on carbon surface.

Activated carbon	Group or functionality	Assignment region (cm^{-1})
AC raw	Quinone	1580
	Carboxylic acid	1178,1699,2924
	Lactone	1178,1699
AC Ox(10%)	Carboxylic acid	1120,1700,2700
	Phenol	2700
AC Ox(20%)	Carboxylic acid	1120,1700,2650
	Phenol	2650
AC T800	C-O in ethers (stretching)	1050
AC T900	None	None
AC NT	Carboxylic acid	1177,1588,3338
	N-H, C = N	1580
	C-N	1177

Abbreviation	**Description**
AC raw	Commercial activated carbon
AC Ox ( )	Oxidized Activated carbon with water or HNO_3.
AC T#	Activated carbon with thermal treatment at temperature #.
AC NT	Activated carbon modified with NH_4OH.
FH	Forced hydrolysis

On the other hand, the spectra obtained from the both activated carbons oxidized with nitric acid indicated absorption bands of C-OH (stretching) and –OH related with phenolic groups, also was identified the carboxylic acid, Moreno *et al.* (2000) reported same groups or functionalities for activated carbons oxidized with 14M HNO_3, nonetheless, other authors (Khelifi *et al.* (2010); Allwar *et al.* (2012)) observed the presence of quinone or conjugated ketone structure and carbonyl groups which have similar absorption bands, this allowed that the peaks of these structures overlapped with other functional groups. Nevertheless Bautista *et al.* (1994) reported that the nitric oxidation introduced a small amount of nitrogen and attributed this observation to the formation of nitro and nitrate aromatic compounds which also have similar absorption peaks (1100-1300, 1560 cm^{-1}) like the acid groups, Chimgombe *et al.* (2006) corroborated this information finding the same behavior with activated carbon oxidized with nitric acid for 9h.

With regard to the thermal treatment, the modification performed at 800^oC provoked the removal of most of the functional groups from the activated carbon as a result just a peak appeared at 1100 cm^{-1} which could be a C-O bond in ether or hydroxyl group as found by Attia et al. (2006).

Nevertheless, when the temperature increased at 900°C, no characteristic peak is observed which is consistent with the results obtain with the Boehm method due to the elimination of all acid groups or volatile compounds from the activated carbon surface, this a typical effect found in the studies performed by Aguilar *et al.* (2003), Bandosz *et al.* (2006) and Ríos *et al.* (2007) those who reported the decomposition of oxygenated groups when the activated carbon is submitted to heat treatment at high temperatures specially under hydrogen atmosphere.

The analysis performed to the spectrum of the activated carbon modified with ammonia solution (AC NT) showed characteristic bands at 1580 and 1177 cm^{-1}, which could be attributed to N-H or C=N and C-N bonds, respectively. In addition, the spectrum have the three absorption bands (1177, 1580 and 3338 cm^{-1}) that characterize the carboxylic acid group, but also at the same wave number could have overlapping bands of O-H and N-H stretching vibrations due to that the nitrogen treatment suggest the formation of nitrogenized species on the activated carbon surface, a similar analysis was performed by Mohammad *et al.* (2011) in the study of ammonia modification of activated carbon and by Adebukola & Min (2013) in their studies about basic treatments of activated carbon for enhanced CO_2.

The main absorption bands obtained from the spectra of the adsorbent materials with forced hydrolysis are shown in Table 17. The effect of the hydrolysis on the adsorbent did not cause changes in the IR spectrum of the commercial activated carbon, this behavior corresponds to the obtained data from the Boehm method (AC raw FH), which showed that the total acid groups remained constant after the forced hydrolysis of the commercial activated carbon , and the oxygenated functional groups were still staying on the activated carbon surface, this could explain why the absorption bands of AC raw FH had not changes compared to the untreated carbon (AC raw).

Table 17. IR Assignments of functional groups on carbon surfaces with forced hydrolysis.

Activated carbon	Group or functionality	Assignment region (cm^{-1})
AC raw FH	Quinone	1580
	Carboxylic acid	1170,1700,2910
	Lactone	1180,1700
AC Ox(10%) FH	Carboxylic acid	1120,1700,2700
	Phenol	2700
AC Ox(20%) FH	Lactone	1120,1740
	Carboxylic anhydride	1120,1740
AC T800 FH	Phenol	1200,3000
	-C-OH (stretching)	1200
AC T900 FH	Phenol	1200,3000
	-C-OH (stretching)	1200
AC TN FH	Carboxylic acid	1200,1750,3000
	Phenol	1200,300
	C-N	1200

Same results were observed with the hydrolysis of the activated carbon oxidized with nitric acid (AC Ox(10%) FH) which have similar behavior like the forced hydrolysis of commercial activated carbon, the spectrum of this adsorbent indicated the presence of carboxylic and phenolic groups mainly. However, according with the potentiometric titrations, this activated carbon suffered a decrease in acid groups but the predominant groups still being phenolic group and in higher amount carboxylic, that are same groups that appeared in the oxidized activated carbon without forced hydrolysis, obtaining as a result the same infrared spectrum. In contrast, AC Ox(20%) FH showed absorption peaks at 1200 and 1740 cm^{-1}, that according with Wenzhong and co-workers, are specific absorption band for carboxylic anhydride and lactone groups, the effect of the hydrolysis in this adsorbent provoked the decrease in acid surface groups, remaining in greater proportion lactone and carboxylic group, this resulted in a grander intensity of the absorption bands at the wave numbers related with these functional groups.

Forced hydrolysis of both heat-treated activated carbons caused the formation of new acid structures although they looked in the spectra with lower intensity. Both adsorbents presented the same absorption peak at 1200 cm^{-1} which is related with the –C-OH (stretching) bond and together with the peak that appeared at 3000 cm^{-1} could suggest the presence of phenolic groups which is the functional group found with the Boehm method through potentiometric titrations.

Even though both thermal-treated activated carbons have the same absorption peaks in the spectra, the activated carbon treated at 900°C and modified with forced hydrolysis presented peaks with lower intensity, the absorption bands decreased about 15% in transmittance compared with the activated carbon treated at 800°C and also modified with forced hydrolysis, this could indicate that the functional groups in the second adsorbent (AC T800 FH) are stronger linked to the activated surface than the first one, resulting in higher vibrations in bonds and also in a greater intensity in the corresponding absorption peaks.

IR spectrum of the activated carbon treated with an ammonia hydroxide solution and modified with forced hydrolysis presented the same peaks like the activated carbon with nitrogen treatment without hydrolysis, however in the wave number range from 1200 to 1750 cm^{-1}, the peaks had higher intensity than the adsorbent without hydrolysis. Nonetheless, the spectrum of the first adsorbent (AC NT FH) showed a lower percentage of transmittance respect to the second activated carbon (AC NT), the absorption bands decreased about 20% transmittance, this could be explained due to the AC NT FH had an increase in the total basic sites this indicate that new structures were formed and they could obstruct the radiation absorption resulting in a spectrum with lesser intensity or lower transmittance percentage.

4.1.4 Physical adsorption of Nitrogen

The modified activated carbons during this research project were characterized by physical adsorption of Nitrogen (Table 18), to obtain the surface area by BET method and pore size distribution by BJH method.

Table 18. Surface area and pore size distribution of the adsorbent materials.

BET analysis			Pore size distribution (BJH)			
Activated carbon	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**% Pore Volume**			**Average pore diameter (nm)**
			Micropores	***Mesopores***	***Macropores***	
AC raw	735.30	3.39	7.21	84.07	8.72	1.60
AC Ox(10%)	858.40	4.23	7.96	84.42	7.62	1.50
AC Ox(20%)	807.70	4.08	7.30	85.00	7.70	1.56
AC Ox(40%)	779.00	3.88	7.16	84.39	8.44	1.68
AC raw FH	746.61	3.85	6.66	84.26	8.32	1.73
AC Ox(10%) FH	752.30	3.81	7.06	83.58	7.70	1.58
AC Ox(20%) FH	807.00	3.94	8.35	85.66	7.58	1.46
AC T800	785.30	4.10	7.67	89.50	8.65	1.71
AC T900	869.10	4.19	7.72	84.21	8.07	1.56
AC T800 FH	730.30	3.72	7.92	84.32	7.76	1.58
AC T900 FH	745.40	3.08	7.59	84.25	8.16	1.55
AC NT	1365.0	11.40	4.81	86.45	8.70	2.91
AC NT FH	1280.1	10.50	4.79	86.43	8.78	2.89

Abbreviation	**Description**
AC raw	Commercial activated carbon
AC Ox ( )	Oxidized Activated carbon with water or HNO_3.
AC T#	Activated carbon with thermal treatment at temperature #.
AC NT	Activated carbon modified with NH_4OH.
FH	Forced hydrolysis

The results of the physical adsorption of nitrogen of the studied activated carbons, showed that oxidation with nitric acid of the adsorbent materials caused an increase in up to 17% of BET surface area and 24% of pore volume regarding commercial activated carbon. Nonetheless, it is suggested that as the degree of the oxidation increased (AC Ox(40%)), activated carbon walls began to collapse being reflected in a decrease of 10% of BET area and 25% of pore volume, this same effect was found by many authors (Aksoylu *et al.* (2001); Nevskaia *et al.* (2003); Stravropolus *et al.* (2008); Pietrzak *et al.* (2009)) whom studied the effects about the oxidation of activated carbons with nitric acid.

