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Wastewater treatment and reuse in textile industries, a review

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Abstract

The choice between the various processes of wastewater treatment is related to many parameters like the exploitation and capital costs, the quantity and the quality of the effluent, the variability of the effluent, the specific applications of recycling the treated effluent. Although many processes do exist, force is to note that the majority of these processes have been developed specifically to treat the urban effluents and are, consequently, unsuited to the industrial liquid waste processes characterized by very strong concentrations in pollutants and low flows. This bibliographical review deals with the processes of treatment for liquid waste of the textile industry. The chemical treatments or advanced oxidation are mainly used to eliminate the dyes from the effluents and do not bring any solutions to remove the strong quantities of salt present in the complex effluents of the textile. The membrane processes are usually used to recover the dyes, but it is often necessary to add upstream a chemical stage of filtration. Considering the increase in the output of the factory's site and the hardening of the standards of rejections, the biological wastewater treatment plants appear under-dimensioned and/or do not allow to reach the specifications required by the legislator. Moreover, to be in conformity with the legislation of rejections of the industrial effluents, new technologies have been developed and tried to be financially attractive. Last techniques of depollution require to associate the biological processes (the bioreactor) and physical processes (membranes): the bioreactor with membranes.

1.- Mobilized resources

The need for water were multiplied by more than 7 between 1900 and 1995; i.e. the rate of growth is twice higher than that of the world population. The world population has more than tripled since the beginning of the century, to reach today more than 6 billion individuals; the United Nations predict an increase of

almost 75% around 2050, thus passing to more than 9,8 billion inhabitants. The more the world population increases the more the needs for water keeps growing. To satisfy these needs, the water is pumped since the ground water which unfortunately is often very slow to be renewed; the reason is that the subsoil water is pumped more quickly than nature can renew it; that creates deficits on great scale.

Consequently, if the international approach of the stock management does not change significantly in the next years, two thirds of the world population could suffer of lacks of water in 2025.

In a report published in 1995, the World Bank estimated that 80 countries, accounting for 40% of the world population, suffer already from water shortages, which causes an obstacle with their development. The degree of vulnerability of a country for water depends on the quantity on water, of its distribution in time, its quality, and the level of consumption and the request. Whereas the climate is the principal factor determining the quantity of water and its distribution in time, the population and the economic development are the dominating influences for quality and the request. The needs increasing, the costs of mobilization of the resources will become higher, as these resources will be difficult to exploit. However, the countries concerned with these problems of shortage are, for most of them under development, and will not be able to assume these financial implications [1]. For some countries, the water problems will constitute a barrier to the development. Any development can be durable without the control of the water resource, particularly for arid countries [2]. From an economic as well as social, cultural or strategic point of view, the water is the most important element of a durable development.

On a world scale, the total pure water consumption (volumes of water not restored in the aquatic environment) is distributed between agriculture (69% of consumed water), industry (23%) and the households (8%). In the developing countries, the share of agriculture can even reach 80%. The largest water user in the world is the irrigation but this water taken for the irrigation is mainly consumed (a part humidifies the grounds and is absorbed by the plants but the greatest part evaporates without same reaching the roots of the plants) or rather

wasted because of ineffective methods of irrigation; this water cannot thus be used for other uses. That's why it is necessary to try "to recover" water from the second large-scale consumer which is the industry; regarding the quality requirements are sometimes very high. In conclusion the degradation of the resources can constitute a barrier to the industrial development and it is besides one of the reasons that led the industrialized countries, before the others, to worry about the state of their resources. Concerning the industrial sectors most consuming water are in particular the agro-alimentary one, the industry of the textile (one needs 2500 litres for one kg of cotton yarn), the industry of the paper pulp (one needs 300 litres of water to manufacture one kg of paper - approximately 1,4 billion litres of water is necessary to produce the world quantity of newsprint used in only one day) and the metallurgy (100 litres for one kg of aluminium).

