EXPLORING THE RE-UTILIZATION OF INDUSTRIAL EXHAUSTION BATHS FROM TEXTILE DYEING PROCESSES BY SOLAR-BASED PHOTO-FENTON TREATMENT

ABSTRACT

The aim of the present paper is to study the decolourization and mineralization of textile industrial wastewaters from dyeing exhaustion baths by means of a solar photo-Fenton treatment. Firstly, the exhaustion dyeing baths have been grouped according to the fibres and dyeing recipes used, so as to verify the effectiveness of the photo-Fenton treatment on each dyeing process separately. Later on, the results previously achieved have been compared to those obtained by mixing all the exhaustion baths together, as it happens with the industrial textile effluents from dyeing and finishing procedures.

After their neutralization and filtration, photo-Fenton treated exhaustion dyeing baths and mixtures have been re-used to carry out laboratory dyeing samples. These re-utilization examples have been tested over several fibres by using the same dyeing procedure that was originally applied, as well as in different dyeing processes and over diverse fibres. The results achieved show that the re-utilization of the aforementioned effluents, either in new exhaustion dyeing baths or in some other textile industrial operations, raise a very important challenge, not only because the water consumption is significantly reduced, but also the wastewater levies for the firms. Furthermore, the contaminating effect of the industrial effluents to be dealt with is also diminished and consequently, this will entail environmental and economic benefits.

1.- INTRODUCTION

Textile wastewaters constitute an important concern due to the hindrance of removing colour and pollutants before their discharge into the receiving media. Apart from the environmental impact that might be caused by the large amount of water consumed during the preparation, dyeing and finishing processes, the potential polluting effects of industrial effluents are to be added. Besides, their chemical composition is very diverse, depending on the nature of the textile material employed and process they come from [1,2].

The re-utilization of these wastewaters by the firms must be aimed at as an alternative to minimize costs and water contamination, seeking not only economic but also ecological goals. Nevertheless, this re-utilization is only possible at certain stages of the productive processes and cannot be widely used. Hence, further accurate research is needed to evaluate the treatment to be applied after each textile process and to determine the final quality required for the re-utilization of the effluent.

In particular, highly coloured textile wastewaters are produced after exhaustion dyeing procedures. These effluents not only contain a huge variety of pigments and dyestuffs but also other chemicals can be found, namely humectants, sequestering agents, solvents, dispersants, softeners, fixing and antistatic agents, as well as inorganic acids, bases and salts. It must be also considered that the effluent composition varies according to daily and seasonal production orders [3]. Their high complexity might constitute a major drawback in the

process of purification and re-utilization. In addition, reactive dye hydrolysis or the presence of electrolytes in wastewaters is an important problem as they cannot be removed by means of chemical or biological treatments [4,5].

Other available treatments, such as reverse osmosis, microfiltration, ultrafiltration or nanofiltration are so far expensive and technically complex. Therefore, new strategies must be found consisting of the pre-treatment of those effluents or a combination of several techniques to make them compatible for their re-use in industrial processes [6-8].

Advanced oxidation processes (AOPs) are an attractive alternative to decolorize and mineralize textile effluents into CO_2, H_2O and inorganic irons, or into biodegradable compounds. These processes are based on the in situ generation of highly reactive and non-selective species, such as hydroxyl radical, which makes them suitable to treat a wide range of pollutants [9,10]. Some examples can be found dealing with different dyestuffs degradation by using ozone [11,12], UV / hydrogen peroxide process [13,14], UV / hydrogen peroxide / Fe^{2+} process [15,16], or Fenton treatment [17,18]. Also combined Fenton and nanofiltration procedure [19], electro-Fenton [20-22], photo-Fenton [23-25], or TiO_2 [26-28].

As the production of photons using artificial light sources require high energy expense, AOPs using solar radiation are especially interesting in areas widely exposed to sunlight, because of their enhancing environmental and economic advantages [29]. Furthermore, the use of solar-based AOPs to improve

biocompatibility of effluents coupling with a biological process is meaningful, as total mineralization of pollutants is not necessary and the energy consumption and reaction time can be reduced [30-32].