Nonetheless, Huang *et al.* (2009) suggested that the decreased in BET surface areas resulted from a pore blockage in the micropores caused by the formation of humic substances or surface oxides during the oxidation process. However, Khelefi *et al.* (2010) reported that the considerable changes in the activated carbon surface was also could be due to by two possible effects: i) the partial destruction of the micropores walls and ii) the restrictions of the accessibility caused by the fixation of oxygen containing groups at the entrance of the pores.

Due to the drastic nature of the acid treatment which partially broke the pores texture (observed in the decrease in BET area) of the activated carbon probably did not favor the formation of ketone and ether groups resulting in a decrease of acid surface groups as was observed in the Boehm method, which also was found by Moreno *et al.* (1995) in their studies about the modification of the activated carbon surface.

On the other hand, both adsorbents (commercial activated carbon such as the activated carbon oxidized with nitric acid) contain up to 85% of mesopores which was confirmed with the adsorption-desorption isotherms of nitrogen type IV, typical for mesoporous materials.

The results of the force hydrolysis of the commercial activated carbon (AC raw HF) showed an increase of 1.5% on the BET surface area and 14% in pore volume respect to the raw adsorbent, this indicated that the hydrolysis provoked the formation of a higher amount of pores in the activated carbon how was expected due to the experimental conditions of the forced hydrolysis which acted like an acid treatment cause by the sulfuric acid media and heating at 70^{o}C.

Furthermore, the effect of the forced hydrolysis in both oxidized adsorbents resulted in a lightly decrease (about 11%) of the BET surface area and pore volume, compared with the adsorbents without hydrolysis, cause by the strong conditions in which the hydrolysis was carried out (acid solution and heating) that could have had a similar effect like the oxidation with nitric acid, causing the breaking down of the walls of the pores modifying the surface area and pore volume, however, after the hydrolysis the oxidized activated carbons still continue being mainly mesoporous.

The analysis of the heat-treated activated carbons showed a slight increase in the BET surface area about 7% and important increase of 20% in pore volume compared with commercial activated carbon, this behavior resulted from the elimination of oxygenated groups or the elimination of volatile matter of the activated carbon surface causing the generation of new pores in the adsorbent increasing BET surface area; Chimgombe *et al.* (2005) reported that thermal treatment removed some of the humic acid lodged in micropores and eliminates some oxygen-containing functional groups that are not stable at high temperatures, increasing surface area. Other authors (Rangel *et al.* (2005); Yoo *et al.* (2005); Ruiz *et al.* (2007)) obtained a physical improve, mainly in BET area and micro and mesopore volumes, on the adsorbent properties as a result of the heat treatment of activated carbon at high temperatures.

Furthermore, forced hydrolysis of the heat-treated adsorbents (AC T800 FH, AC T900 FH) showed a decreased in BET surface area, compared with the thermal-treated activated carbons without hydrolysis, as a result of the acid solution used in the forced hydrolysis modification which could be collapsed the walls of the activated carbon diminishing the surface area and obtaining a slight increase in pore volume, also this behavior could suggest that the iron particles were distributed on the activated carbon surface diminishing the BET area, this effect have been reported by many authors (Ang *et al.* (2000); Park *et al.* (2003); Bulushev *et al.* (2004)) who modified the surface of catalyst supports with a foreign material mainly metals such as iron, copper, gold, silver among others.

The incorporation of nitrogen on the commercial activated carbon (AC NT) caused an important effect on the adsorbent surface increasing the BET area about 85% and 3 times the pore volume in comparison with the raw activated carbon; however, forced hydrolysis of this nitrogen-containing activated carbon (AC NT FH) showed a slight decrease in the surface area around 6% and 8% in pore volume compared with AC NT, that is a similar behavior obtained from the others activated carbons with anchored iron particles. Both adsorbents AC NT and AC NT FH showed a decrease about 50% in their densities as a result of the changes in the surface area and pore volume caused by the strong nitrogen treatment.

Biniak *et al.* (1997) modified the activated carbon surface by an ammonia treatment at high temperature, and they observed an increase of microporosity that was in agreement with data for other ammonia treated carbons; the same author in 1999, reported that the amination process alters the surface area (BET) only slightly, but strongly influences the surface chemical structure of the activated carbon. Same results were obtained by Mangun *et al.* (2001) who reported that the ammonia treatment allowed the increasing of pore size and surface area, also Lei *et al.* (2002) observed amination had little effect on micropore volume and BET surface area, then had no noticeable effects on pore size distribution.

4.2 Batch adsorption-desorption test

4.2.1 Cr(VI) adsorption test

The adsorption test of hexavalent chromium were performed up to the equilibrium was reached, using the different adsorbent materials generated during this researcher project, isotherms were classified according to the modification performed to the activated carbons also the parameters of the adsorption isotherm model which were used to adjust the data are shown.

4.2.1.1 Adsorption isotherms: Commercial activated carbon

In Figure 15, are shown the adsorption isotherms of the commercial activated carbon as well as its modification with forced hydrolysis; data fitting was performed to different models of adsorption isotherms reporting the best fit in Table 19.

Table 19. Parameter of the fitting to Freundlich for adsorption isotherms.

Specie	K (mg/g)*(mg/L)$^{-1/n}$	1/n	Correlation factor R^2	q_{max} (mg/g)
AC raw	0.8745	0.6490	0.9959	45.6
AC FH	**5.3350**	**0.3676**	**0.9856**	**49.5**

From the analysis performed to adsorption isotherms, a same tendency of the isotherm of the activated carbon with forced hydrolysis was observed in comparison with the isotherm of the commercial activated carbon.

The hydrolysis of the commercial activated carbon presented as important effect a greater adsorption capacity (50%) by the adsorbate to concentrations lesser than 150 mg/L and about 25% at upper concentrations compared with the raw material. Equilibrium data of the batch adsorption tests of both adsorbents were fitted to different adsorption isotherms models, however, the fitting which better described the behavior of the experimental data was the Freundlich model.

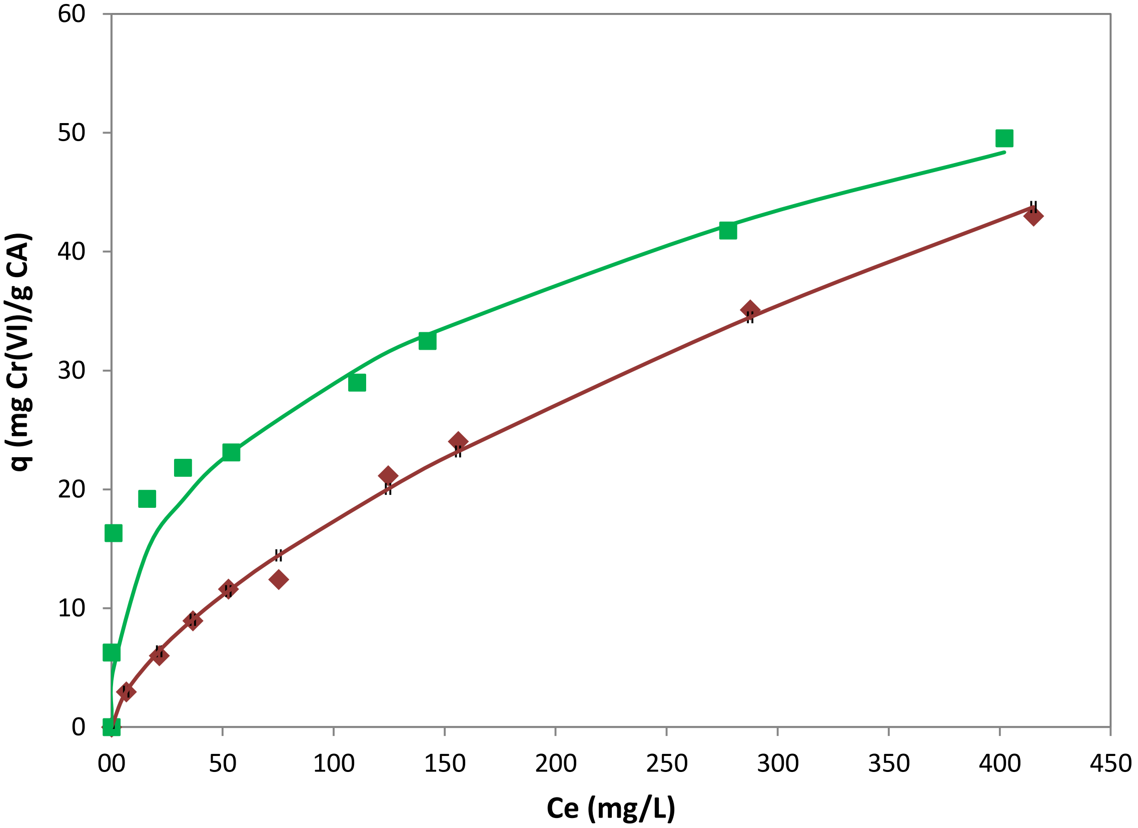

Figure 15. Adsorption isotherm of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and temperature of 25°C); Freundlich fit (continuous line): ◆ AC raw, ■ AC raw HF.

4.2.1.2 Adsorption isotherms: Oxidized activated carbons with HNO_3

Adsorption equilibrium data of Cr(VI) of the adsorbents oxidized with nitric acid as well as its modification with forced hydrolysis are shown in Figure 16. Analysis of the adsorption tests indicated that the activated carbons oxidized with HNO_3 presented a lesser adsorption capacity in all the range of concentration of the adsorbate studied in comparison with the commercial adsorbent.

