

FS-TER-002

**TECHNICAL SHEETS
FOR EFFLUENT TREATMENT PLANTS
IN TEXTILE INDUSTRY**

ACTIVATED CARBON ADSORPTION

SERIES: TERTIARY TREATMENTS

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INDITEX

ACTIVATED CARBON ADSORPTION

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INDEX

- 1.- INTRODUCTION**
- 2.- FUNDAMENTALS OF ADSORPTION ONTO ACTIVATED CARBON**
 - 2.1.- Factors influencing adsorption**
 - 2.2.- Kinetics of adsorption**
 - 2.3.- Transport mechanisms**
 - 2.4.- Adsorption equilibrium**
- 3.- DESIGN AND OPERATION**
 - 3.1.- Description**
 - 3.2.- Operation**
 - 3.3.- Design variables**
 - 3.4.- Typical design values**
- 4.- PARAMETERS AND CONTROL STRATEGIES**
 - 4.1.- Breakthrough curve**
 - 4.2.- Activated carbon regeneration and activation**
- 5.- PERFORMANCE**
- 6.- PARTICULAR TECHNICAL CONDITIONS**
- 7.- SPECIFICATIONS FOR THE TREATMENT OF WASTEWATER OF TEXTILE INDUSTRY**
- 8.- OPERATION TROUBLESHOOTING**

BIBLIOGRAPHY

ANNEX 1 MILLS EXAMPLES WITH AC ADSORPTION ON ITS EFFLUENT TREATMENT PLANTS PROCESS
ANNEX 2 GRAPHICAL DESCRIPTION OF UNIT PROCESSES

1.- INTRODUCTION

Granular activated carbon (GAC) adsorption is a process used as tertiary treatment of municipal and industrial wastewater (physical-chemical treatment, followed by secondary treatment) or as a step in the physical-chemical treatment (coagulation, sedimentation, filtration, GAC adsorption) instead of the secondary treatment. In case of being applied as a tertiary treatment, GAC is fundamentally used for organic molecules adsorption incorporated to effluent from the biological treatment. It normally requires a pretreatment, such as lime precipitation followed by rapid filtration.

In industrial water treatment, the GAC adsorption can be used to meet pretreatment discharge standards to municipal wastewater treatment plants or to meet discharge standards to environment.

This document is based on the text *Activated Carbon for Water and Wastewater Treatment* of Ferhan Çeçen and Özgür Aktas (2012), with contributions and specific documents for water treatment in the textile industry.

2.- FUNDAMENTALS OF ADSORPTION ONTO ACTIVATED CARBON

2.1.- Factors influencing adsorption

In summary, a number of factors influencing the adsorption process in AC can be listed:

- **Surface area of adsorbent**
- Physical and Chemical **characteristics of the adsorbate**: as molecular weight and solubility in the water media.
- **Adsorbate polarity**: A polar solute is preferably adsorbed by a polar adsorbent, whereas a nonpolar solute is more easily adsorbed by a nonpolar adsorbent. Activated carbon adsorbs nonpolar molecules better than polar molecules.
- **pH**: Adsorption of most organic compounds is higher at neutral pH conditions (around pH 7).
- **Temperature**: Temperature influences on solvent affinities and compounds diffusion in water
- **Porosity of the adsorbent**: The total porosity is usually classified into three groups: micropores less than 2 nm, mesopores pores between 2 and 50 nm and macropores above 50 nm pores. Most of the total surface area is found in the micropores and the contribution of the macropores to the total surface area is very low.
- **Surface chemical characteristics**: Adsorption capacities of thermally activated carbons have been found to be relatively higher than those of chemically activated carbons, although it varies depending on the adsorbate.

2.2.- Kinetics of adsorption

The rate of adsorption is usually limited by various mass transport mechanisms and depends both on the properties of the adsorbent and the adsorbate. Figure 1 shows the main transport mechanisms of an adsorbate to a carbon surface and the adsorption phenomena.

2.3.- Transport mechanisms

Bulk solution transport (advection): Adsorbates must first be transported from the bulk solution to the boundary layer of water (liquid film) surrounding the activated carbon particle.

External diffusion: Transport of adsorbate from the bulk of solution across the stationary layer of water, called the hydrodynamic boundary layer, liquid film or external film that surrounds the adsorbent particles. It occurs by molecular diffusion.

Intraparticle (Internal) diffusion Intraparticle diffusion involves the transfer of adsorbate from the activated carbon surface to sites within the particle. In modeling of the adsorption of pollutants from water or wastewater, the surface diffusion is usually assumed to be the dominant intraparticle transport mechanism.