An increasing number of papers have been published on the decolourization and mineralization of solutions containing textile dyestuffs by means of solar homogeneous photo-Fenton process [33-35], solar heterogeneous photo-Fenton process [36-39], and comparing processes [40-44]. However, the real applicability of these AOPs has to be evaluated with real effluents because, as stated above, the presence of other species in the matrix might have a remarkable effect on the process and the future reuse of the effluent. In fact, some researchers have studied simulated textile effluents [45-46], but research on the application of photo-Fenton treatment on real textile wastewaters is still scarce [47].

In particular, our research group has reported on the possible re-utilization of laboratory exhaustion dyeing baths for further dyeing processes after a photo-Fenton process [48]. Results were encouraging and hence, this issue deserves further research to clarify the extent and potential application of this methodology.

With this background, the aim of this paper is to assess the possible reuse of complex industrial wastewaters from dyeing exhaustion baths after a solar homogeneous photo-Fenton treatment. For this purpose, decolourization and mineralization of exhaustion dyeing baths showing different characteristics have

been analyzed. Then, treated effluents have been recycled for further use in dyeing processes.

2.- EXPERIMENTAL

2.1.- Reagents

Exhaustion Dyeing Baths (EDBs) employed in this work were obtained from industrial dyeing processes. EDB 1 was the proportional mixture obtained from dyeing acrylic fibre with wool and polyamide blends in purple, coffee and black colours respectively; in EDB 2 acrylic fibres were dyed in orange and brown; EDB 3 was taken from polyester fibres dyed in pink, green and violet; in EDB 4 the fibre was viscose dyed in turquoise, purple, red and green respectively; and EDB 5 was obtained from dyeing cotton fibre in black.

Finally, EDBs 1 to 5 were combined in different proportions to simulate a typical textile exhaustion dyeing effluent more closely. Accurate calculations have been made to adjust the exhaustion dyeing baths proportions to those of the industrial effluents in firms according to the average fibres and dyeing processes production percentages, taking into account several yearly productions. EDB 6 and EDB 7 were obtained by this procedure. Main parameters of EDB 1-7 are summarized in Table 1.

Insert table 1 about here.

All other chemicals employed in this work were supplied by Panreac. Solutions were prepared with deionised water Milli Q grade (Millipore Elix3).

2.2.-Photochemical reactions

Laboratory scale solar photo-Fenton treatments were performed in 250 ml cylindrical Pyrex vessels (55 mm internal diameter) magnetically stirred. Deionised water was added periodically to compensate for evaporation loss. Then, reactions were scaled-up in a 4 litre pilot plant (Solardetox Acadus-2001, Ecosystem) for solar decontamination of wastewaters, described in detail elsewhere [48, 49]. Solar irradiation was performed during summer sunny days in Eastern Spain.

For the photo-Fenton process, sulphuric acid was used to adjust pH to 2.7 and Fe^{2+} (10 mg/l) was added as iron (II) sulphate. After mixture homogenization, hydrogen peroxide was added to start the reaction. As the main target of this paper was the decolourization of the EDBs, hydrogen peroxide quantities were much smaller than the stoichiometric amounts required to mineralize the organic matter of each EDB [42]. As shown in Table 2, peroxide concentrations between 60 and 900 mg/l were employed for EDBs treatment, using 1/3 initially. The photo-Fenton reaction was kept until complete consumption of H_2O_2, determined by Merckoquant® 1.10011 Peroxide Test (analytical strips 0.5 – 25 mg/l H_2O_2).

Insert table 2 about here

After EDBs treatment, pH was adjusted with NaOH between 8 - 8.5 in order to precipitate iron into ferric hydroxide $Fe(OH)_3$; then all EDBs were filtered through polypropylene (VWR, 0.45μm).

Blank experiments were also performed for all 7 EDBs. The exhaustion dyeing baths were exposed to sunlight and even after forty days all EDBs were still coloured.

2.3.-Chemical analysis

Following EDBs collection from the textile mill, they all were initially filtered through cellulose filters. UV-visible absorption spectra were recorded by means of a Thermo Scientific Helios Gamma γ spectrophotometer, and the predominating peak was taken to estimate decolourization.

Dissolved organic carbon (DOC) was determined with a Shimadzu model TOC-V CSH apparatus provided with a chemoluminescence detector, able to analyse total dissolved nitrogen (TN).

Chemical oxygen demand (COD) was determined spectrometrically, according to the dichromate method [50]. Digestions were done in a Thermoreaktor TR300 (Merck) and for the photometric determination a Spectroquant NOVA 60 (Merck) was employed.