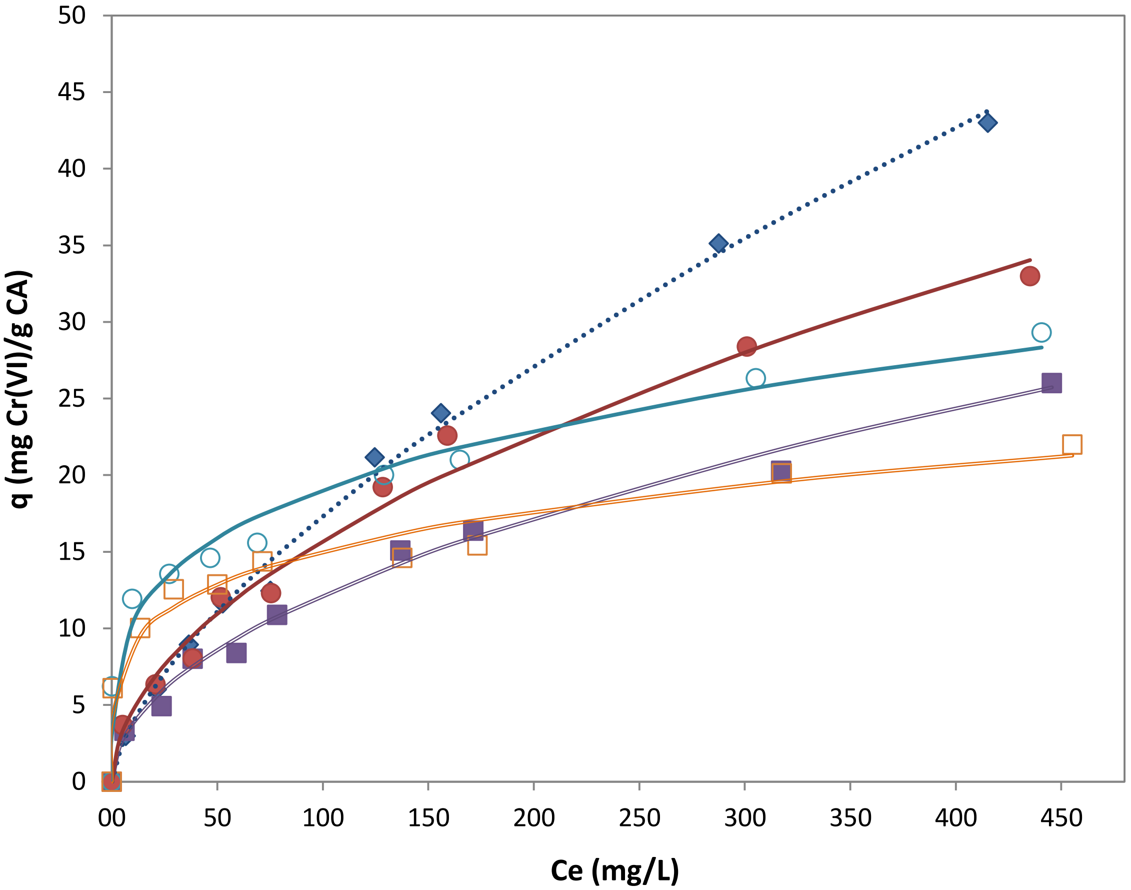

Figure 16. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and temperature of 25°C); Freundlich fit (continuous line): ◆ AC raw, ■ AC Ox(10%), ● AC Ox(20%), □ AC Ox(10%) FH, ○ AC Ox(20%) FH.

Nevertheless, the oxidized and modified adsorbents with forced hydrolysis showed an increase of 25% on adsorption capacity of the commercial activated carbon only at concentrations of Cr(VI) < 80 mg/L, and above this value of concentrations the equilibrium data showed a similar behavior to the activated carbons only oxidized with nitric acid, which presented a lower Cr(VI) adsorption capacity compared to the raw adsorbent.

The equilibrium data obtained were fitted to different adsorption isotherm models, obtaining the best fit with the Freundlich model. The summary of the parameters of the model is shown in Table 20, where it was observed that the commercial activated carbon presented the greater adsorption capacity (45.6 mg/g) compared with the others activated carbons oxidized with nitric acid as well as the modification of these carbons with forced hydrolysis.

Table 20. Parameter of the fitting to Freundlich for adsorption isotherms (Oxidation HNO_3).

Activated carbon	K $(mg/g)*(mg/L)^{-1/n}$	1/n	Correlation factor R^2	q_{max} (mg/g)
AC raw	**0.927**	**0.634**	**0.9965**	**45.60**
AC Ox(10%)	1.207	0.507	0.9798	27.82
AC Ox(20%)	1.405	0.525	0.9808	32.99
AC Ox(10%) FH	5.603	0.2662	0.9695	30.23
AC Ox(20%) FH	5.258	0.2284	0.9687	22.99

4.2.1.3 Adsorption isotherms: Activated carbons with thermal treatment

Adsorption equilibrium data of Cr(VI) of the activated carbons with thermal treatment, Figure 17, followed a similar behavior to the commercial activated carbon; on the other hand, forced hydrolysis of these adsorbents caused an increase of 26% on maximum adsorption capacity of raw adsorbent and a higher affinity to concentrations of Cr(VI) lesser than 200 mg/L.

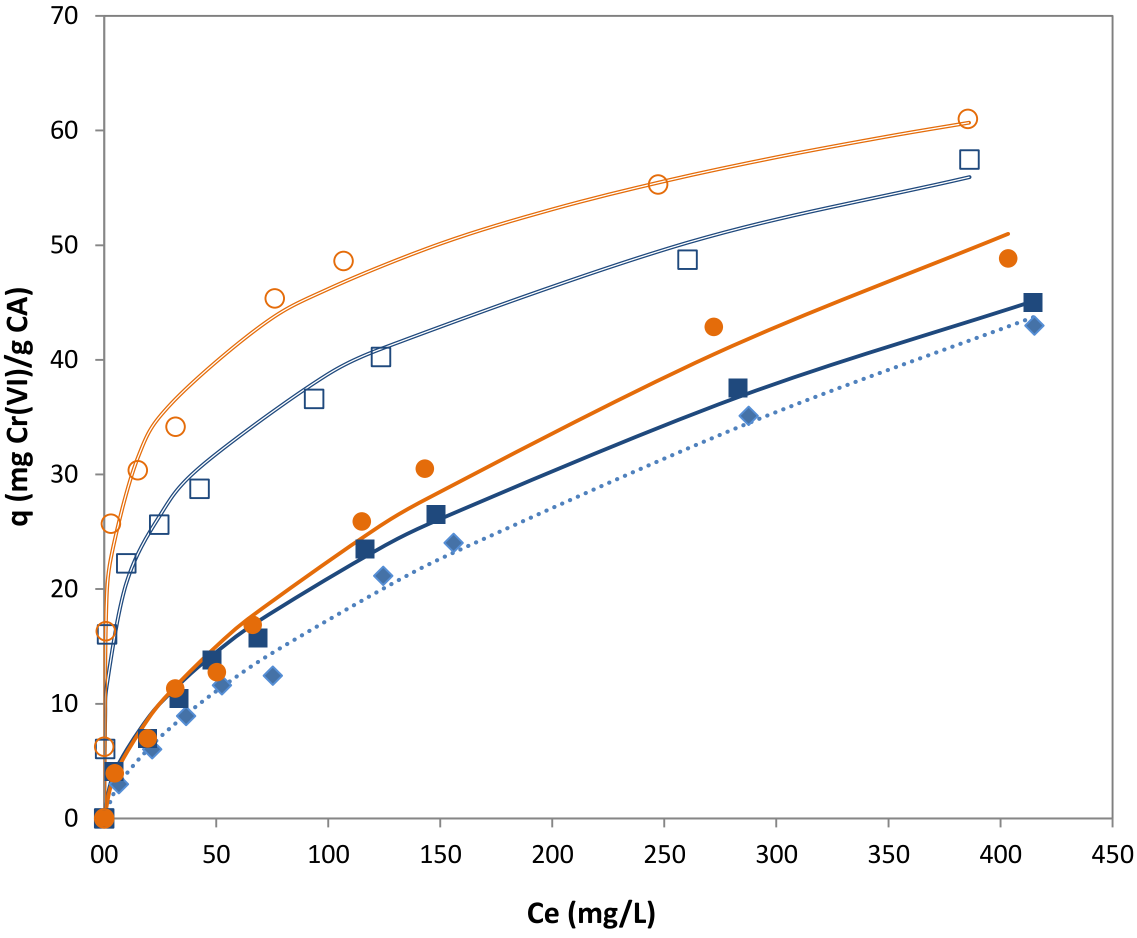

Figure 17. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6,and temperature of 25°C); Freundlich fit (continuous line): ◆ AC raw, ■ AC T800, ● AC T900, □ AC T800 FH, ○ AC T900 FH.

Adjusting of equilibrium data obtained for the different adsorbents with thermal treatment was performed, resulting Freundlich model the most adequate for data and summarizing the information obtained in Table 21, in which it was observed that the activated carbon with thermal treatment at 900°C and modified with iron particles presented the greater adsorption capacity (59.82 mg/g) in comparison with the rest of the adsorbents.

Table 21. Parameter of the fitting to Freundlich for adsorption isotherms (Thermal treatment).