Adsorption. After the transport of the adsorbate to an available site, an adsorption bond is formed. In the case of physical adsorption, the actual physical attachment of adsorbate onto adsorbent is regarded as taking place very rapidly. Therefore, the slowest step among the preceding diffusion steps (advection, external diffusion or internal diffusion), called the rate-limiting step, will control the overall rate at which the adsorbate is removed from solution. However, if adsorption is accompanied by a chemical reaction that changes the nature of the molecule, the chemical reaction may be slower than the diffusion step and may thereby control the rate of removal.

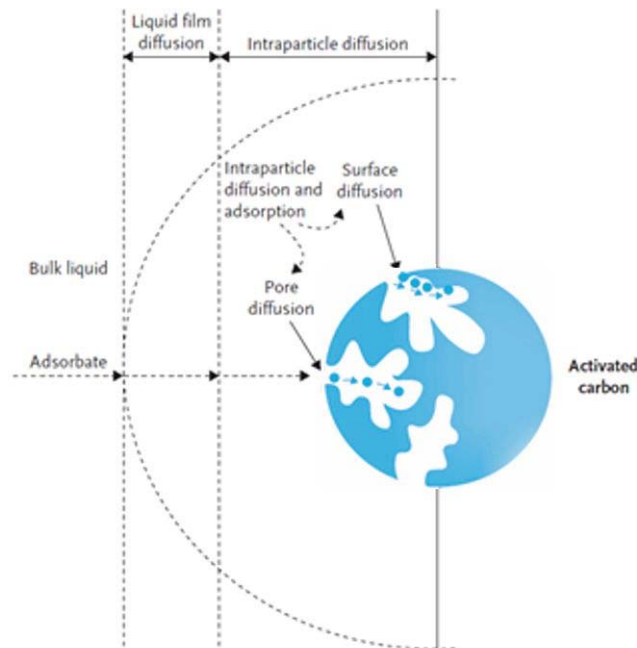


Figure 1 External and intraparticle transport of an adsorbate in an activated carbon particle

2.4.- Adsorption equilibrium

Adsorption equilibrium is often studied through those called adsorption isotherms, which represent the main source of information on the adsorption process.

$$Q = Q(S_e) \text{ at temperature } T$$

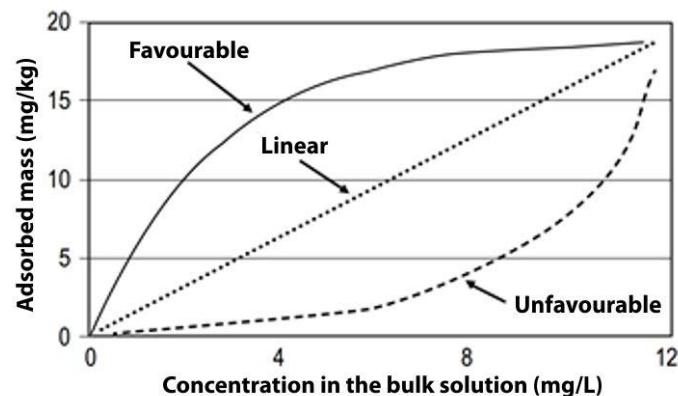


Figure 2 Representation of the general types of adsorption isotherms of solutes in porous media (Martin, 1997).

The amount of adsorbed material per unit mass of adsorbent increases with increasing concentration, but not in direct proportion. Generally, an isotherm is favorable if its form is convex, and unfavorable if concave. Any point of an isotherm curve describes an amount of pollutant adsorbed per unit weight of active carbon, or alternatively, the adsorption capacity at a particular concentration.

As practical issues, the isotherms can be used to select the correct type of active carbon, to estimate the lifetime of the adsorbent and to study the remaining adsorption capacity of an adsorption unit under continuous operation.

3.- DESIGN AND OPERATION

3.1.- Description

Continuous flow GAC systems are usually composed of carbon filters, virgin and spent carbon storage, carbon transport systems and carbon regeneration systems. The carbon filter typically consists of a linear steel column or a rectangular steel or concrete tank in which carbon is deposited as "filter bed".