Biochemical Oxygen Demand for 5 days (BOD$_5$) values were performed in the dark by means of an Hg free WTW 2000 Oxytop$^®$ unit at a thermo-stated temperature of 20 ºC. A Crison Basic 30 conductimeter equipped with an automatic temperature controller was utilized to determine conductivity. Surface tension was measured with a Krüss K9 tensiometer. Ferrous ions Fe(II) were determined by the standard spectrophotometric method based on absorbance measurements of the Fe(II)-phenanthroline complex at 510 nm.

2.4.-Laboratory dyeing

The obtained solutions were employed for further dyeing processes. For this purpose, 10 g of textile material were dyed with the chosen dyestuff (50 mg/l, which is 0.5% over fibre or fabric weight) following standard procedures. Most important data and dyeing method conditions are summarized in Table 3. Commercial dyes containing different chromophores were tested: C.I. Disperse Blue 35 (anthraquinone) for polyester *Trevira*® roving fibre, Basic Red 46 (azoic) for acrylic *Courtelle*® roving fibre, Direct Red 80 (azo) and Reactive Blue 15 (phtlalocyanine) for bleached cotton satin.

Insert table 3 about here

An "*All-in*" dyeing exhaustion method was used adjusting pH and adding the required auxiliaries. Exhaustion open baths were employed for the dyeing of satin cloth and hermetic vessels for the roving fibres. Paramount Dyemaster™ and Tint-Control Multi-Mat Renigal equipments were used. The same textile materials were also dyed following the identical procedure and using the same dyestuffs using Milli Q grade water.

2.5.-Colour evaluation

The colour of the dyed fibres and fabrics was determined by means of reflectance measurements using a Minolta CM-3600D spectrophotometer. Using diffuse illumination standard D65 and observer standard angle 10º. CIE *L*a*b** equations for surface colour measurements ISO 105 J01 and for colour

differences ISO 105 J03. Reflection spectra were recorded in the visible range (400 and 700nm, band gap 10nm) comparing colours against the pattern sample having used deionised water. Colour differences according to $\triangle E^*$ cmc (2:1).

3.- RESULTS AND DISCUSSION

3.1.- Chemical results

EDBs 1-7 were submitted to a solar photo-Fenton process until complete reaction of the hydrogen peroxide. Figure 1 shows that important decolourization was achieved in all cases (64 – 98 %) and the final absorbance of the filtered EDBs was systematically below 0.087 (Table 4). Best results were reached for EDB 2, 4 and 5 (more than 90 % decolourization). However, it is important to remark that also for the more complex EDB 6 and 7, ca. 80 % colour removal was obtained.

Insert table 4 about here

Mineralization and oxidation of organic matter were determined according to DOC and COD respectively. Results were strongly dependent on the textile dyeing process which produced the effluent. More than 80 % of the organic matter in EDB 4 and 5 was mineralized, while this value was in the range 60-70% for EDB 6 and 7. Again in this case, EDB 1 (mixture of acrylic, wool and polyamide fibres utilizing cationic and acid dyestuffs) and EDB 3 (disperse

dyestuffs employed for polyester dyeing) showed worse results than the ones of the other EDBs treated.

Insert figure 1 about here

Surface tension was also determined before and after irradiation. The initial values were in the range 37-50 mN/m, far below the 73 mN/m corresponding to distilled water; this is attributable to the presence of high concentration of organics, especially those showing surfactant properties. Although some increase was observed after the photo-Fenton, values kept in the range 45-61 mN/m, which were still clearly below the desirable 73 mN/m, thus confirming that significant amounts of surfactants remained in the solution. Regarding to conductivity, only a slight variation was observed and hence, high values remained after the treatment. This is expectable as the oxidative process is efficient in the oxidation of organic matter but has no influence on inorganic ions.

3.2.- Re-Utilization of industrial dyeing baths

Results reported above show that photo-Fenton can improve the quality of the studied textile effluents, although complete decontamination could not be achieved. Hence, it seems interesting to check if the quality of treated waters is compatible with their re-use in dyeing processes.