Activated carbon	K $(mg/g)*(mg/L)^{-1/n}$	1/n	Correlation factor R^2	q_{max} (mg/g)
AC raw	0.927	0.634	0.9965	45.60
AC T800	1.776	0.537	0.9891	43.33
AC T900	1.518	0.5867	0.9884	48.85
AC T800 FH	10.970	0.274	0.9819	57.82
AC T900 FH	**18.200**	**0.202**	**0.9839**	**59.82**

The increase on the adsorption capacity of the adsorbents with thermal treatment in comparison with the commercial activated carbon was attributed to the removal of the electrostatic repulsion generated by acid sites of the surface of the adsorbents surface, in addition of the increase of basic sites available for adsorption of Cr(VI) anions; moreover, the incorporation of iron species onto activated carbons with thermal treatment acted as anchor sites of Cr(VI) causing an increase of 50% on the adsorption capacity of the commercial activated carbon at concentration of Cr(VI) lesser than 200 mg/L.

4.2.1.4 Adsorption isotherms: Activated carbon with nitrogen treatment

The effect of the modification of the activated carbon surface with ammonium hydroxide resulted in an increase on the adsorption capacity of the commercial activated carbon by 7% in the studied concentration range (Figure 18), the changes on the adsorption capacity were attributed to increase of basic sites generated by the nitrogen treatment. In addition, hydrolysis of the adsorbent with nitrogen treatment produced a higher affinity for the adsorbate up to concentrations of Cr(VI) lower than 250 mg/L.

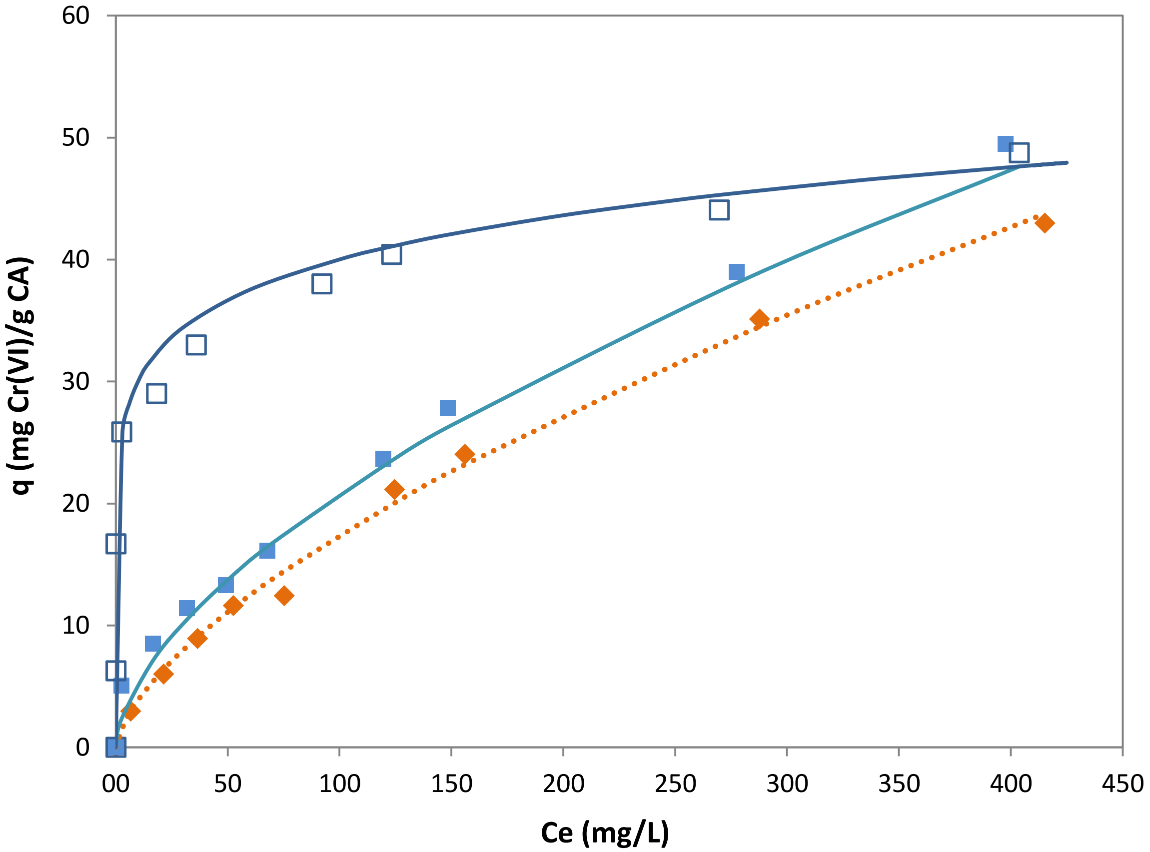

Figure 18. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/ml, pH = 6, temperature of 25°C); Freundlich fit (continuous line): ◆ AC raw, ■ AC NT, ☐ AC NT FH.

The analysis of the adsorption equilibrium data of Cr(VI) shown that the incorporation of iron species on the nitrogenized activated surface increased affinity for the adsorbent to low concentrations about 60% on the adsorption capacity of the commercial activated carbon. Isotherms were fitted to Freundlich model, parameter values of the model are reported in Table 22, where even though nitrogenized activated carbon (AC NT) presented the greatest adsorption capacity, its modification with forced hydrolysis (AC NT FH) was chosen since it presented a higher affinity for the adsorbent at low concentrations.

Table 22. Parameter of the fitting to Freundlich for adsorption isotherms (Nitrogen treatment).

Activated carbon	K $(mg/g)*(mg/L)^{-1/n}$	1/n	Correlation factor R^2	q_{max} (mg/g)
AC raw	0.927	0.634	0.9965	45.60
AC NT	1.334	0.596	0.9939	48.51
AC NT FH	**22.500**	**0.125**	**0.9850**	**48.41**

4.2.2 Cr(VI) reduction analysis

Reduction analysis of Cr(VI) during the adsorption process was an important factor that helped to elucidate how interacted the species of chromium with the functional groups present on commercial activated carbon as well as its diverse performed modifications.

4.2.2.1 Adsorption isotherms: Commercial activated carbon

In Figure 19, adsorption isotherms of total chromium and Cr(VI) are shown for the commercial activated carbon (AC raw) as well as for its modification with forced hydrolysis (AC raw FH); in the pair of isotherms for each adsorbent was observed a similar behavior of the equilibrium data for the Cr(VI) as for total chromium indicating that the conditions in which took place the adsorption process achieved a reduction about 2% from Cr(VI) to Cr(III) as a result of the activated carbon surface charge and the low available of protons in solution.

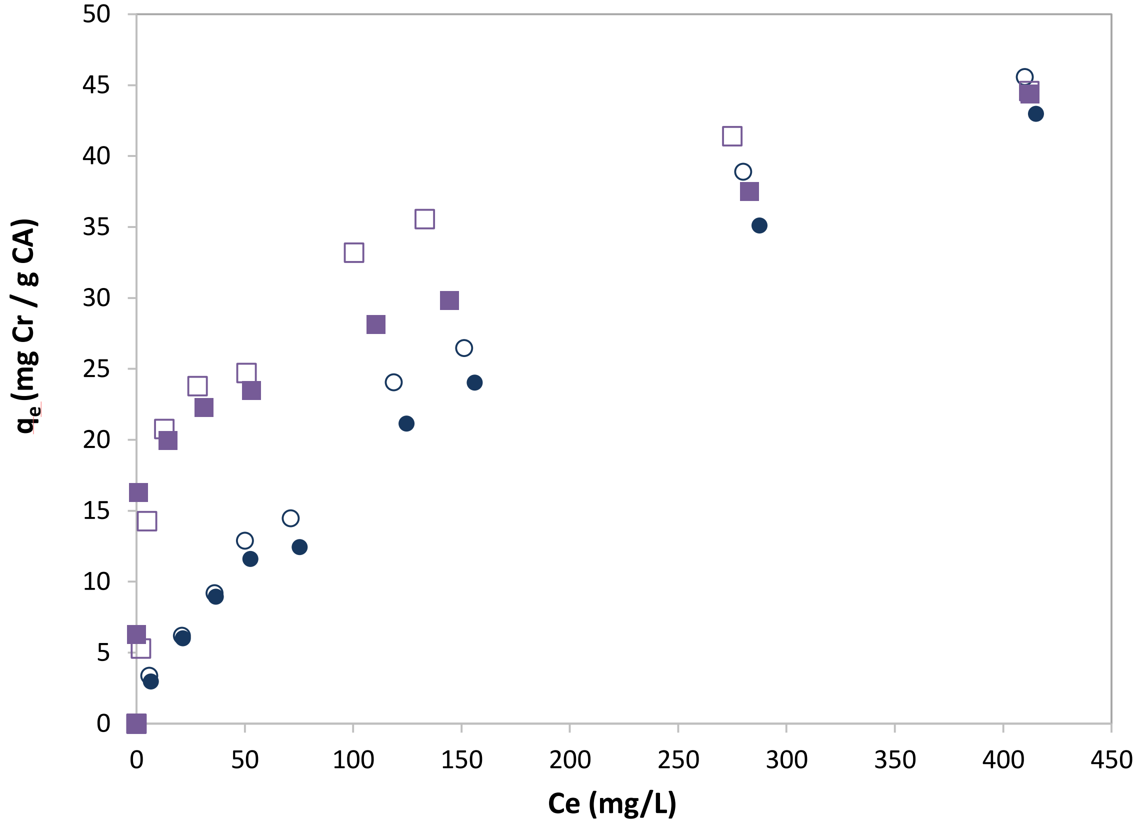

Figure 19. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and T = 25°C): ● AC raw Cr(VI), ○ AC raw total Cr, ■ AC raw FH Cr(VI), □ AC raw FH total Cr.