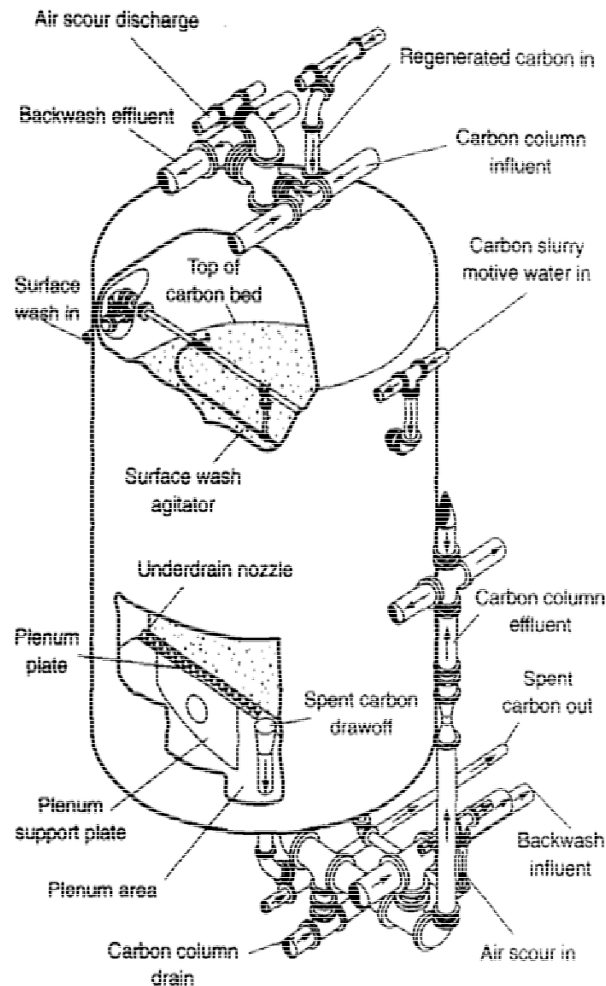


Figure 3 Typical activated-carbon contactor in a pressure vessel (Metcalf & Eddy, 2002)

3.2.- Operation

Types of GAC Adsorbers

A fixed-bed GAC column is used most commonly for contacting wastewater with GAC. Fixed-bed carbon adsorbers may be operated under **pressure or gravity** flow. Wastewater is applied at the top of the carbon column, flows downward through the carbon bed, and is withdrawn at the bottom of the column. As the wastewater flows through the column, the contaminants are adsorbed. The carbon is held in place with a drain system at the bottom of the contactor. Provisions for **backwash and surface wash** of the carbon bed are required to prevent buildup of excessive head loss due to accumulation of solids and to prevent the bed surface from clogging.

The main reactor configurations for GAC adsorption systems are **the fixed (packed), expanded, and fluidized beds**. A downflow adsorber with low fluid velocities essentially functions as a fixed-bed reactor. Fixed-bed operation provides filtration as well as adsorption. The fixed-bed configuration is suitable in the case of low-strength wastewaters containing little or no suspended solids.

3.3.- Design variables

In sizing of GAC columns, the following factors are mainly taken into consideration: the empty-bed contact time (EBCT), the hydraulic loading rate, the carbon depth, and the number of contactors. GAC filters may be designed as up or downflow systems consisting of one or more vessels in series or in parallel. The main parameters characterizing the GAC operation are as follows:

Empty-Bed Contact Time (EBCT)

The EBCT is calculated as the total volume of the carbon bed divided by the flow rate of water:

$$EBCT = \frac{V_B}{Q}$$

Where

V_B =volume of the GAC bed (L3)

Q =flow rate (L3/T)

EBCT can also be expressed as follows:

$$EBCT = \frac{L_B}{Q/A}$$

Where

L_B =depth of GAC bed, (L)

A = cross-sectional area of bed, (L2)

Q/A =hydraulic loading rate (HLR), (L3/L2.T)

The EBCT represents the theoretical residence time in the filter in the absence of packing media. Therefore, it is actually a fictive parameter whose meaningfulness has been discussed in water treatment.

Effective Contact Time: Since the GAC bed has a void fraction, the effective contact time (τ) of the fluid is as follows in an adsorber:

$$\tau = \frac{V_B \varepsilon_B}{Q}$$

Where

ε_B = void fraction in the carbon bed

Filter Velocities

In water and wastewater treatment the superficial velocity shows the velocity of liquid in an empty bed with a cross-sectional area A and corresponds to the hydraulic loading rate (HLR). It is also termed the surface loading rate.

$$v_F = \frac{Q}{A}$$

On the other hand, the interstitial velocity in an adsorber is a more meaningful parameter, and is defined as follows:

$$v_i = \frac{Q}{A_{\varepsilon_B}}$$

Filter Operation Time

The filter operation time (t_F) is the time until the replacement of activated carbon with regenerated or new activated carbon.

