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REMOVAL OF DYES FROM WATER BY GALVANOCOAGULATION

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Abstract

Galvanocoagulation (GC) utilizing metallic iron chips and granular coke was studied as a potential technique for decolorization of dye-containing aqueous solutions. GC and chemical coagulation by inorganic metallic coagulants such as iron sulfates (Fe^{2+}, Fe^{3+}) were examined for the removal of individual dyes, used in the fur industry, from model aqueous solutions. The role of metal cations when progressively electrogenerated *in situ* was compared to when they are added simultaneously. The superiority of GC over chemical coagulation was established for the removal of the tested dyes as chemical coagulation required relatively high dosages of coagulant. Additionally, the specific dye removal ability, expressed as q (g/g), which is the maximum amount of dye removed per gram of iron, for GC was considerably higher compared to the one obtained from chemical coagulation. The efficiency of GC was also tested on real wastewater. The average percent removal of chemical oxygen demand (COD) and color was 90 % and 99 %, respectively, during 30 min of treatment. GC is considered a cost-effective and environmentally friendly method which, in the presence of hydrogen peroxide, may also be considered a Fenton-like Process. Using Acid Yellow as a model dye it was observed that the decolorization efficiency increased to 40% when a GC/H_2O_2 combination was used as compared to GC alone. UV treatment further increased the efficiency of the GC/H_2O_2 system. The dye removal is attributed to both the oxidation by the photo-Fenton reagent and the following adsorption.

Keywords: coagulation, dye removal, Fenton process, galvanocoagulation, wastewater treatment

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1. Introduction

The fur production industry is highly detrimental to the environment. There are prominent problems concerned with the high pollution load generated, complex composition of wastewater, multiple pollution management steps required, and large amounts of energy and water consumption. Additionally, the industry has received criticism on environmental grounds, mainly in developing countries, on account of the little effort put in towards promoting cleaner production processes. Wastewater originates from various technological steps and is characterized by complex ingredients, high chromaticity, high chemical oxygen demand (COD) and biochemical oxygen demand (BOD), high suspended matter content etc. In order to carry out wastewater treatment in the most effective manner,

flow segregation is useful to allow preliminary treatment of concentrated wastewater streams.

Wastewater produced from the dyeing and finishing processes is known to be one of the most problematic wastewaters to treat due to resistance of commercial dyes to biodegradation (Forgacs et al., 2004; Holkar et al., 2016). A large quantity of the dyes is lost in residual liquors. The structure of the dyes is becoming more complex and their properties more stable, as they are generally designed to withstand microbial, chemical, and photolytic degradation. Additionally, auxiliary chemicals such as surfactants act as obstacles in the wastewater treatment process.

The decolorization of those effluents remains a main goal in the global treatment of fur wastewaters. Various studies have reported color removal techniques which can be classified into chemical, physical or physicochemical, biological, and
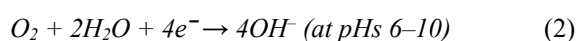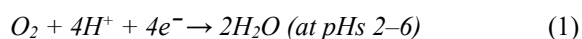
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electrochemical methods (El-Ashtoukh et al., 2017; Eslami et al., 2016; Dükkancı et al., 2014; Fajardo et al., 2017; Martınez-Huitle and Brillas, 2009; Mezzanotte et al., 2013; Ozkan-Yucel and Gokcay, 2017; Reddy and Lee, 2013; Rodrigues et al., 2017; Wang et al., 2017; Xiao et al., 2017; Zheng et al., 2013).
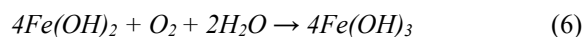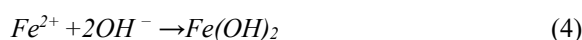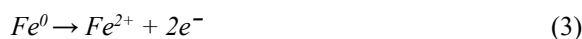
Coagulation has been reported as an efficient and cost-effective preliminary (at the source) treatment (Bratby, 2006; GilPavas et al., 2017; Verma et al., 2012; Yukseler et al., 2017). It may not only reduce pollutants before biological treatment but also allow for the safe reuse of water from dyeing baths to be further treated with membrane processes. Inorganic metal coagulants such as ferrous, ferric, and aluminum salts are widely used in water and wastewater treatments because they are cheap and relatively effective (Duan and Gregory, 2003). There are major disadvantages with Al coagulants, such as neurotoxicity of aluminum and the problem of sludge dewatering (Banks et al., 2006; Polizzi et al., 2002). Several research works have been oriented towards using natural coagulants of vegetable and mineral origin in water treatment. However, such coagulants were not able to compete effectively because of the fact that they tend to increase the concentration of organic matter in the treated water (Ndabigengesere and Narasiah, 1998). Many studies have focused on different combinations among physicochemical systems for the treatment of dye-containing wastewaters. Combinations of conventional physicochemical techniques with Advanced Oxidation Processes appeared as an attractive option (Rodriguez-Narvaez et al., 2017; Yukseler et al., 2017).