For this reason, the possible reuse was checked under different conditions, according to the final characteristics of each EDB. For instance, EDB 1, EDB 2, EDB 6 and EDB 7 were used to dye acrylic, since EDB 1 and EDB 2 were effluents from acrylic dyeing. That is why they can be expected to be compatible for this use, and EDB 6 and EDB 7 are a mixture of EDB 1- EDB 5 and their reuse was checked with different fibres. Fibres and fabrics (polyester, acrylic and bleached cotton satin) were dyed in an "*All-in*" procedure according to the aforementioned conditions in table 3.

The CIELAB colour scale is an approximately uniform colour scale. The differences between points plotted in the colour space correspond to visual differences between the colours plotted. The colour space is organized in a three-dimensional elliptic shape. The L* axis runs from top to bottom: maximum 100 (which represents a perfect reflecting diffuser), minimum zero (which represents black). The a* and b* axes represent the colour-opponent dimensions (+a* red, -a* green; +b* yellow, -b* blue). $\triangle$L*, $\triangle$a*, and $\triangle$b* indicate how much a standard and sample differ from one another in L*, a* and b*. In addition, there are two other delta values that are related to this scale: $\triangle$C* and $\triangle$h*. The $\triangle$C* is the difference in chroma and $\triangle$h* is the difference in hue angle between the sample and standard as described in a polar coordinate system.

The total colour difference $\triangle$E* is a single value which takes into account the differences between the L*, a*, and b* of the sample and standard. If the $\triangle$E*

value is below 1 or 1 the colour difference is acceptable, CMC colour evaluation described in detail [51].

The colour differences, as calculated by CIE L*a*b* using the standard ISO 105 J03 are presented in the following tables 5, 6, 7 and 8.

Insert figure 5, 6, 7 and 8 about here

As it can be seen from the results of the tables, most of the values are within tolerance. In dyeing acrylic fibre and bleached cotton using direct dyestuff only EDB 2 and EDB 6 respectively were out of tolerance. In bleached cotton using reactive dyestuff, two EDBs out of four were out of tolerance. The reason why this happened was because the reactive dyestuff used had a pale blue pastel hue.

4.- CONCLUSIONS

Textile dyeing and finishing processes making use of exhaustion baths are facing increasing and more restrictive environmental laws. Worldwide factories must improve continuously their wastewater treatments or adapt new eco-friendly methods for the sustainability of their manufacturing techniques and attain corporate social responsibility. The photo-Fenton treatment has been proved to be an effective means to decolourize and oxidize organic matter present in these textile wastewaters after their industrial use, although colour intensity must be taken into account for a good effectiveness of the process.

Due to its scarce oxidative selectivity, the photo-Fenton treatment has demonstrated their application in the oxidation of the most common dyestuff cromophores industrially used, as well as complex mixtures of them and auxiliary products. This fact confirms the successful application in exhaustion baths textile wastewaters, especially when sunlight is used compared to artificial UV-light, because it enhances sustainability in areas with long solar exposition periods.

As it has been verified, 99% absorbance decrease was achieved in some particular exhaustion baths whereas 90% absorbance decrease was reached in sample 7 with all the exhaustion bath waters mixed. 85% DOC decrease was measured for sample 4 and an average of 70% COD decrease for mixed samples. 95% COD decrease was confirmed for sample 4 and an average of 65% COD decrease for wastewaters mixed samples. The biodegradability ratio (BOD$_5$/COD) of the exhaustion dyeing effluents did not suffer significant changes but a partial treatment of these wastewaters could offer a possibility for a coupled photo-Fenton and biological process.

The high concentration of mineral salts in the samples after the treatment did not have any interference in their re-use. In some cases no more NaCl or Na$_2$SO^4 was added and when necessary, only a proportion was poured to copy the pattern electrolyte.

The water quality obtained in the samples after the treatment allowed their re-use in new dyeing procedures without dilution, not only with the same fibres and dyestuffs firstly used but also with different materials and colours. The reflexion spectra of the new dyeing samples compared to patterns using deionised water

were coincident in the majority of tests. Besides, these treated effluents could be re-used in other industrial textile processes as washing, rinsing or cooling. By using this technique gives us the possibility of savings in the consumption of fresh water, NaCl or Na_2SO_4 and in the wastewater levies. Moreover, it entails significant environmental benefits because it reduces the polluting effects of the industrial effluents and eradicates the problem of coloration of dyeing effluents.

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FIGURE CAPTIONS

Figure 1.- DOC (☐), COD (█), Absorbance (█) decrease percentages in EDBs.