Throughput Volume

The throughput volume is the water volume which passes through the reactor during the filter operation time (t_F).

$$V_L = Q \cdot t_F$$

Bed Volume

The bed volume (BV) shows the normalization of throughput volume to the carbon bed volume V_B . As such, it allows a comparison of removal efficiencies of different adsorbers.

$$BV = \frac{V_L}{V_B} = \frac{t_F}{EBCT}$$

Carbon Usage Rate

The breakthrough curve can be used to determine the activated carbon usage rate (CUR), which is defined as the mass of activated carbon required per unit volume of water treated until breakthrough

$$CUR \left(\frac{\text{masa}}{\text{volumen}} \right) = \frac{\text{mass of GAC in column}}{\text{volume treated to breakthrough}}$$

3.4.- Typical design values

Ranges of the principal design and operation parameters for granular active carbon filters are included on Table 1

Table 1 Typical values for design and operation in GAC filters (Çeçen, 2012)

	Range	Unit
Flow rate, Q		
Water treatment	1200–9600	m ³ d ⁻¹
Tertiary treatment of municipal wastewaters	5000–380000	m ³ d ⁻¹
Physicochemical treatment of municipal wastewaters	2200–19000	m ³ d ⁻¹
Industrial wastewater treatment	19–16000	m ³ d ⁻¹
Empty-Bed Contact Time (EBCT)		
General	10–50	min
Typical	30	min
Water treatment	5–30	min
Tertiary treatment of municipal wastewaters	17–50	min
Physicochemical treatment of municipal wastewaters	20–66	min
Industrial wastewater treatment	30–540	min
Hydraulic Loading Rate, HLR		
General	5–25	m h ⁻¹
Typical	12	m h ⁻¹
Water treatment	5–15	m h ⁻¹
Tertiary treatment of municipal wastewaters	7–16	m h ⁻¹
Physicochemical treatment of municipal wastewaters	6–15	m h ⁻¹
Carbon Usage Rate (CUR)		
Tertiary treatment of municipal wastewaters	0.12–0.23	kg GAC/m ³
Physicochemical treatment of municipal wastewaters	0.29–1.04	kg GAC/m ³
Typical values of the GAC bed		
Bed volume, V_B	10–50	m ³
Cross-sectional area, A	5–30	m ²
Length, L_B		
General	3–9	m
Water treatment	1.8–4	m
Tertiary treatment of municipal wastewaters	3–10	m
Physicochemical treatment of municipal wastewaters	2.7–11	m
Void fraction in GAC bed, ε_B	0.3–0.6	m ³ /m ³
Apparent filter density, ρ_B	430–480	kg solids/m ³ bed
GAC particle density, ρ_P	0.92–1.5	kg solids/m ³ solid

4.- PARAMETERS AND CONTROL STRATEGIES

4.1.- Breakthrough curve

As the wastewater flows naturally through GAC adsorbent, contaminants are eliminated by adsorption. The adsorption of contaminants takes place in zone A, called the mass transfer zone (MTZ) (Figure 5). While in operation, the transfer zone moves in the direction of flow. In this zone moves downwards, generating the saturation zone (Zone-Sat) which is saturated with pollutants and is in equilibrium with the influent concentration.

Inside an AC filter pollutant concentration changes along the adsorption column, the area of rapid change of length is known as concentrations wave front. Inside an adsorber, the concentrations of contaminants change with respect to both time and reactor length. The region of rapid change in concentration with the length z is termed the wave front.

The plot of effluent concentration divided by influent concentration (S/S_0) as a function of elapsed time, processed volume, or bed volume generates the "breakthrough curve". The point at which a predetermined concentration (S_B) appears is defined as the "Breakthrough point". This point is rather arbitrary and is selected according to purity requirements.