Galvanocoagulation (GC), also known as internal microelectrolysis, was developed as a new method to dispose wastewater in the 1970s and has been successfully utilized for the removal of heavy metals used in the galvanic industry, toxic Cr^{6+} and As^{3+}, phosphates, solid household leachate, etc. (Batoeva et al., 2010; Chanturia and Solozhenkin, 2005; Sokolova et al., 2004). Internal microelectrolysis is believed to operate on principles very similar to those of the electrochemical methods with the exception that the electrons are supplied from the galvanic corrosion of many micro-scale sacrificial anodes instead of from an external power supply. For example, when a mixture of iron chips and coke particles are in contact with wastewater (electrolyte solution), numerous microscopic galvanic cells are formed between the particles of iron and carbon.

Based on the different standard potentials of coke and iron, the half-cell reactions occurring at microscopic corroding surfaces can be represented as Eqs. (1-2):

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (at pHs 2–6)} \tag{1}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (at pHs 6–10)} \tag{2}$$

while on the iron surface, anode corrosion and transition to solution take place in the form of Fe^{2+} ions as active coagulant precursors *in situ*.

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{3}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{4}$$

$$4Fe(OH)_2 + O_2 \rightarrow 4FeOOH + 2H_2O \tag{5}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \tag{6}$$

The *in situ* production of coagulating ions involves three stages: (I) formation of coagulants by oxidation of the sacrificial electrode; (II) destabilization of the contaminants, particulate suspension, breaking of emulsions; and (III) aggregation of the destabilized phases to form floc.

During the operation, the cathode material is not consumed to any great extent, whereas the anode is dissolved continuously, without passivation. This is a principal advantage of this method. Moreover, the utilization of metal scraps (chips, pellets, filings, etc.) instead of chemical reagents noticeably decreases salt content. The generation of substantial amounts of Fe^{2+} makes it possible to apply GC under acidic pHs and in the presence of hydrogen peroxide to oxidize recalcitrant organic compounds by Fenton reagents (Fe^{2+}/H_2O_2) (Fenton, 1894; Haber and Weiss, 1934). This method was named galvanic chemical oxidation (GC/H$_2$O$_2$) (Zhalsanova et al., 1998). It may also be considered a Fenton-like process (Bremner et al., 2006; Rima et al., 2005; Tang and Chen, 1996), when Fe^0 is used as a source of Fe^{2+} ions to replace inorganic salts.

The purpose of this work was to investigate the ability of GC alone along with combinations of GC/H$_2$O$_2$ and GC/H$_2$O$_2$/UV to remove dyes from aqueous solutions. The GC efficiency was compared to that of coagulation by inorganic metallic coagulants such as iron sulfates (Fe^{2+}, Fe^{3+}).