2. -Water pollution

Each year, approximately 450 wastewater km³ are carted in the coastal areas by the rivers. One needs 6 000 km³ fresh water, that is to say the equivalent of two thirds of all stable surface waters on a planetary scale, to dilute this load of pollution [3]. The sources of pollution can be grouped in four great classes, i.e.:

- Domestic and urban sources (the wastewater rejected by the collective installations, such as hospitals, schools, shops, hotels and restaurants, etc). This wastewater contains, in particular, greases (organic pollution), soaps and detergents (chemical pollution), suspended matter and also organic or mineral dissolved matters. One can consider that one finds almost all the types of micro-organisms in domestic wastewater [4].
- Agricultural sources (nitrogen contributions and, especially, its derivatives, nitrates and

nitrites, pesticides);

- Industrial sources (domestic waters from some industries and hygiene water). Contrary to domestic wastewater, the industrial wastewater is characterized by its great diversity, and depends on the water use that is made during the industrial process. This pollution varies with the industrial sector, even for each establishment. According to the industrial activity, one will find pollution as various as:

- Organic matter and greases (slaughter-houses, food industry's...),
- Hydrocarbons (oil industries, transport...)
- Metals (surface treatments, metallurgy...),
- Various acids, bases, chemicals (chemical industries, tanneries...),
- Hot water (coolant circuits of the power stations...),
- Radioactive materials (nuclear thermal power station, radioactive waste processing...)
- Natural sources (excretions of the warm-blooded animals).

In spite of the strong development of the analytical techniques, the characterization of the industrial effluents remains very complex and the majority of the organic components present in the effluents still are not identified, having for consequence some unknown environmental risk [5].

3. - Current processes

The principal objective of the re-use of water is not only to provide additional quantities of water of good quality by thus accelerating the natural cycle of water, but also to ensure the balance of this cycle and the protection of the surrounding medium. The re-use of wastewater can have either an immediate use after treatment, transport and storage, or an indirect

use, after passage by a natural or artificial basin [6].

According to the quality requirements, the activities of re-using the wastewater are mainly destined to the irrigation of green parks (parks, golfs, grounds sporting), national development (cascades, fountains, water level), streets or vehicles cleaning and the fire-protection. The standards that govern the quality of the used water destined to such uses are very severe and close to those are in force for drinking water.

By now it is necessary to use complex technologies to treat polluted water. The choice of the processes depends on several factors of which most significant are the composition of the effluent, the type of re-use, the quality requirements and the size of the installations; this choice remains however also guided by the operation and capital cost. According to the local conditions and technico-economic criteria, various processes to treat the effluents can be considered: chemical treatments, physicochemical treatments, membrane filtration, chlorination, irradiation, UV, ozonization. Unfortunately systematic procedures cannot be used because the effluents are very different and the applications various. However, some general tendencies can be released. Basic processes can be classified in several categories: (i) the physical processes which allow the elimination of particulate pollution, at least the coarse particles fraction responsible for obstructing the secondary treatments. One finds processes such as cleaning, sifting, decantation, flotation, ultraviolet radiation, filtration (realized on traditional materials (sands) or adsorbents (activated carbon in grains) or on membranes). (ii) Physicochemical processes such as coagulation-flocculation. (iii) Chemical processes such as ozone, chlorination, the dechlorination, the acid peracetic, ferrates. (iiii) Biological processes take into account some

processes such as the treatment by activated sludge, purification by fixed cultures (bacterial Bed, Biofiltres, Lagunage).

4. – Implementations of these processes: the case of the Textile industry

4.1. – Introduction

The respect of the environmental legislation to which industries are subjected contributes to the protection of the natural environment but also to the development of their image and their competitiveness. The industrialist is at the same time conscious and constrained by increasing the severity of the legislation and the need for limiting the polluting effect of his production on the river. However, his first objective is to manufacture on better account products of quality. It does not consider the water treatment like an added value but rather like a financial overload. It is necessary for him thus to reconcile protection of environment and costs, while taking into account the various constraints of production. In an often difficult economic context, the industrialists must reconcile ecological and economic stakes that supports the development of processes often innovating and contributing to optimize the operating costs. Our objective is to put forward some of these processes being used to treat the effluents of the textile industry. The choice of

this type of industry has been determined by two essential reasons:

- it is a strong industry consuming water and thus rejecting many wastewater (approximately 40 to 65 litres to manufacture 1 kg of fabric),
- these effluents present serious environmental problems.