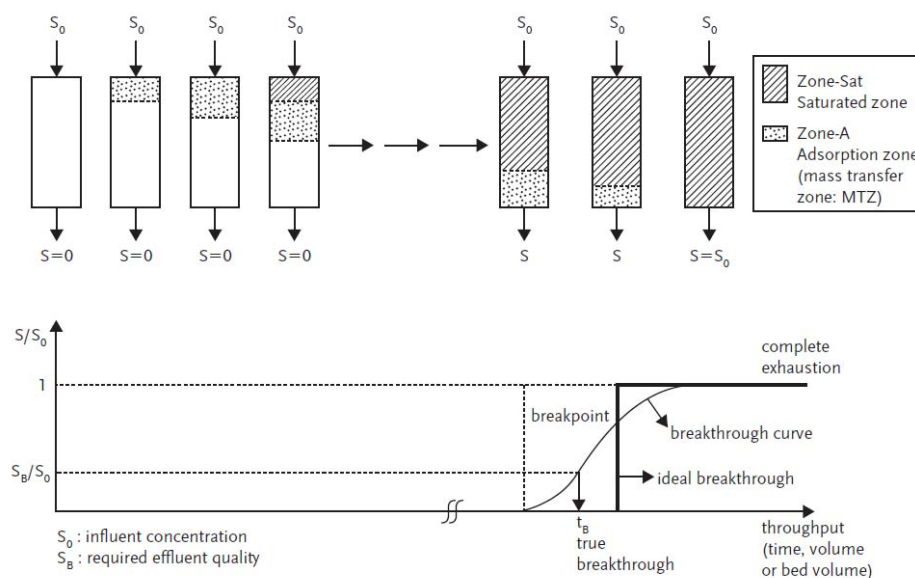


Figure 4 Breakthrough characteristics in a fixed-bed GAC adsorber (Çeçen, 2012).

4.2.- Activated carbon regeneration and activation

The carbon adsorption capacity gradually deteriorates with use. When the quality of the effluent reaches the minimum level set in quality standards, the spent carbon should be regenerated, reactivated or removed.

Activated carbon is a high capital investment and operating cost to operate in both batch and continuous, mainly due to system regeneration need. The regeneration of the spent adsorbent is the most difficult and expensive part of the adsorption technology. It carries about 75% of the cost of operation and maintenance of a filtration unit in fixed bed GAC.

- Regeneration represents carbon contaminant removal without destroying contaminants.
- Reactivation involves the destruction of contained matter and reactivation of coal, which normally occurs at high temperatures.

If regeneration of spent carbon is not feasible or it is irreversibly contaminated by the adsorbed substance, used carbon used will be removed.

The most used techniques for regeneration are thermal, chemical and electrochemical regeneration.

5.- PERFORMANCE

Table 3 shows qualitative active carbon filtration performance values in comparison with a conventional activated sludge treatment and improved integrated adsorption and biological treatment process. According to this reference, the use of both biological treatment and GAC, whether combined or in different steps of the process line, allow to improve wastewater effluents.

Table 2 Reduction in pollutant groups parameters obtained by adsorption, biodegradation or both processes integrated.

Parameters/pollutant groups	Importance in water (W), groundwater (GW) or wastewater (WW) treatment	Activated Carbon Adsorption	Biological Removal or Transformation	Removal in Integrated Adsorption and Biological Treatment
Organic pollutants				
<i>Oxygen demand parameters</i>				
BOD	WW	F to G	G to E	E
COD	WW	G	L to G	G to E
<i>Organic carbon parameters</i>				
TOC	W, WW, GW	G	L to G	G to E
DOC	W, GW, WW	G	L to G	G to E
VOC ^e	W, GW, WW	L to G	L to G	G to E
BDOC	W, GW	F to G	G to E	E
AOC	W, GW	F to G	E	E
<i>Other organic parameters</i>				
AOX	W, GW, WW	G to E	L to F	G to E
UV ₂₅₄	W, GW, WW	G	L	G to E
<i>Organic Pollutant Groups</i>				
THMs	W, GW	G	P to L	G
HAAs	W, GW	G	G	G to E
Pesticides	W, GW	F to E	L to F	G
Pharmaceuticals	W, WW	F to E	F to E	G to E
Endocrine Disrupting Compounds (EDCs)	W, WW	G	P to G	G to E
Chlorinated hydrocarbons	GW, WW	F to E	L to G	G to E
<i>Inorganic Pollutants</i>				
Bromate	W	L to F ^a	F to G ^d	G ^d
Perchlorate	GW	N	G	G to E
Ammonia	W, WW	N	G	G to E
Nitrate	GW, WW	N	G	G to E
Heavy Metals	W, GW, WW	P to G ^b	F ^c	G ^c

E: excellent, G: good, F: fair, L: low, P: poor, N: none

^areduction at surface

^bdependent on type and conditions

^cpossible transformation and/or biosorption

^duncertain

^eVolatile Organic Carbon: Volatile Organic Compounds are measured based on the surrogate 'carbon.' They can also be measured as individual compounds.