2. Experimental

2.1. Reagents

Commercially available dyes such as Alizarine Blue T, Lowalan Black BH, Lowalan Braun TRM, Lowanil Braun DR, Lowanil Black TH, and Lowocene Blue BC were supplied by Jos. Y. Lowenstein & Sons (USA); Acid Yellow was supplied from Ecros Inc. (Russia). The reason for the selection of these dyes is that they are used in a local fur plant (Ulan-Ude, Russia). To the best of our knowledge, detailed structural information (i.e. chemical classification) was not available for the chosen dyes. Table 1 shows the available information of the dyes with their industrial classification and application as well as the experimentally determined wavelength of maximum absorbance in the visible region.

Table 1. Characteristics of dyes

Commercial name	Abbreviation	Industrial classification	λ_{max}, nm[a]	Application[b]
Alizarine Blue T	ABT	Acid	590	Acid dye for fur
Lowalan Black BH	LBBH	Acid	400	Metal Complex dyes for fur
Lowalan Braun TRM	LBTRM	Direct	490	Metal Complex dyes for fur
Lowanil Braun DR	LBDR	Acid	490	Dyes for leather
Lowanil Black TH	LBTH	Basic	400	Dyes for leather
Acid Yellow	AY	Acid	417	Dyes for leather
Lowocene Blue BC	LBBC	Direct	590	Mordant for fur
Methyl Orange	MO	Acid	463	-

[a]In aqueous solution; [b] Supplier Information

Because azo dyes represent the most extensive group of dyes used, Methyl Orange (Ecros Inc., Russia) was used as a model azo dye with known structure. The model solutions were prepared by dissolving a dye in distilled water to a final concentration of 20 mg L^{-1}. Ferrous and ferric sulfate FeSO$_4$×7H$_2$O, Fe$_2$(SO$_4$)$_3$×9H$_2$O, H$_2$O$_2$ (30-35% w/w), and NaOH were all obtained from Ecros Inc.(Russia). All chemicals were of analytical grade and were used without any further purification.

2.2. Wastewater characteristics

GC methods were also tested on real wastewater produced after dyeing sheep wool to a black color (intermixed bath effluent and rinse water). The pH, color, and COD were measured throughout the experiment. The wastewater (COD 2440 mgO$_2$ L^{-1}, pH 5.6) contained Aluzarine Blue T, Lowalan Black BH, formic acid, surfactant, and leveling agents.

2.3. Analytical methods

The UV-VIS spectra of dyes were monitored using an Agilent 8453E UV-VIS spectrophotometer (Agilent Technologies Deutschland GmbH, Germany) at a characteristic wavelength with a 1 cm cell (Table 1). The COD was measured by the standard dichromate method (PND F, 2004). The temperature was maintained at 20°C±0.2. The pH and the conductivity were measured using a Universal Pocket Meter MultiLine P4 (WTW, Weilheim, Germany). Total dissolved iron content was measured by the standard o-phenanthroline colorimetric method (Lurie, 1984).

2.4. Experimental procedures

The chemical coagulation experiments were performed by a Jar test method at room temperature (ASTM, 1995). A predetermined dose of coagulant was added to the solution under rigorous stirring. The dosage was ranged from 10 to 200 mg L^{-1} of Fe^{2+} or Fe^{3+}. Afterwards, the solutions (200 mL) were mixed for 3-5 min. The pH was adjusted up to 7.5-8 and left to precipitate for 30 min. The supernatant was sampled at regular time intervals, filtered with normal filter paper, and analyzed immediately.

The study of GC was carried out using active loading of a galvanic pair Fe^0 (cast-iron filings) – C (coke) with particle size 2 mm at a mass ratio of 2:1. Previously degreased cast-iron filings (industrial waste) were used as a source of Fe^{2+}. The detailed experimental methodology for GC and GC/H$_2$O$_2$ (alone and photo-assisted) treatments have been described previously (Aseev et al., 2009). The photoreactor was equipped with a low-pressure mercury lamp DB30-1 with an output of 30 W that mainly emits irradiation at 254 nm (MEK ElTOS, Russia). The specific dose of radiation obtained by the solution in this reactor was determined by means of chemical actinometry described in (Gordon and Ford, 1972); it was 1.64 W/cm^2. H$_2$O$_2$ was added as 0.1 % solution. The contact time of a treated solution with the active load was up to 30 min. Most of the experiments were conducted thrice under identical conditions and the error between consecutive experiments was less than 8 %.