4.2.2.2 Adsorption isotherms: Oxidized activated carbons with HNO_3

In the analysis of isotherms of Total and hexavalent chromium for the activated carbons treated by a oxidation with nitric acid (Figure 20), presented around 33% of reduction of Cr(VI) to Cr(III) at concentrations greater than 100 mg/L, obtaining a high percentage of reduction in comparison with 2% achieved by commercial activated carbon. On the other hand, no reduction was shown at low concentrations due to basic surface groups allow the hexavalent chromium adsorption and there was not enough protons to the electron donors to provoke a Cr(VI) reduction.

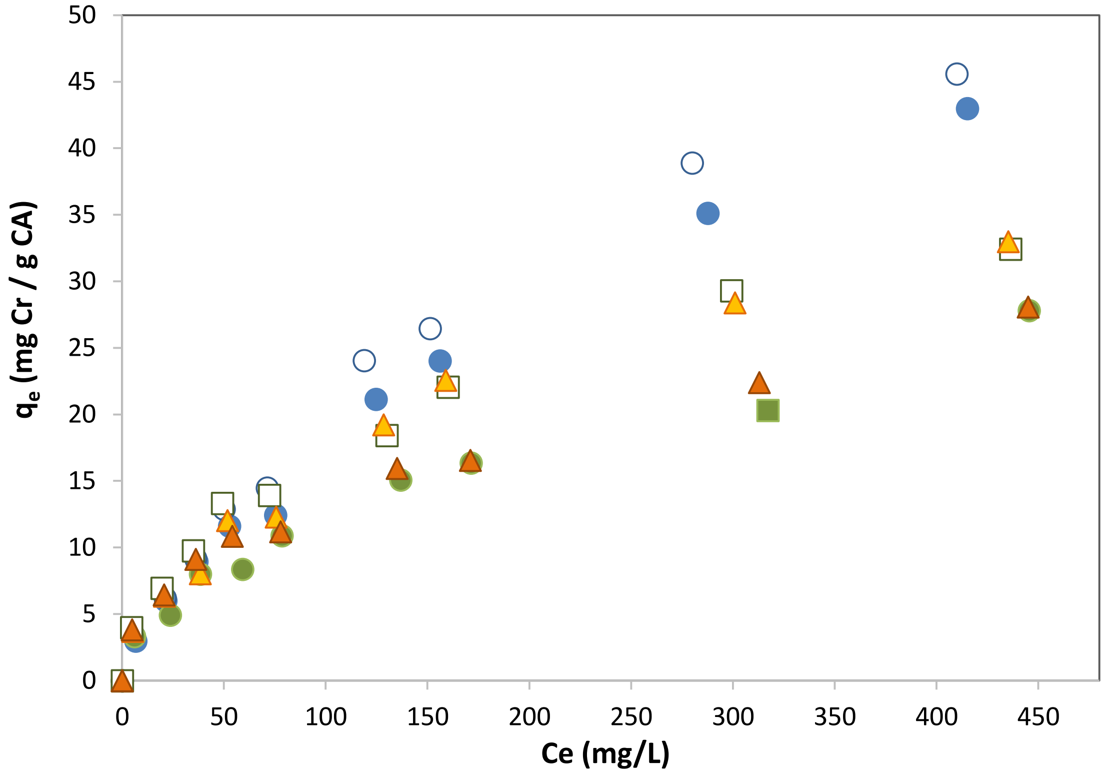

Figure 20. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and T = 25°C): ● AC raw Cr(VI), ○ AC raw total Cr, ■ AC Ox(10%) Cr(VI), ☐ AC Ox(10%) total Cr, ▲ AC Ox(20%) Cr(VI), ▲ AC Ox(20%) total Cr.

On the another hand, in the analysis of the isotherms of the adsorbents oxidized with nitric acid and modified with forced hydrolysis was obtained a 50% of reduction of Cr(VI) to Cr(III) at concentrations greater than 100 mg/L, this effect was attributed mainly to the density of acid sites that acted as electron donors causing the Cr(VI) reduction, standing out the commercial activated carbon as the best adsorbent of hexavalent chromium anionic species.

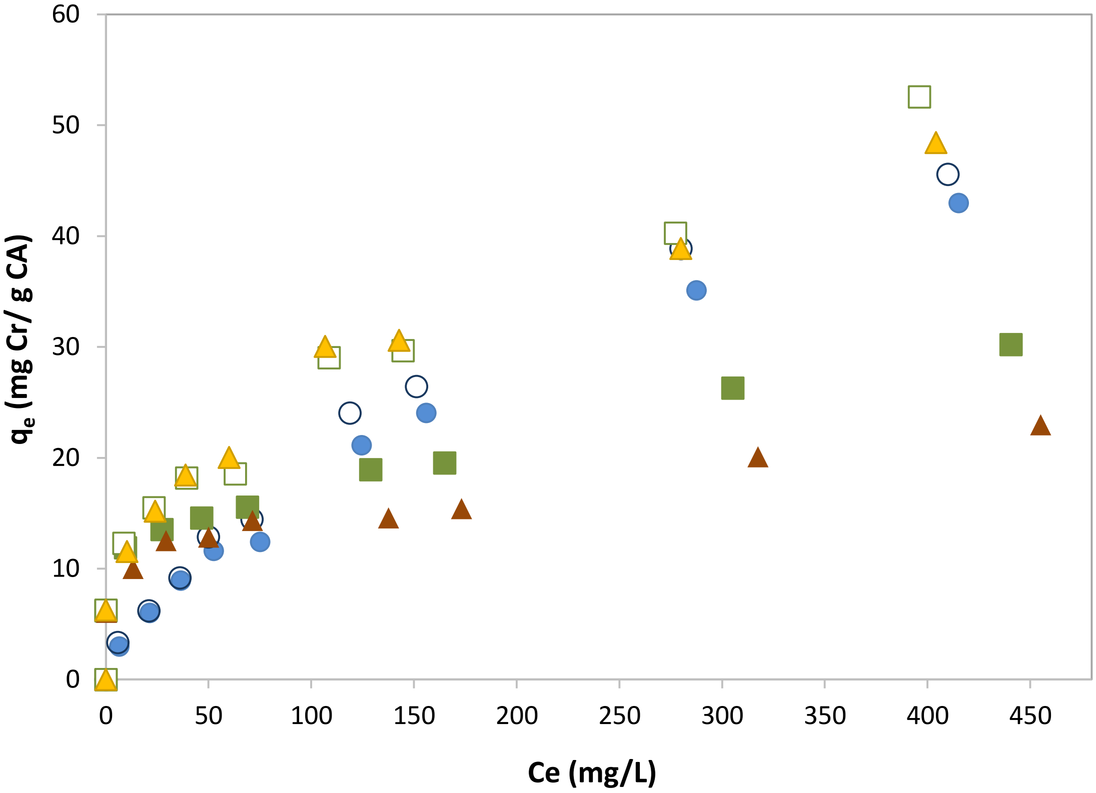

Figure 21. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and T = 25°C): ● AC raw FH Cr(VI), ○ AC raw FH total Cr, ■ AC Ox(10%) FH Cr(VI), □ AC Ox(10%) FH total Cr, ▲ AC Ox(20%) FH Cr(VI), ▲ AC Ox(20%) FH total Cr.

4.2.2.3 Adsorption isotherms: Activated carbons with thermal treatment

Regarding thermal treatment, isotherms of total chromium and Cr(VI) for the obtained adsorbent materials, Figure 22, showed a similar tendency to the behavior obtained from the activated carbons oxidized with nitric acid, which involved a 35% of Cr(VI) reduction at concentrations above 100 mg/L , nonetheless presented a higher adsorption capacity with regard to these adsorbent materials as a result of the increase in the quantity of basic surface groups by the thermal treatment.