In the field of industrial water, there is unfortunately no standard solution considering the characteristics of wastewater are very different. Each type of activity, each site is a particular case of industries with their own effluents and their own rejections (Table 1). Also before any intervention on the water cycle of an industrial production chain, it is necessary to establish a precise diagnosis.

Textile industry asks for great quantities of water, which must be pure, but their rejections (which are clearly visible when they are discharged without treatment in public water) constitute enormous harmful effects for human health. These effluents pose an environmental problem mainly in term of color, COD, toxicity and salinity. The different dyes used cause serious problems because of their stability and their low biodeterioration. The most used dyes are azo type (more than 3000 listed) and constitute 60 à 70% of the whole of the produced dyes. They are used in the industry of the textile but also in printing works. These dyes are characterized by -N=N- connections

Table 1.
Principal characteristics of the rejections in textile industry

Type of industry	Origin of the principal polluting effluents	Principal characteristic of the rejections
Laundry	Washing of fabrics	High percentage of alkalinity and organic, detergent matter
Manufacture of fibres	Fibres synthetic, viscose, polyamides, polyesters, vinyl	Presence of solvents, dyes, neutral water charged with organic matter
Preparation of fibres	Washing, boiling off, bleaching, dyeing, impression and finish, combing of wool	Suspended matter high or average, alkaline or acid water, organic matter (COD) very high and variable, dyes, chemicals, reducing or oxidizing sometimes sulphides, grease, suint

which are the most common shape of the "reactive" dyes. It is estimated that 50% of the initial dyes are not fixed on fibres and finally remain in the effluents of the baths of dyeing. They are present in a state hydrolyzed in wastewater of the baths of dyeing, a form that cannot be re-used in the processes of colouring. Moreover, textile industry often uses precious dyes; among them some precursors of the trihalomethane precursors (THMPs) which has carcinogenic properties. The toxic salinity and solvents affect the biological treatment and the effluent quality; the solids in suspension obstruct the primary decantation; an increase in the nitrogen concentration complicates its elimination; an increase in COD involves an increase in the initial fraction in inert COD which sets a problem in effluent [7]. The increase in salinity involves also a reduction in the flow of permeate when one uses as treatment of the membrane modules.

There are some elementary processes intended to treat them and the combination of several processes can be carried out according to specific cases. Moreover, each process will be able to play a different part according to the place that it takes into the treatment and the way in which it is implemented.

4.2. – Chemical processes

Recent experiments show that the "reactive" dyes can be eliminated by advanced oxidation processes (AOP). The AOP allow the formation of radical's hydroxyls (OH) which degrade all types of organic and inorganic pollutants present in wastewater [8,9]. In many studies, one finds processes of oxidation by hydrogen peroxide (H_2O_2) which presents a potentiality to eliminate mainly the dyes, but it is necessary to pay a detailed attention to the quantity of hydrogen peroxide injected. Ince (1999) finds an increase in the kinetics of discoloration with

the increase in the hydrogen peroxide amounts, until a breaking value ($H_2O_2/\text{colorant} = 14$ is $520 \text{ mgH}_2\text{O}_2/\text{L}$) [10]. Beyond a certain quantity it thus exerts a harmful effect on the microbial growth on the biological breakdown (the optimal amount would be of $1,5 \text{ cm}^3 H_2O_2$ for wastewater 1 dm^3) [11]. A pretreatment by chemical oxidation with hydrogen peroxide also makes it possible to reduce the COD (63%) [12], but the hydrogen peroxide alone is less effective like oxidant than its association with Fe^{2+} [13]. Many authors [9,14-17] degrade the molecules of dyes with the reagent Fenton ($H_2O_2+Fe^{2+}$) which has the advantage of being easily set up, this reduce the COD and the color but has the disadvantage of increasing the sludge formation, of requiring a long reaction time, of forming salts [14] and of depending on the pH [9]. To improve the outputs of purification mainly of the color and the COD, the addition of an UV source with the treatment by H_2O_2/Fe an interest presents. This association UV/ H_2O_2 , employed in many work [10, 14, 19, 20] produce neither sludge nor salts and does not require significant reaction time. Considering the economic point of view, this system of advanced oxidation is most attractive to treat the "reactive" effluents of the baths of dyeing [19]. It has however the disadvantage not to be appropriate to all types of dyeing and requires the installation of a separation of the solid particles in suspension. Moreover, the kinetics of discoloration depends on the molecular structure of the dyes [20].