The concentration was quantified by measuring the adsorption intensity at λ_{max} (Table 1). The decolorization efficiency (%) of an individual dye was determined as follows (Eq. 7):

$$Decolorization\ efficiency = (1 - \frac{C_t}{C_0}) \times 100 \qquad (7)$$

where C_0 and C_t are the initial and final concentration of a dye, respectively.

Experimentally, the decolorization efficiency or percentage color removal and the abatement of COD (%) during the treatment of real wastewater were determined by the expressions (Eqs. 8, 9):

$$Color\ removal = \frac{ABS_0 - ABS_t}{ABS_0} \times 100 \qquad (8)$$

where ABS_0 and ABS_t are the average absorbance before and after treatment, respectively, at the maximum visible wavelength (λ_{max}).

$$COD\ decay = \frac{\Delta COD}{COD_0} \times 100 \qquad (9)$$

where ΔCOD is the corresponding removal in COD (mgO$_2$ L^{-1}) at treatment time t; COD_0 is its initial value before treatment.

3. Results and discussion

3.1. Coagulation

The limited information on the chemical structure of commercially available dyes creates the necessity for the appropriate method and reagent for treatment to be empirically selected in each case. The efficiency of dye removal depended on both the kind of dye and the coagulant dosage. The effect of chemical coagulant dosage on dye removal efficiency was investigated at first. For this purpose, different amounts of coagulant were dosed into the dye-containing solution. The experimental data for individual dyes are presented in Figs. 1 (a, b). As expected, the efficiency of dye removal increased with the dosage up to a certain limit and then reached a constant value. With the increase of dosage, no restabilization phenomenon or removal reduction was observed.
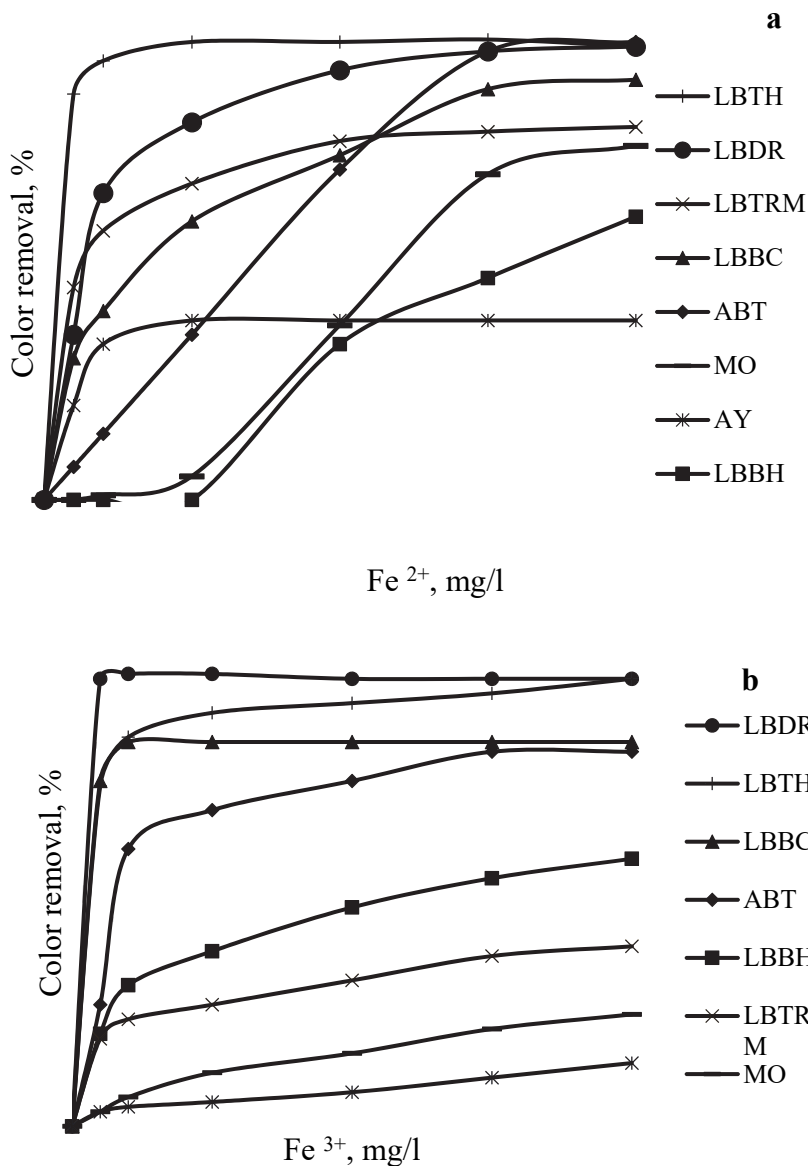