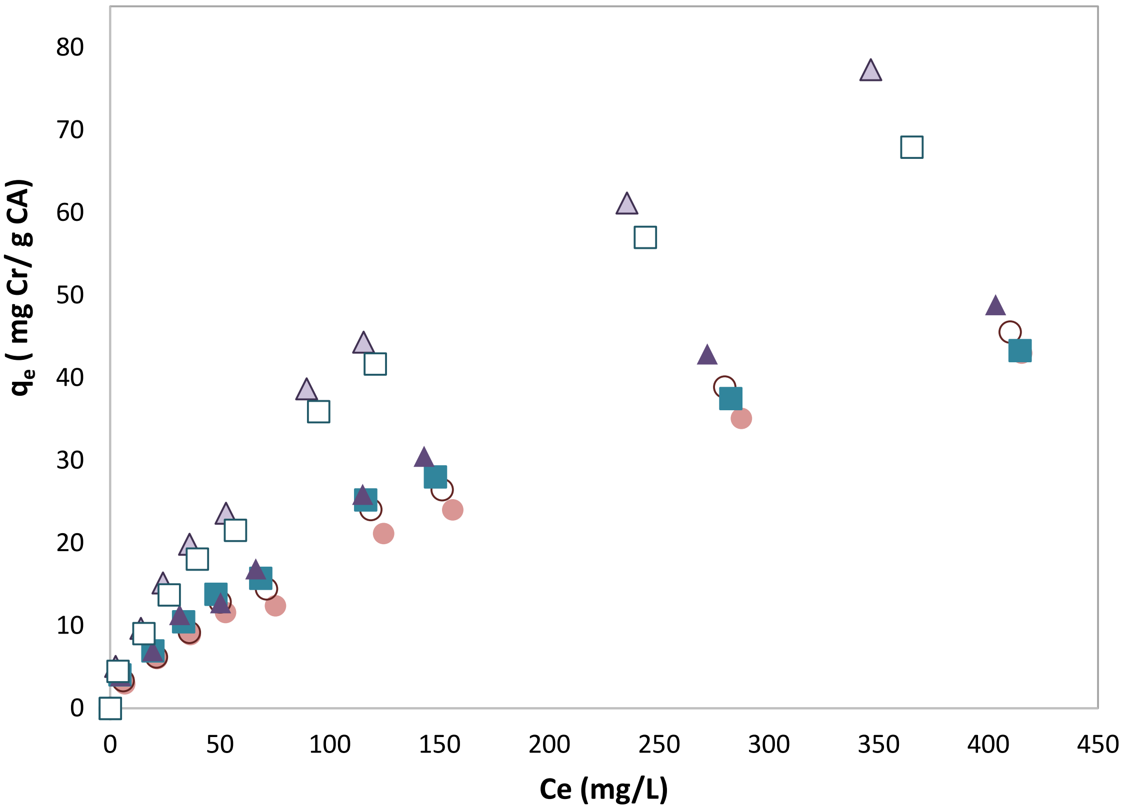

Figure 22. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and Temperature of 25°C): ● AC raw Cr(VI), ○ AC raw total Cr, ■ AC T800 Cr(VI), □ AC T800 total Cr, ▲ AC T900 Cr(VI), △ AC T900 total Cr.

Forced hydrolysis of the adsorbents treated thermally, Figure 23, caused that iron species anchored on the activated carbon surface showed 20% lower reduction of Cr(VI) to Cr(III) compared with the materials without hydrolysis, this effect was attributed to the interaction of electron donors with iron species inhibiting the Cr(VI) reduction during the adsorption process, however, it was observed that was achieved only 1% of reduction to concentrations lesser than 100 mg/L and a maximum of 10% at higher concentrations for these adsorbents allowing anionic adsorption at low concentrations.

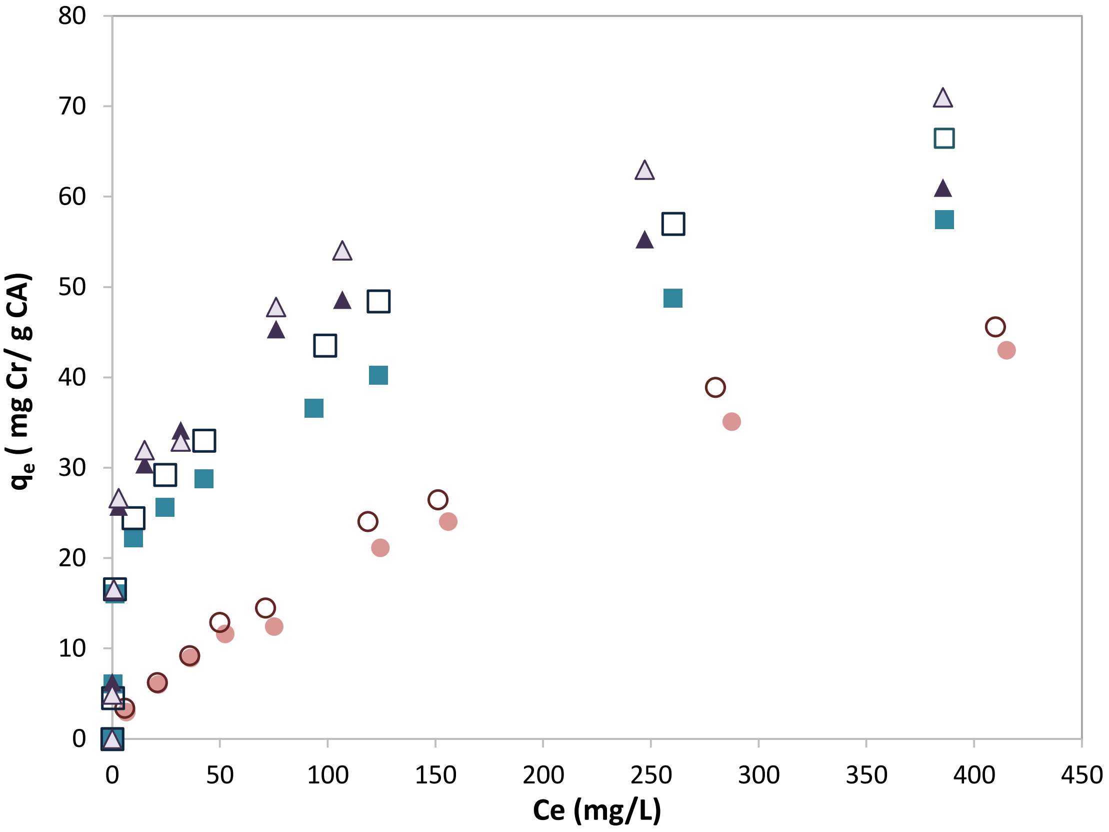

Figure 23. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and Temperature of 25°C): ● AC raw Cr(VI), ○ AC raw total Cr, ■ AC T800 FH Cr(VI), □ AC T800 FH total Cr, ▲ AC T900 FH Cr(VI), ▲ AC T900 FH total Cr.

4.2.2.4 Adsorption isotherms: Activated carbon with nitrogen treatment

Isotherm of the nitrogen-containing activated carbon (AC NT) showed a hexavalent chromium reduction about 30% between 100-200 mg/L compared with the commercial activated carbon (Figure 24). However, at upper concentration values (> 200 mg/L) the quantity of trivalent chromium increased about 50%, this behavior suggested that some electron donor groups from the activated carbon surface reduced the anionic chromium species. In another hand, forced hydrolysis of activated carbon (AC NT FH), did not show reduction at concentrations below 150 mg/L, nonetheless above this concentration a 20% of reduction of Cr(VI) was obtained, this behavior could explain that the hydrolysis provoked changes in the chemistry surface of the adsorbent and iron particles allowed the anionic adsorption of Cr(VI).

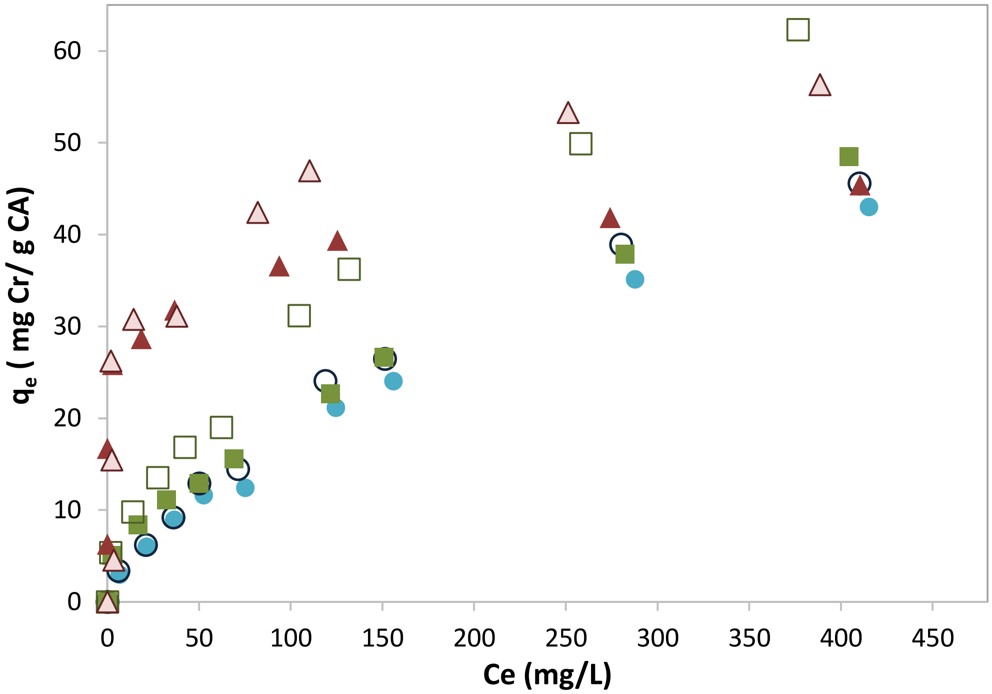

Figure 24. Adsorption isotherms of Cr(VI) on activated carbon (2 mg CA/mL, pH = 6 and Temperature of 25°C): ● AC raw Cr(VI), ○ AC raw total Cr, ■ AC NT Cr(VI), □ AC NT total Cr, ▲ AC NT FH Cr(VI), △ AC NT FH total Cr.

4.2.2.5 General discussion: Hexavalent chromium adsorption

Commercial activated carbon showed a high adsorption capacity compared with some adsorbents that have been studied, Table 23, most of the adsorption studies were carry out in acid media because of the nature of the adsorbent that allowed the adsorption of hexavalent chromium species but also provoked up to 98% of reduction to trivalent chromium.

The obtained results showed that the commercial activated carbon (AC raw) had a great adsorption capacity (45.60 mg/L) at room temperature and pH = 6. In addition, forced hydrolysis of the raw adsorbent (AC raw FH) caused an improvement about 46% in the adsorption capacity (Figure 15) especially at low concentration of hexavalent chromium (lesser than 200 mg/L), also the forced hydrolysis provoked a slightly increase about 5% in the maximum adsorption capacity (49.50 mg/L) of the commercial adsorbent.