Because of its strong oxidizing capacity, the disinfection by ozone (alone or associated other treatments such as O_3/H_2O_2 , $O_3/UV/H_2O_2$ or biological) is practised more and more because of its excellent effectiveness to eliminate viruses [21,22], bacteria and protozoa [23], to degrade organic pollutants, and seem to be an acceptable solution to treat large installations. On the environmental level, the ozonization of wastewater constitutes an advantageous

solution: the organic matter is oxidized with oxygen rather than with chlorine, which prevents the formation of organochlorinated products thus. According to Szpyrkowicz and alt. (2001) ozone gives excellent results to eliminate the color but on the condition that the colloidal particles and those in suspension shall be removed from wastewater by pretreatments. This colloidal organic matter interferes besides with the measurement of the color [24]. However, it should be noticed that the installation of an ozonization process brings not only additional costs [25] but sets also the problem of its instability; because of this instability, ozone must be produced on the spot, usually by passing the carrying gas through electrodes narrowly spaced under a high tension. The disadvantages of this method, in addition to its cost, come from the complexity of its implementation and owing to the fact that ozone does not maintain an activity which remains in water. Moreover, one major advantage of the ozone which is an application in a gas state (one thus does not increase the volume of wastewater), can be a disadvantage because the application in the form of gas bubbles sets problems of foam [26]; to avoid the development and the accumulation of this foam, the effectiveness of the ozone transfer in the liquid phase must be controlled [27].

4.3. – Physical processes

The physical process, usually applied, generally in pretreatment, is the sand filtration or the activated carbon adsorption to activated carbon which makes it possible to reduce solids in suspension, organic matter and to get a light influence on the color. The process of activated carbon adsorption brings a solution to eliminate more than 50% from the COD, and also to eliminate from surface-active and products from discoloration [28]. But the activated carbon filters only contribute to eliminate a tiny quantity from COD [29] and, it is necessary to

remain vigilant on the granulometry of the activated carbon, since an increase in the size of the particles involves a reduction in the elimination of the color [30]. Adsorption on activated carbon is, moreover, limited for the "reactive" dyes due to their relatively weak molecular weight, their very great solubility in water and their weak affinity for these adsorbents [31]; furthermore the activated carbon is very expensive [32].

In order to get water which can be re-used in cycles of production, particularly for processes of dyeing, more thorough and more effective physical treatments are necessary; these treatments pass by the membrane processes, alone or associated to other treatments. In the current studies, it is difficult to suggest a preponderance for a membrane or a type of membrane (MF, UF, NF and RO - organic or mineral); the choice is rather guided by the quality of the desired permeate knowing, for example, that the membranes of ultrafiltration make it possible to retain the organic components with high molecular mass whereas the membranes of nanofiltration are rather used to retain the made up organic compounds of small sizes.

- Microfiltration (MF) is adapted to eliminate the dyes colloidal [33], but it cannot be used alone. It remains interesting each time that an effective method is required to eliminate colloids and the suspended matter like, for example, in pretreatment for another membrane process (NF or RO) [34] or in partnership with chemical treatments.
- Ultrafiltration (UF) is effective to eliminate the macromolecules and the particles, but it is strongly dependent on the type of material constituting the membrane. The elimination of the polluting substances is never complete (COD between 21 and 77%, color between 31 and 76% and surface-active agents between 32

and 94%). Even in the best of the cases, the quality of the effluent, relating to particularly residual colouring, does not make it possible to re-use the treated effluent to feed significant processes such as the wire dyeing with a light colouring. And when a residual salinity is not a problem, approximately 40% of the water treated by UF can then be recycled to feed from the processes known as "minor" in the industry of the textile (rinsing, washing) [29]. On the other hand, if the salinity of water becomes a problem, a part of recycled water must be replaced by "fresh" water, which involves a weaker rate of recycling and an increase in the operating costs. As the UF does not eliminate the low-weight compounds molecular, it is preferable to use nanofiltration [35].