Fig. 1. Effect of Fe^{2+} (a)/ Fe^{3+} (b) dosages on color removal during chemical coagulation

Removal of color by chemical coagulants is interpreted to be due to specific chemical interactions (chelation/complex formation) between dye ligands and aqua metallic ions resulting in the formation of insoluble metal-dye complexes and/or physico-chemical factors such as adsorption, interaction between metal hydroxy species, dye aggregates, and charge neutralization leading to aggregation. It was observed that different type of dyes exhibited different degrees of color removal with the two coagulants. Color removal varied even within the same class, according to the industrial classification. This behaviour is probably due to differences in structure of dyes and the reaction products of the dyes with a coagulant in the aqueous solution. These variations made generalization in terms of the class of dyes difficult. However, it can be stated that for Lowanil Black TH, Acid Yellow, Methyl Orange and Alizarine

Blue T Fe^{2+} is more effective than Fe^{3+}, at the same coagulant dosage. For example, at a coagulant dosage of 150 mg L^{-1} decolorization of Alizarine Blue T was 77% and 95% for Fe^{3+} and Fe^{2+}, respectively, although an exact dosage of Fe^{2+} was required. The maximum color reduction was achieved for Lowanil Black TH (98% at 50 mg L^{-1} of Fe^{2+}), while the lowest one was for Acid Yellow (3% and 20% at 50 mg L^{-1} for Fe^{3+} and Fe^{2+}, respectively). Generally, the dosage of coagulants required to achieve the highest color removal was relatively high (up to 200 mg L^{-1}).

The specific dye removal ability, expressed as *q* (g/g), which is the amount of dye removed after treatment at the optimal coagulant dosage per gram of iron, was calculated using the following expression (Eq. 10):

$$q = Color\ removal \times C_0 / (100 \times D_{Fe}), \qquad (10)$$

where *Color removal* is the percentage color removal after treatment at the optimal coagulant dosage, %; C_0 is the initial dye concentration, mg L^{-1}; D_{Fe} is the optimal coagulant dosage, mg L^{-1}.

The same parameter was determined for GC. In the case of GC, the total iron concentration generated *in situ* was accepted as the D_{Fe} in Eq. (10). Table 2 summarizes the comparison between chemical coagulation at the optimal coagulant dosage and GC. It can be seen that in general for all dyes, the specific dye removal ability, *q*, of GC is >1, which is notably higher compared to *q*'s obtained from chemical coagulation. This might be explained by differences in chemical and electrochemical coagulation processes.