Table 23. Cr(VI) adsorption capacity for different adsorbent materials.

Raw material	mg Cr^{6+}/g	pH	Adsorption system	Reference
Hazelnut shell	17.70	2.0	Batch	Cimino *et al.* (2000)
Activated carbon, FS-100	69.30	3.0	Batch	Hu *et al.* (2003)
Activated carbon, fabric cloth	22.29	2.0	Batch	Mohan *et al.* (2005)
Terminalia arjuna nuts	28.40	1.0	Batch	Mohanty *et al.* (2005)
Bituminous coal	7.00	5.0 - 8.0	Batch	Natalie *et al.* (2007)
AC raw	45.60	6.0	Batch	This study (2014)
AC raw FH	49.50	6.0	Batch	This study (2014)

On the another hand, reported researches about the hexavalent chromium adsorption did not involve the study of the adsorption mechanism, just some authors reported that during the adsorption of chromium species in acid media or low pH values, a higher quantity of hexavalent chromium was reduced to its trivalent form. However, the analysis of total chromium performed to the activated carbons at pH = 6 showed only a 2% of reduction by the commercial activated carbon because of the pH conditions in which the adsorption process was carried out there were not an enough quantity of protons to interact with electron donors provoking reduction to Cr(III); On the other hand, AC raw FH presented a reduction of up to 12% at concentrations greater than 150 mg/L as a result of the acid surface groups incorporated in the activated carbon surface during the hydrolysis step and at low concentration iron particles working as an adsorption site of anionic chromium species decreasing the reduction rate.

Analysis performed to the oxidized activated carbon with nitric acid allowed to identify the pair of the best adsorbents that resulted from the modification (AC Ox(10%), AC Ox(10%) FH) which had a higher adsorption capacity than other modified adsorbents, Table 24. However, most of the adsorption test performed by acid-treated adsorbents were carry out in acid media causing an important amount of reduced hexavalent chromium (greater than 90 %). On the contrary, adsorption test at pH = 6 allowed to decrease the reduction rate due to AC Ox(10%) showed only a 33% of reduction at concentrations greater than 100 mg/L.

In addition, AC Ox(10%) FH increased the adsorption capacity about 25% at concentration lower than 100 mg/L without reduction to trivalent chromium, but above this concentration value about 50% of reduction was shown.

Table 24. Cr(VI) adsorption capacity for activated carbons oxidized with minerals acids.

Raw material	Technique used	pH	mg Cr^{6+}/g	Reference
Commercial	Oxidation using HNO_3	-	10.40	Babel *et al.* (2004)
Commercial	Oxidation using sulfuric and nitric acid	-	13.30	Zhao *et al.* (2005)
Commercial	Oxidation using HNO_3	2.0	13.70	Liu *et al.* (2007)
Commercial	Oxidation using HNO_3 and heat treatment	2.0	10.93	Kumar *et al.* (2009)
Commercial	Oxidation using sulfuric and nitric acid	4.0	16.10	Huang *et al.* (2009)
AC Ox (10%)	Oxidation using nitric acid	6.0	27.82	This study (2014)
AC Ox (10%) FH	Oxidation using nitric acid and forced hydrolysis	6.0	30.23	This study (2014)

Thermal treatment did not cause an important effect on the adsorption capacity of the commercial activated carbon, both heat-treated activated carbons (AC T800, T900) showed a very similar adsorption isotherms behavior compared with the raw adsorbent, there are few studies about the adsorption of hexavalent chromium by adsorbents modified thermally, most of them were coupled to another treatment such a oxidation using mineral acids (Table 25).

Besides, forced hydrolysis of the heat-treated activated carbons (AC T800 FH, AC T900 FH) caused an important effect on the adsorption capacity of the adsorbents increasing 26% on maximum adsorption capacity of raw adsorbent and a higher affinity at concentrations of Cr(VI) lower than 200 mg/L. Even though AC T900 FH showed the greatest adsorption capacity, AC T800 FH was chosen as a better adsorbent because of the increase of 100°C on temperature only generated an increased about 15% on the adsorption capacity at concentration lesser that 150 mg/L, and above this concentration both adsorbents had almost the same value in the adsorption isotherms reaching similar maximum adsorption capacities, therefore is not justify the increase in the consumption of energy with the improvement in the adsorption capacity.

Table 25. Cr(VI) adsorption capacity for activated carbons modified by thermal treatment.

Raw material	Technique used	pH	mg Cr^{6+}/g	Reference
Commercial	Oxidation using mineral acid and thermal treatment	-	13.30	Zhao *et al.* (2005)
Commercial	Oxidation using HNO_3 and heat treatment	2.0	10.93	Kumar *et al.*(2009)
AC T800	Thermal treatment at 800°C	6.0	43.33	This study (2014)
AC T800 FH	Thermal treatment at 800°C and forced hydrolysis	6.0	57.48	This study (2014)

On the another hand, the adsorbents with thermal treatment presented about 35% of Cr(VI) reduction at concentrations greater than 100 mg/L, nonetheless heat-treated activated carbons modified with forced hydrolysis showed 20% lower reduction of Cr(VI) to Cr(III) compared with the materials without hydrolysis as a result of the iron particles anchored on the activated surface which allowed an anionic adsorption of chromium species diminishing the quantity of reduction to trivalent chromium.

The modification of commercial activated carbon with ammonium solutions (AC NT) resulted in an increase on the adsorption capacity about 7% compared with the raw adsorbent, however, hydrolysis of the activated carbon containing nitrogen produced a higher affinity (26%) for Cr(VI) up to concentrations lesser than 250 mg/L. The obtained adsorption capacities had an average value compared with that obtained with other adsorbents, Table 26, as a result of the method used to modify the activated carbon surface.

Table 26. Cr(VI) adsorption capacity for activated carbons modified by ammonia treatment.

Raw material	Technique used	pH	mg Cr^{6+}/g	Reference
ACF-307	Oxidation using ammonium persulphate	-	19.00	Aggarwal *et al.* (1999)
Coconut Pitch	Amine modification	3.0	123.40	Unnithan *et al.* (2004)
Activated carbon	Amine-crosslinked copolymer	5.0	102.88	Sun *et al.* (2013)
AC NT	Oxidation using Ammonia solution	6.0	48.51	This study (2014)
AC NT FH	Oxidation using Ammonia solution and forced hydrolysis	6.0	45.41	This study (2014)

In addition, many of the adsorption studies performed with activated carbon modified with an ammonia source did not analyze neither the reduction of Cr(VI) to Cr(III) nor the effect of the nitrogen functional groups on the adsorption capacity. The results of the total chromium isotherms showed that AC NT surface caused up to 50% of reduction of hexavalent chromium at concentration greater than 100 mg/L; On the other hand, forced hydrolysis of the activated carbon (AC NT FH) improved the adsorbent surface resulting in a 20% of Cr(VI) reduction at concentration greater than 150 mg/L.

4.2.3 Cr(VI) desorption test

Desorption test were carried out from different adsorbents studied using a solution of NaOH-NaCl 0.1 N, a desorption with this eluent suggested the way in which species of Cr(VI) and activated carbon interacted indicating anionic adsorption, the obtained results are shown in Figure 25. Adsorbents that shown the best results were commercial activated carbon with forced hydrolysis (AC raw HF), activated carbon with thermal treatment 800°C and it forced hydrolysis (AC T800 FH) as well as activated carbon with thermal treatment at 900°C and also it forced hydrolysis (AC T900 FH), resulting the activated carbon modified with thermal treatment and forced hydrolysis as the best adsorbents in both adsorption and desorption. Some researchers have reported an excellent desorption rate using acid solutions such as HNO_3, HCl or EDTA (Gupta *et al.* (2010); Kumar *et al.* (2011)), reaching up to 75% of the adsorbed chromium.

However, desorption with acid solutions indicated cation exchange, therefore trivalent chromium was the specie of chromium that took place in the adsorption process. On the contrary, anion exchange was reported by Selvaraj *et al.* (2003) who achieved 82% of Cr(VI) desorption using 0.014 M NaOH; and Deng *et al.* (2004) reported a 96% of hexavalent chromium desorption using 0.5 M NaOH. The studied activated carbon achieved different desorption capacities which is related with the adsorption process because of nitrogen and acid nitric oxidation treatment caused a high reduction of hexavalent chromium while commercial and heat-treated activated carbon showed a short reduction at low concentration; In addition, forced hydrolysis improved the anionic adsorption of the adsorbent material, therefore the best selected adsorbents (AC T800 FH, AC T900 FH) showed about 96% of Cr(VI) desorption using 0.1 N NaOH-NaCl indicating also anion exchange during the desorption process.