6.- PARTICULAR TECHNICAL CONDITIONS

Installing two or more identically sized columns in series is common practice. When the effluent of the column 1 reaches the breakpoint, the water to be treated is fed directly to column 2, leaving column 1 off-line. Then the saturated carbon is removed from the column 1, being exchanged for fresh coal. At this time, the output of column 2 is connected to the input column 1 renewed (Figure 6). When the column 2 reaches the breakpoint, it is again extracted off-line to be renewed and so on. In this way always a second, relatively new bed is positioned to maintain the level of pollutants in the effluent as low as possible (Cooney, 1999).

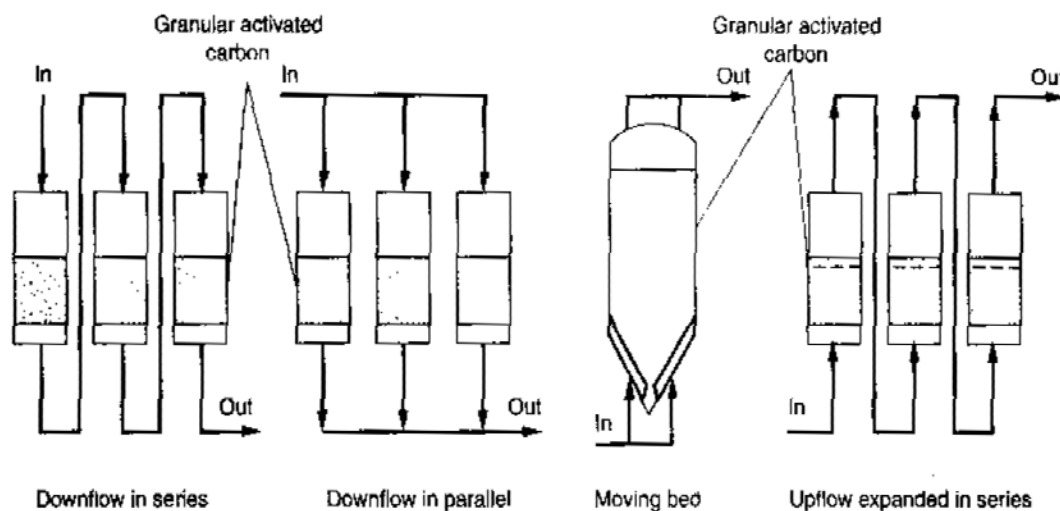


Figure 5 Activated carbon dispositives. A) Downflow in series. B) Downflow in parallel. C) Moving bed. D) Upflow expanded bed. (Metcalf, 2002)

The design must also provide:

- Pressure probes to the input and output in AC filtration
- Bypass possibility in case of good influent quality

7.- SPECIFICATIONS FOR THE TREATMENT OF WASTEWATER OF TEXTILE INDUSTRY

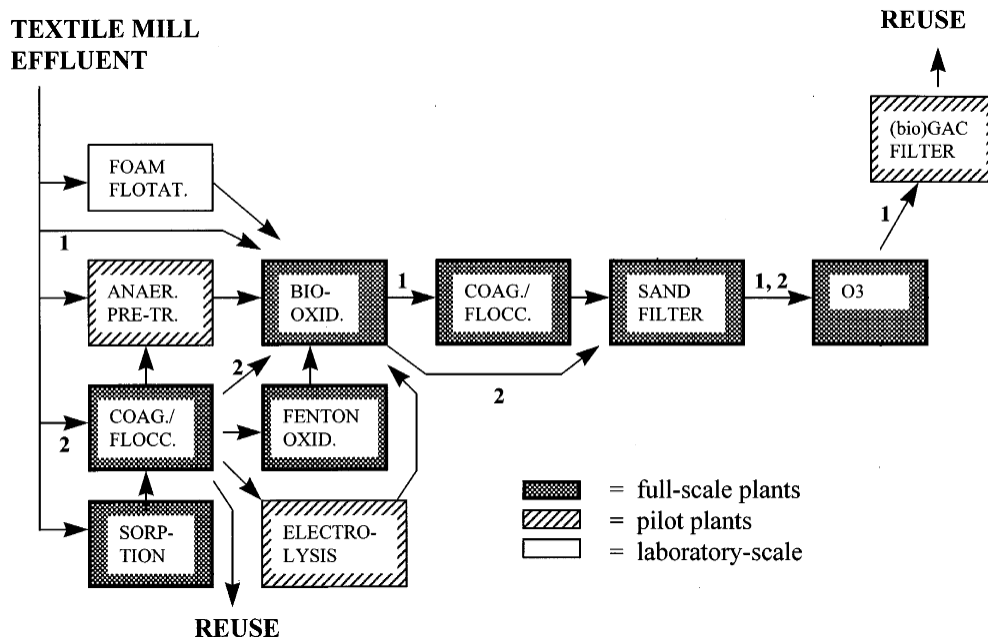
The specific characteristics of the Activated carbon adsorption process, turn it into a flexible process that can be located in different places within the plant configuration (Figure 7) with different effluent quality targets. For various applications in the textile industry it can be found as:

- Process water pre-treatment
- Tertiary treatment with discharge quality objectives
- Tertiary treatment prior to reuse.