■ Nanofiltration (NF) used as a separation process is in development; this technique could become more significant in the future [36,37]. It enables to eliminate the compounds with weak molecular weights and salts. Nevertheless it is necessary to pay attention with the salt concentration in the effluent: increasing this concentration by 1 g/l with 10 g/l generates, according to the type of membrane of nanofiltration, a fall of the flow from 3 to 17% [38]. Then, when directly treating baths of dyeing by filtration, it leads to a reduction in the flow that strongly limits the applicability of the nanofiltration; some problems can occur with osmotic pressures (too much) high. This makes the process strongly dependent on the composition of the dyeing bath and on the good choice of membrane (diameter of the pores). But once the operational parameters are regulated, the results obtained with the NF are such as they can be compared with those of opposite osmosis (RO). The NF and the RO produce a permeate great quality, with a very high elimination of COD (NF between 79 and 81% and RO between 89 and 91%), of color (NF and RO > 96%), of the surface-active agents (> 99,8%) and of salinity (NF between

81 and 89% and RO between 95 and 99%). The NF may not reach the RO rates of elimination but it constitutes a interesting process because it offers a greater productivity with less demanding operating conditions. The results obtained by the NF on the dyes usually employed in this type of industry and on other components (hardness, metals, chlorides, sulphate, BOD, COD) are sufficient to allow the re-use of the worn water treated like water of process, providing of this fact a considerable economy out of water [39]. It has also the advantage of reducing the energy cost of the treatment since it separates with lower pressure than the RO.

By taking into account their little differences, it is used to associate various membrane technologies, and here, all associations are possible. For example, when adding at exit of the UF a NF (the effluent is previously treated by activated sludge followed by a sand filtration) we obtain an improvement of purification from approximately 30% in COD; and if the NF is replaced by the RO, the combination UF + RO gives excellent results in term of COD (95% removed), SS (90%), turbidity (93%) and color (> 95%) [33]. As for the result of the NF and RO combined treatment, the permeate is such as it can be recycled to feed the whole of the wet processes of the textile industry, including more strict on quality of water.

4.4. – Biological processes

The first function of the biological treatments is to eliminate the organic matter [40]. The low biodeterioration of the most of the dyes and the chemicals of the textile industry makes that the biological treatment by activated sludge is not always a success in the treatment of this wastewater. Almost 70% of the "reactive" dyes are of azo type and most of these dyes resist to

the aerobic biological treatment. The dye is a kind of organic matter refractory and thus not easily usable like source of carbon and source of energy for the microorganism. But it can be broken up by anaerobic biological breakdown into simple intermediate products (aromatic amines) by a division of connections $-N=N-$ and then treated in an aerobic phase. The compounds azo with an amine group or hydroxyl are most easily degraded [41]. For a good discoloration in a biological reactor (sequential batch - SBR), the anaerobic stage is essential and must be added upstream of the aerobic stage [42]. According to their operating conditions and with sludge retention times of 8 day (6.3 anaerobic day, 1.7 aerobic day) the principal reduction of the color take place at the time the first two hours of the anaerobic stage with a very light increase with longer hydraulic retention time (18 h.). According to the substrate used (glucose alone or nutritive agents + sodium acetate), they find a discoloration total ranging between 63,1% and 73,3% with mainly a suppression of the color at the time of the anaerobic phase (71.5% for 18h.) and a very small additional discoloration at the time of the aerobic stage (1.6% for 5h.). Furthermore, the biological process enables to eliminate between 93.3 and 97.3% of the COD. The addition of substrate (glucose and acetate) seem besides to stimulate the cleavage of the connections azo and thus to increase discoloration [60].