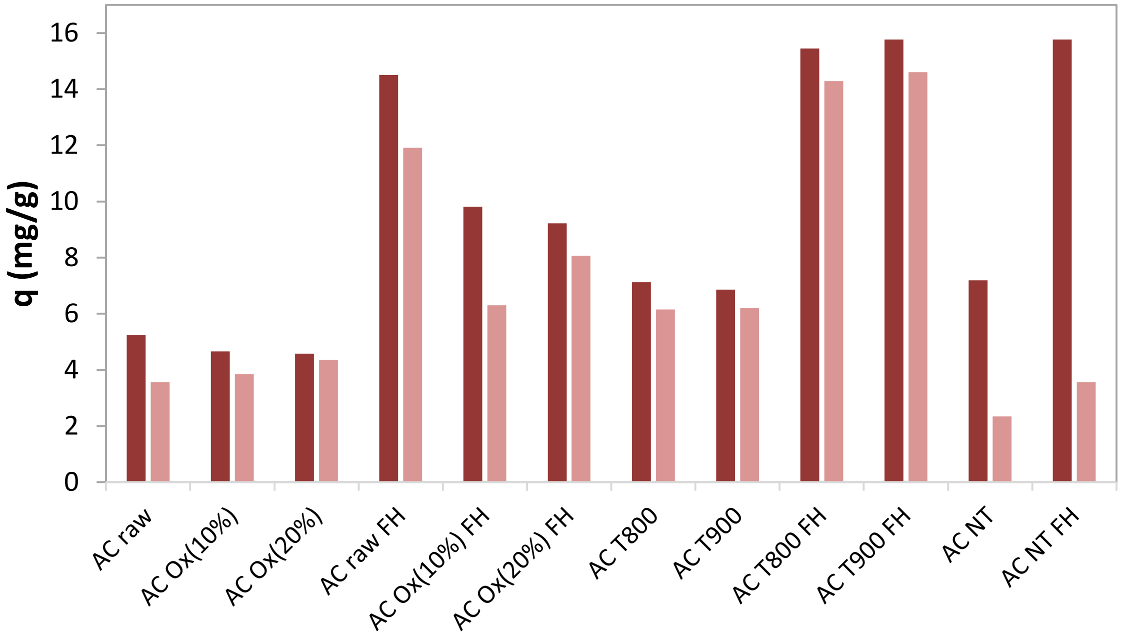

Figure 25. Histogram of the adsorption-desorption analysis of the different adsorbent materials: ■ Adsorption capacity (mg/g), ■ Desorption capacity (mg/g); Initial concentration: 30 mg/L Cr (VI), pH = 6.

4.2.4 Cr(VI) adsorption kinetics

The analysis of the adsorption kinetics of the selected adsorbents (Figure 26) showed a faster adsorption of hexavalent chromium achieved by the heat-treated activated carbon with forced hydrolysis (AC T800 FH) diminishing the equilibrium time (1031 min) about 30% compared with the activated carbon without hydrolysis AC T800 (1300 min) and about 55% in comparison with the commercial activated carbon (1600 min) indicating that thermal treatment coupled the iron particles adsorption sites helped to the adsorbent surface to attach hexavalent chromium ions improving both capacity as adsorption rate of the activated carbons.

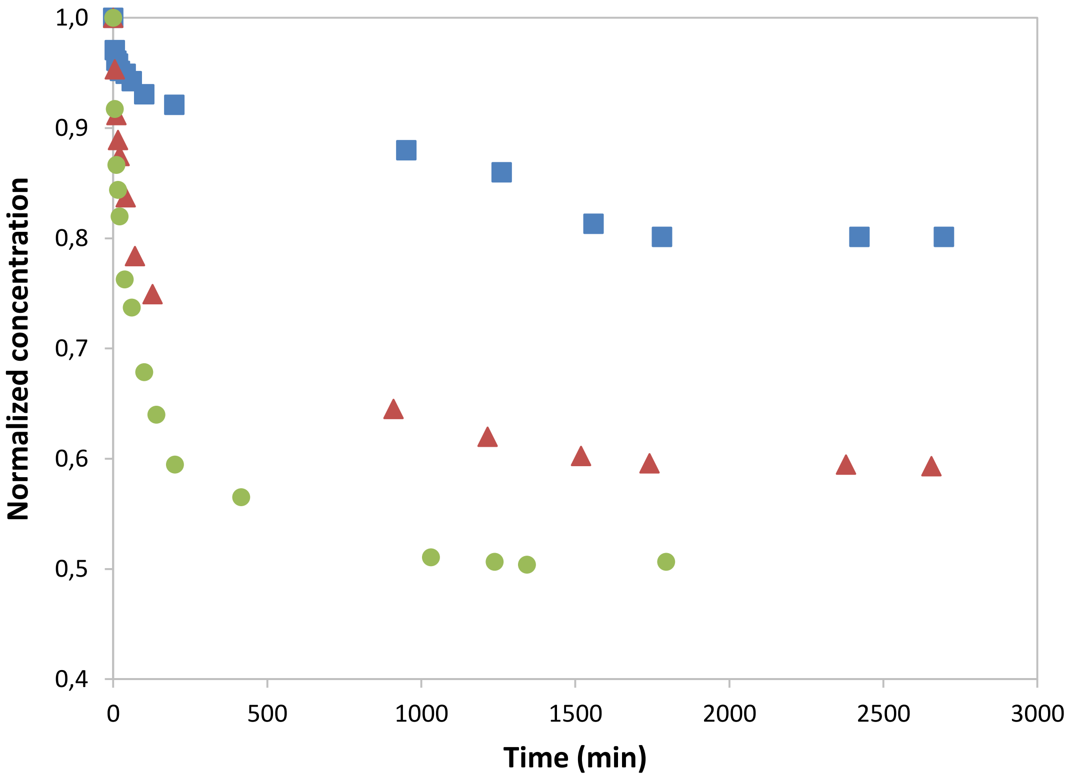

Figure 26. Adsorption kinetics analysis of the different selected adsorbent materials: ■ AC raw, ▲ AC T800, ● AC T800 FH. Initial concentration: 30 mg/L Cr (VI), pH = 6.

Adsorption kinetic data (AC T800, AC T800 FH) were pretty adjusted to a Pseudo-second order model (Eq. 4.1), the main parameter were obtained and they are shown in Table 27.

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad \text{(Eq. 4.1)}$$

In the contrary, adsorption kinetic data of the raw activated carbon could not be adjusted because its kinetic curve showed two adsorption steps, indicating the simultaneous adsorption-reduction mechanism of hexavalent chromium.

Table 27. Adsorption kinetic parameters.

Adsorbent	K_2	q_e	R^2
AC T800	0.00144	12.42	0.99986
AC T800 FH	0.00162	15.08	0.99975

Ho *et al.* (1999) reported an extensive study about the pseudo-second order model for sorption processes and they concluded that in their 12 different studied systems, chemical reaction seems significant in the rate controlling step and the pseudo-second order model provides the best correlation of the experimental data. Khezami *et al.* (2005) reported that pseudo-second order model well mimics the adsorption kinetic data in the removal of chromium (VI) by activated carbon. In addition, AL-Othman *et al.* (2012) reported the kinetics of Cr(VI) followed both pseudo-first order and pseudo-second order rate expressions in the removal of hexavalent chromium by activated carbon prepared from peanut shells.

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CHAPTER 5

Conclusions

> **"A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales."**
>
> *Marie Curie*

CONCLUSIONS

The oxidation treatment with nitric acid caused the increase in quantity of surface acid groups, mainly fenolic and carboxylic groups according with Boehm titrations and the obtained infrared spectra. Also the oxidized activated carbons showed an slightly increment in the BET surface area about 16%; however, an increase in the oxidation degree caused that activated carbon walls collapsed and, therefore, a 10% surface area and 25% pore volume were shown.

Thermal treatment removed all the surface acid groups from the activated carbon surface increasing the quantity of basic groups as a result of the decomposition of oxygenated groups or volatile compounds causing the generation of new pores in the adsorbent that slightly increase the BET surface area about 7% and 20% in pore volume compared with commercial activated carbon.

Nitrogen treatment increased the quantity of nitrogen groups on activated carbon according with the obtained results from elemental analysis and infrared spectra; In addition, Boehm titrations showed that nitrogen containing activated carbons presented an increment in the quantity of surface basic groups. On the other hand, nitrogen treatment caused an important effects increasing the BET surface area about 85% and 3 times the pore volume.

Forced hydrolysis of the commercial and modified activated carbon did not show important changes on surface chemistry of activated carbon, but decrease both BET surface area and pore volume about 15 % as a result of pore blocking by anchored iron particles. Iron analysis showed that activated carbon with higher quantity of acid functional groups had the greater quantity (0.15%) of anchored iron particles and the adsorbents without acid groups and high content of surface basic groups had the lower quantity (0.01 %) of iron over adsorbent surface.

Commercial and modified activated carbon are able to sequester metal ions such as hexavalent chromium from aqueous solution; however, oxidized and nitrogen containing activated carbons caused about 40-50% of reduction of Cr(VI) to Cr(III), resulting as better adsorbents those which were treated thermally.

On the other hand, the anchoring of iron particles improved the hexavalent chromium adsorption of the activated carbons at concentration lower than 150 mg/L. All equilibrium data of the different studied adsorbents were well-fitted to Freundlich model.

Even though, oxidized activated carbon had the higher iron quantity, heat-treated adsorbents and modified by forced hydrolysis showed the best adsorption capacity (57 mg/g) of hexavalent chromium from aqueous solutions.

Hexavalent chromium desorption test showed that commercial and oxidized activated carbons could desorb about 80% of hexavalent chromium, and nitrogen containing activated carbon just could desorb about 30%; these low desorption percentages indicated that the chromium removal was through a reduction coupled adsorption mechanism.

In addition, heat-treated activated carbons presented the higher desorption (98%) of hexavalent chromium indicating that the main adsorption mechanism was carried out by anion adsorption.

The best adsorbents resulted the heat-treated activated carbons and modified with forced hydrolysis (T800 FH, T900 FH) who achieved an adsorption capacity of 57 mg/g and 98% of Cr(VI) desorption.

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> **“It isn't that they can't see the solution.**
> **It is that they can't see the problem.”**
> *G.K. Chesterton*

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AUTOBIOGRAPHIC SUMMARY

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