During GC, in oxygenated water and at a lower pH, generated *in situ* Fe^{2+} ions immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides (Goncharuk et al., 2010). The insoluble metal hydroxides of iron can remove dye molecules by surface complexation. A dye molecule can act as a ligand to bind a hydrous iron moiety through precipitation and adsorption mechanisms. Additionally, the decolorisation in the presence of Fe^0 may be attributed to the formation of iron complexes between iron ions and dye molecules preferably with the chromophore azo group (Cao et al., 1999). Although, maximum decolorization in some cases was observed for chemical coagulation, relatively high dosages of coagulant were required, especially for Fe^{2+}. The superiority of GC over chemical coagulation was established for removal of all tested dyes, as excessive amounts of inorganic salts generate considerable volumes of toxic sludge that must be incinerated or handled otherwise while GC produces minimal sludge. Additionally, the *q* parameter for GC was considerably higher (except for the case of LBDR with Fe^{3+}) compared to the one obtained from chemical coagulation. To support this conclusion, real wastewater was treated by GC and chemical coagulation. The optimal amount of ferrous coagulant to be used was chosen to be 200 mg L^{-1} of Fe^{2+}. Color and COD of the supernatant were measured after centrifugation for 10 min at 4000 rpm and treatment efficiency was defined using Eqs. (8) and (9). As can be seen from Table 3, the GC values are more favorable than those obtained by chemical coagulation; in good agreement with the results achieved using the model dye solutions. The average percent removal of COD and color was 90% and 99%, respectively, during 30 min of treatment.

3.2. Galvanochemical oxidation

It is well known that some proportion of the soluble matter in effluents is not removed by coagulation only.

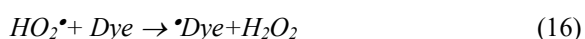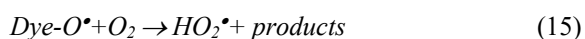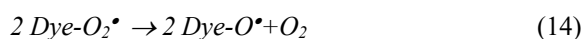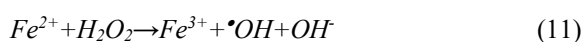**Table 2.** Results of decolorization of dye solutions

| Dye | Chemical coagulation | | | | GC^a | |
| | Fe^{3+} | | Fe^{2+} | | | |
	Efficiency, %	q, g/g	Efficiency, %	q, g/g	Efficiency, %	q, g/g
LBDR	93	1.86	95	0.19	72	1.44
LBTH	85	0.34	98	0.39	71	1.42
LBBC	79	0.79	88	0.12	54	1.08
ABT	77	0.10	95	0.13	71	1.42
LBBH	50	0.07	60	0.06	93	1.86
LBTRM	32	0.06	78	0.10	79	1.58
MO	15	0.03	75	0.08	58	1.16
AY	5	0.02	38	0.15	45	0.90

^{a} An average concentration of total iron generated in situ at GC was observed to be about 10 mg L^{-1}

Table 3. Results of lab tests for real wastewater

| Parameter | Before treatment | After treatment | |
		Chemical coagulation	GC
pH	5.6	8.5	8.5
Color removal, %	0	61	99
COD, mg L^{-1}	2440	1200	100

In order to achieve a high quality of treated water, the application of oxidation methods is needed. Among the oxidation methods, Fenton reagent is one of the best technologies for the total removal of dyes from water (Rodriguez-Narvaez et al., 2017; Yukseler et al., 2017). As mentioned above, upon Fe^0 dissolution, Fe^{2+} is released to the bulk solution. Dissolved iron content is appropriate for utilization in iron-catalysed Fenton processes. Upon adding H_2O_2, the decomposition of oxidant occurs with the generation of extremely powerful intermediate oxidizing hydroxyl radical ($^\bullet OH$) species (Eq. 11). Apparently, the Fe^{2+} and H_2O_2 concentrations largely determine the amount of $^\bullet OH$ being formed, which then interact at a high rate with the substrate to give organic radicals (Eqs. 12-16) (Alshamsi et al., 2007).