Textile wastewaters are generally strongly colored with a high organic content. They are difficult to treat by conventional biological treatment processes because of the presence of refractory dyes and complex ingredients. The high color of these wastewaters results from a number of dyestuffs. The BOD₅/COD ratio in these wastewaters is generally too low (<0.2) to support biological treatment. In many cases, activated sludge can be effectively combined with PAC to decolorize textile effluents since PAC serves as a deposit for dye molecules. For example, it was shown that in the treatment of a wool-dyeing wastewater the decolorization yield reached 86% upon the addition of PAC to a batch activated sludge reactor (Chen, 2000).

In addition, BAC filters can be used for dye removal. Simulated aqueous discharge from a carpet printing plant comprising a mixture of acid dyes was treated for color removal in an aerobic batch BAC reactor dominated by the bacteria *Pseudomonas putida*. This BAC system outperformed the combined application of conventional GAC adsorption and biological treatment. Enhanced color removal was achieved in the BAC system due to the high utilization of biodegradable anthraquinone dyes. The main factor underlying the enhanced utilization was the accumulation of dye at the carbon surface. For non-biodegradable azo dyes, biosorption was an important removal mechanism. In any case, in BAC systems biosorption was higher than the one in conventional immobilized systems.

An upflow biological aerated filter packed with two different layers consisting of GAC and ceramsite (artificial foundry sand) was employed for tertiary treatment of a secondary textile effluent (Lin, 2008). The reactor performed well under steady-state conditions. The average COD, NH₄⁺-N, and total nitrogen (TN) in the effluent were, 31, 2 and 8 mg/L respectively, satisfying the standards for domestic reuse in China. At a constant dissolved oxygen (DO) concentration, the increase in hydraulic loading rate (HLR) from 0.13 to 0.78 m³/m²/h decreased COD NH₄⁺-N, and TN removal efficiencies from 52% to 38%, 90% to 68%, and 45% to 33%, respectively. When the DO concentration was raised from 2.4 to 6.1 mg/L, the efficiency of COD and NH₄⁺-N removal increased from 39% to 53% and 64% to 88%, respectively.



1: Alto Lura WWTP managed by CIDA Srl in Como area (Italy) treating 22.000 m³/d in a mixture consisting in 17% domestic WW, 32% stormwater, 51% homogenized textile finishing factories effluent (cellulosic, wool, silk and synthetic fibers). 2: Levi's Strauss WWTP, Wervik (Belgium).

Figure 6 Compilation of possible technological, commercial and experimental processes for the treatment and reuse of textile effluents with GAC (modified from Vandevivere, 1998).

Anaerobic processes combined with activated carbon were also considered from the treatment of textile effluents. For example, the wastewater of a carpet dyeing factory with COD and BOD₅ concentrations up to 9000 and 1500 mg/L, respectively, was anaerobically treated in a GAC-UASB (upflow anaerobic sludge blanket) reactor with about 80% efficiency (Kuai, 1998).

Activated carbon use in the supply chain

In the review work to the effluent treatment plants of INDITEX's supply chain, it is observed that factories use activated carbon filters as a tertiary treatment prior to discharge into the natural environment. In all cases rapid sand filtration precedes GAC filters (Annex I).

8.- OPERATION TROUBLESHOOTING

Filters clogging

The suspended solids present in municipal and industrial wastewaters and the potential for biological growth can lead to **problems if fixed beds are used**. Passing wastewater upwards at velocities sufficient to expand the bed is a way of minimizing the problems of fouling, plugging and increasing pressure drop in municipal and industrial wastewater treatment. For this purpose, expanded moving, or fluidized bed systems may be used. In an expanded bed system, water or wastewater introduced at the bottom expands the bed when it flows upward.