Nevertheless it is necessary to remain vigilant on the way of implementing the biological process because the output depends on it. Regarding the use of sequential batch reactor: in the first system both phases aerobic/anaerobic are realized in the same bioreactor whereas in the second system these phases are dissociated in two distinct bioreactors [43]. In the first system, 64% of the dyes slightly biodegradable are eliminated in anaerobic phase and only 2% in aerobic phase are on the whole 66%. According to authors',

such a difference comes, on one hand, from a aeration time of only 20h on 48h of operation and, on the other hand, from a concentration in nutritive element abundant in the anaerobic and not very sufficient phase in the aerobic phase. Moreover, after the anaerobic reduction, difficulties of mineralisation of the intermediate azo dyes are frequently met; these difficulties can be explained by the absence in the biomass of an adequate aerobic population microbial able to metabolize these compounds [44]. An increase in the time of aeration from 8h to 12h (on a cycle of 24h) is ineffective to develop such a microbial population, suggesting that the addition of adapted aerobic bacteria seems to be necessary for a total mineralisation of the reactive dyes azo in the anaerobic/aerobic SBR. Besides some authors advise to add a source of carbon in the anaerobic engine when discoloration decreases [44,45]. This carbon converted into methane and carbon dioxide releases from the electrons which will react with the dye by reducing the connections azo and finally cause the decolorisation. In the second system of the study of Fu and alt.[43], the fact of dissociating the phases anaerobic and aerobic in two separate stages involves a suppression of 50.4% of the dyes in anaerobic phase and 30.4% in aerobic phase are in total 80.8%. It thus proves that the composition of the microorganisms changes according to the system employed, with different dominant species for the anaerobic stages (system 1 and 2); that explains also the divergences in the effectiveness of color elimination. To explain such a difference in discoloration between the phases anaerobic and aerobic, one can base oneself on the work of Kapdan and Kargi (2001) which announce that discoloration by the aerobic bacteria rather occurs mainly by adsorption from the dyes on surface from the cells than by degradation [32]. That justifies a great elimination of the color by adsorption of some dyes as of the first days of treatment in

Table 2
Examples of processes for wastewater treatment

Process	Results - Industry of Textile						Reference
	COD (%)	TSS (%)	Color (%)	Salt (%)	PH	Cost	
Nanofiltration (NF)	95 80-85				10.2 5.5		[53]
Electrochemistry	71.9						[52]
Coagulation	72.8		97.3				
Ion exchange	95.5		100				
H ₂ O ₂ /Fe			95-97.5		4.7 - 9.2		[9]
UV/H ₂ O ₂	70		> 99.9		7 → 3		[18]
Coagulation + filtration + reverse osmosis (RO)	22-29 92	85					[51]
Membrane Bioreactor (MF) + reverse osmosis	30-40 92	100					
NF 53 l/m ² h NF 38 l/m ² h RO 38 l/m ² h	54 63.3 85.3		98.7 99.6 99.7	20.5 16.6 80.4			
Activated sludge							[39]
NF (UTC-20)	85.6				8.6		
NF (NF-70)	92				9.3		
NF (NTR-7450)	86.5			21-87	8.6		
Activated sludge							[55]
Sand Filtration + Ultrafiltration (UF) + reverse osmosis (8 bar)	38 47 87		6 16 >95		7.9 8 6.3	0.97 €m ³	
Activated sludge							
Sand filtration + Ozone (2 contacts) Electroflocculation Electroflocculation+flotation	35-67 60-78 48 68.6	78.7 88.2	95-99 80-100		7.3 - 7.5 7.3 - 7.5 7.2-8.3 7.7-6.6	0.4 €m ³	[56]
Filter (5 µm) Pump high Pressure Nanofiltration							[38]
ES20 charged negatively			97.8	94.8			
NTR-729HF neutral			82.5	54.1			
LES90 charged negatively			96.0	86.3			
Ultrafiltration (UFTA PS10)			75-99		7.7 - 8.0		[57]
Electrofiltration (NF45)				99.8			[35]
Sand Filtration + Ultrafiltration + Nanofiltration	67 93	58 58			8.2 8.1 7.7		[33]
Sand Filtration + Ultrafiltration	53	90					
+ Reverse Osmosis	94.6	90	> 95				
Activated sludge + adsorption	82				5		[32]
Sequential Batch Reactor	80 - 85		75-90				[44]
Sequential Batch Reactor	92 - 97.3		60 - 77		7.2 - 8.5		[42]
Sequential Batch Reactor			66 - 80.8				[43]
Activated sludge + additives	94		65 - 86		7 - 7.5		[49]

the anaerobic bioreactor [24]. And the capacity of adsorption of the biomass depends in particular on the chemical structure and the molecular weight of the molecules of dyes [46]. Moreover some changes in the duration of the phases anaerobic/aerobic could cause deterioration in the microbial population, affecting discoloration negatively [44]. And on various tests of sludge retention time (SRT) optimization, these authors indicate that a SRT of at least 15 days is necessary to effectively eliminate the color in the bioreactor. Previously, some authors showed that the bacteria needs at least 10 days to acclimatize themselves to the dyes at the time of the anaerobic phase [47]. In the biological treatments it is necessary for the bacteria to get a certain time of acclimatization.