Table 1. Main parameters of the Exhaustion Dyeing Baths (EDBs).

EDB	1	2	3	4	5	6	7
pH	2.7	3.7	3.7	11.4	7.4	3.9	3.7
Conductivity (mS/cm)	0.74	1.33	2.21	86.6	8.30	33.6	12.2
Surface tension (mN/m)	37.1	49.5	40.1	45.7	43.1	42.2	45.5
COD (mg/l)	1180	1202	2350	1984	854	1143	1114
BOD_5 (mg/l)	480	470	1000	10	180	500	800
DOC (mg/l)	423	769	855	205	238	506	585
Absorbance (AU)	0.376	0.037	0.103	0.954	1.832	0.423	0.215
Total nitrogen (mg/l)	28	153	235	25	25	118	126

COD: Chemical Oxygen Demand; BOD_5: Biochemical Oxygen Demand after 5 days; DOC: Dissolved Organic Carbon.

Table 2. Hydrogen peroxide concentrations employed for

EDBs treatment.

EDB	1	2	3	4	5	6	7
COD (mg/l)	1180	1202	2350	1984	854	1143	1114
H_2O_2 (mg/l)	180	60	180	450	900	450	230

Table 3: Dyeing procedures and conditions.

Dye C.I.	Disperse Blue 35 (anthraquinone)	Basic Red 46 (Azoic)	Direct Red 80 (Azoic)	Reactive Blue 15 (phthalocyanine)
Material	Trevira® (Polyester)	Courtelle® (Acrylic)	Bleached cotton	Bleached cotton
Liquor ratio	1:25	1:25	1:40	1:40
Procedure	Standard for disperse dyes	Standard for basic dyes	Standard for direct dyes	Standard for reactive dyes
Temp.	120ºC	98 ºC	98º C	95 ºC
pH	3.7 (Formic Acid)	4.0 (Formic Acid)	8.6	12.6
Chemicals			30 g/L Na2SO4	4ml/l (300g/L) NaOH 60g/L Na2SO4

Table 4. Absorbance decrease in the EDB samples.

EDB	1	2	3	4	5	6	7
Initial Absorbance (AU)	0.376	0.037	0.103	0.954	1.832	0.423	0.215
Final Absorbance (AU)	0.087	0.002	0.037	0.007	0.028	0.071	0.046
Decrease %	77	95	64	99	99	83	79
Time (min)	360	30	60	420	480	90	290

Table 5. Colour differences in samples after acrylic dyeing.

ACRYLIC	L*	a*	b*	C*	h	△E*cmc
Deionised water	46.307	63.410	10.039	64.200	8.996	
M1_REUSED	46.973	62.885	9.688	63.627	8.758	0.403
M2_REUSED	44.214	60.762	9.854	61.556	9.212	1.369
M6_REUSED	45.745	63.543	9.880	64.306	8.838	0.288
M7_REUSED	46.989	63.797	9.050	64.436	8.074	0.652

Table 6. Colour differences in samples after polyester dyeing.

POLYESTER	L*	a*	b*	C*	h	△E*cmc
Deionised	46.855	-4.181	-29.862	30.153	262.030	
M3_REUSED	47.516	-4.444	-29.724	30.055	261.497	0.387

Table 7. Colour differences in samples after bleached cotton dyeing with Direct red 80.

BLEACHED COTTON	L*	a*	b*	C*	h	△E*cmc
Deionised water	55.833	54.057	2.247	54.103	2.381	
M4_direct_REUSED	54.808	53.831	1.513	53.851	0.227	0.227
M6_direct_REUSED	54.102	51.317	0.633	51.321	0.707	1.546
M7_direct_REUSED	55.120	53.862	1.719	53.889	1.828	0.431

Table 8. Colour differences in samples after bleached cotton dyeing with Reactive blue 15.

BLEACHED COTTON	L*	a*	b*	C*	h	△E*cmc
Deionised water	79.359	-24.048	-18.196	30.156	217.113	
M4_reactive_REUSED	84.177	-13.704	-17.958	22.593	232.674	0.831
M5_reactive_REUSED	88.037	-12.364	-17.763	21.642	235.171	0.834
M6_reactive_REUSED	89.414	-10.733	-16.982	20.084	237.682	2.073
M7_reactive_REUSED	89.772	-11.049	-18.114	21.223	238.617	1.934