In the moving bed system, spent carbon is continuously replaced so that no head loss builds up. Another option in water and wastewater treatment is to use fluidized bed reactors (FBRs), in which the upflowing liquid suspends the fine solid particles, which remain in the reactor. Fluidized beds minimize clogging and unintentional filtration. The carbon can be continuously removed from the reactor while fresh carbon can be added to the top at the same rate. In contrast to fixed-bed operation, this process will eliminate the need to shut down the contactor after exhaustion occurs.

Problems related to activated carbon replacement

- Regeneration, revitalization and replacement of activated carbon costs are the main expense in O&M of AC filters.
- 5-10% of the carbon to be replaced is due to losses in the transport processes of activated carbon.
- The adsorption capacity of regenerated carbon is slightly lower than that of virgin carbon.

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ANNEX 1

MILLS EXAMPLES WITH AC ADSORPTION ON ITS EFFLUENT TREATMENT PLANTS PROCESS

BEXIMCO CONTINUOUS DYEING UNIT

Code

BAN01

WATER CONSUMPTION: 1640 m³/dayETP CAPACITY: 150 m³/h

STAGES OF THE EFFLUENT TREATMENT PLANT	Chemicals added		Additional notes
Equalization tank			
Dissolved Air Flotation Clarifier	←	<i>Ferrous sulphate</i> <i>Lime</i> <i>Polyelectrolite</i>	
Biological reaction tank	←	<i>Sulphuric acid</i>	
Sedimentation tanks			
High rate filtration (multilayer)			
Granular Activated Carbon Filter			
Discharge to river			

REEDISHA KNITTEX LIMITED

Code

BAN05

EFFLUENT TREATMENT PLANT 2

ETP CAPACITY: 40 m³/h

STAGES OF THE EFFLUENT TREATMENT PLANT	Chemicals added		Additional notes
Equalization tank	←		
Chemical coagulation		<i>Ferrous sulphate</i> <i>Lime powder</i>	
Flocculation	←	<i>Polyelectrolyte</i>	
Sedimentation tanks			<i>Tube settler</i>
Biological reaction tank		<i>Hydrochloric acid</i>	<i>2 Uds.</i>
Sedimentation tanks	←		<i>Tube settler</i>
High rate filtration (single layer)			
Granular Activated Carbon Filter			
Discharge to river			



UNIQUE WASHING

Code

BAN20

WATER CONSUMPTION: 27.000 m³/year (approx.. 90 m³/day)**MAXIMUM WATER CONSUMPTION:** 173 m³/day**ETP CAPACITY:** 34 m³/h

STAGES OF THE EFFLUENT TREATMENT PLANT	Chemicals added		Additional notes
Screening			
Equalization tank			
Demulsifier			
pH regulation	←	Acid / Base	
Chemical coagulation	←	Ferrous sulphate, PAC,	
Flocculation	←	Polymer	
Primary sedimentation tank			
Activated sludge process	←	Nutrients	
Secondary sedimentation tank			
Decoloring agent	←	Chlorine	
Sand filter			
Activated Carbon Filter			
Discharge pipe			

SASHA DENIM LTD.

Code

BAN22

WATER CONSUMPTION: 471600 m³/year (approx.. 1580 m³/day) – 45% public supply, 55% groundwater.

ETP CAPACITY: 30 m³/h (24h/day)

Only 260.000 m³/year go to discharge. Human consumption, heat production and cooling water go directly to discharge (no WWTP downstream). Insufficient ETP capacity even to give treatment to 55% of water (process water).

STAGES OF THE EFFLUENT TREATMENT PLANT	Chemicals added		Additional notes
Screening??			<i>It is not indicated</i>
Equalization tank			<i>Includes aeration system</i>
Chemical coagulation	←	<i>PAC</i>	<i>2 lines</i>
Decoloring agent addition	←	<i>Decoloring agent</i>	<i>2 lines</i>
Flocculation	←	<i>Polymer</i>	<i>2 lines.</i>
Reaction tank			<i>2 lines. It seems all 3 chemicals are added in the same step</i>
Clarifier			
Treated water tank with pH regulation	←		<i>Includes aeration</i>
Carbon filter			
Sand filter			
Post-aeration			
Discharge pipe			

ANNEX 2

GRAPHICAL DESCRIPTION OF UNIT PROCESSES



Figure 1. GAC adsorption for taste and odor removal in water purification system (ETAP-Lugo).



Figure 2. Industrial GAC filtration system
<http://www.aesasa.com.mx/>



Figure 3 High rate anthracite filtration followed by AC adsorption
<http://www.proton-colombia.com/>.



Figure 4. AC adsorption system in Chennai (India)
<http://www.indiamart.com/>.