In the bioreactor, it often occurs an "elimination" of the dyes by adsorption in the flocs of the activated sludge; more often these dyes are resistant to the biological breakdown. If the biological treatment is not sufficient, a complete suppression of these dyes is only possible by the addition of chemical pretreatments (AOP). Some authors add chemical oxidants to modify the molecular structure of the dyes and thus allow the bacteria present in the activated sludge to recognize them more easily and to degrade them more easily [48]. There are also many other pretreatments, like injecting organic flocculating agents directly into the activated sludge (120 mg/L) [49].

Finally, in these biological processes, it is singular to couple the effluents of the textile with the urban ones [50, 51]. Generally this wastewater comes for 80% from the textile and for 20% from domestic; the domestic effluent thus brings the substrates missing and necessary to the aerobic biological process, stimulating the microbial growth. The process is often based on an anaerobic digestion to

adsorb the dyes and to precipitate (if there are some) heavy metals on the sludge anaerobic, followed by an aerobic biological stage to oxidize the nitrogenized compounds and to eliminate the biodegradable organic matter and, finally, a process of separation by membrane. An ozone process can be installed after filtration on the loop of recirculation of the retentate towards the biological stage; the recycling of the retentate increases the concentration in pollutants and can this way be treated by ozone.

5. - Conclusion

Textile industry keeps searching how to preserve water and to make benefits when recycling the dyes. By now, a systematic approach in the liquid waste processing of the textile is not considered yet because gaps persist in the type of effluent to treat, in the choice of the chemical treatments, the type of membranes to be used or in the combination of treatments to be implemented. The effectiveness of the processes depends on the type of dye present in used water, and consequently, the individual processes have limited applications; it is thus often necessary to set up a combination of processes. But the association of these processes lead to increase, on one hand, the costs of the treatment and, on the other hand, the production of sludge; consequently, this sets the problem of the storage of these sludge and their treatments.

■ The chemical treatments or of advanced oxidation are mainly used to eliminate the dyes from the effluents if the volumes to be treated are not too important. Moreover, they do not bring any solution to remove the strong quantities of salts present in these complex effluents. Textile industry also uses non-biodegradable synthetic agents (which set problems in their treatment) as well as non-toxic dyes.

■ The membrane processes are usually used to recover and re-use these agents and these dyes, thus avoiding costs of expensive chemicals. But, unfortunately, it is often necessary to add a chemical stage upstream filtration [58].

■ The majority of the current treatments of the textile effluents are made by the biological processes anaerobic/aerobic, which enable simultaneously to eliminate the organic matter and the toxic dyes. In these biological treatments, under aerobic conditions the azo dyes are not really metabolized but it is essential to create aerobic phases because they can degrade the aromatic amines resulting from the cleavage of the connections azo in anaerobic phase, amines which are carcinogenic or toxic [59]. However, because of increase in the output of the factory's site and the hardening of the standards of rejections, these biological stations of purification occur often under-dimensioned and/or do not allow to reach the specifications required by the legislator. Moreover, to be in conformity with the legislation of rejection of the industrial effluents, new technologies were developed trying to be financially attractive. The last techniques as regards depollution call upon the coupling of the biological processes (bioreactor) and of the physical processes (membranes). It is a biological purifying plant that combines the action of the activated sludge supplemented by a phase of filtration on membrane; this process is called the membranes bioreactor (MBR). The specialists are unanimous to consider the membrane bioreactor as a real progress in the wastewater treatment, then why not apply it to the liquid waste processing of the textile industry. In the literature, one notes (Table 2) by now, there are very few studies with the MBR concerning this type of effluent.

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