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+{}^\bullet OH+OH^- \tag{11}$$

$$^\bullet OH+ Dye \rightarrow {}^\bullet Dye+H_2O \tag{12}$$
$$^\bullet Dye+O_2 \rightarrow Dye\text{-}O_2{}^\bullet \tag{13}$$

$$2\,Dye\text{-}O_2{}^\bullet \rightarrow 2\,Dye\text{-}O^\bullet+O_2 \tag{14}$$

$$Dye\text{-}O^\bullet+O_2 \rightarrow HO_2{}^\bullet+ products \tag{15}$$

$$HO_2{}^\bullet+ Dye \rightarrow {}^\bullet Dye+H_2O_2 \tag{16}$$

From coagulation results, it was obvious that color removal efficiency of Acid Yellow by both GC and chemical coagulation was lowest among all tested dyes. Thus, this dye was subjected to further treatment. As shown in Fig. 2, the addition of H_2O_2 increased the GC removal of Acid Yellow by 40%. This can be due to the formation of hydroxyl radicals as shown in Eq. (11). To accelerate the oxidation process an additional UV-treatment was also applied. It enhanced the decolorization rate of Acid Yellow and improved its destruction (Figs. 2, 3).

The UV absorption spectra at different times were obtained to study the destruction of the dye molecules. Acid Yellow exhibited absorption bands at 417 and 220 nm. The disappearance of the visible band was due to the fragmentation of a bond in the chromophore group. In addition to this rapid bleaching effect, the decay of the absorbance at 220 nm was considered as an evidence of the degradation of aromatic groups in the dye molecules and their intermediates.

The enhancement of the decolorization rate of Acid Yellow could be attributed to the additional generation of $^\bullet OH$ during photodisproportionation of H_2O_2, the cleavage of iron complexes (hydroxy-, oxalate and similar) present in the system, and reduction of Fe^{3+} to Fe^{2+} (Eqs. 17, 18).

$$H_2O_2+hv \rightarrow 2OH^* \tag{17}$$

$$Fe(OH)^{2+}+hv \rightarrow {}^*OH+Fe^{2+} \tag{18}$$

The dye removal is attributed to both oxidative destruction by photo-Fenton process and the following coagulation.

4. Conclusions

GC was used to remove color from dye solutions and its color removal efficiency was compared with that of chemical coagulation. The superiority of GC over chemical coagulation was established for all tested dye removals as in chemical coagulation, relatively high dosages of inorganic coagulants were required in order to achieve maximum decolorization.

Additionally, the specific dye removal ability, expressed as q (g/g), which is the maximum amount of dye removed per gram of iron, for GC was considerably higher compared to one obtained from chemical coagulation.
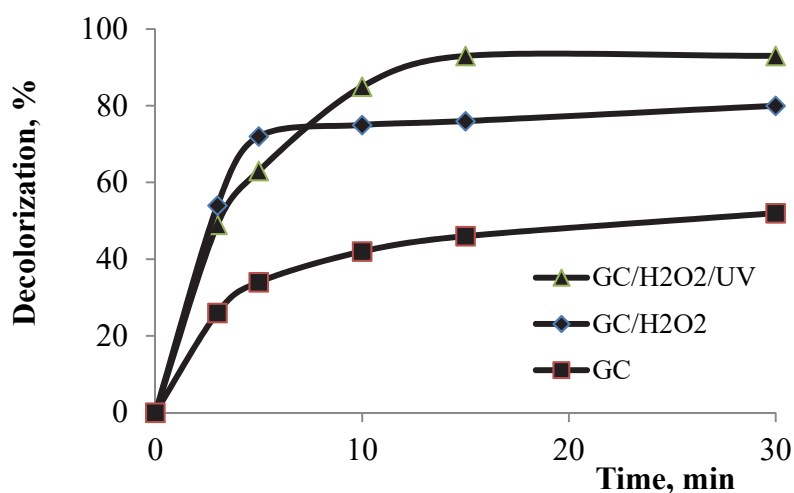

Fig. 2. Decolorization of Acid Yellow (20 mg L^{-1}) at GC, GCO and photo-assisted GCO treatments. $C_0(H_2O_2) = 100$ mg L^{-1}, pH 6.2
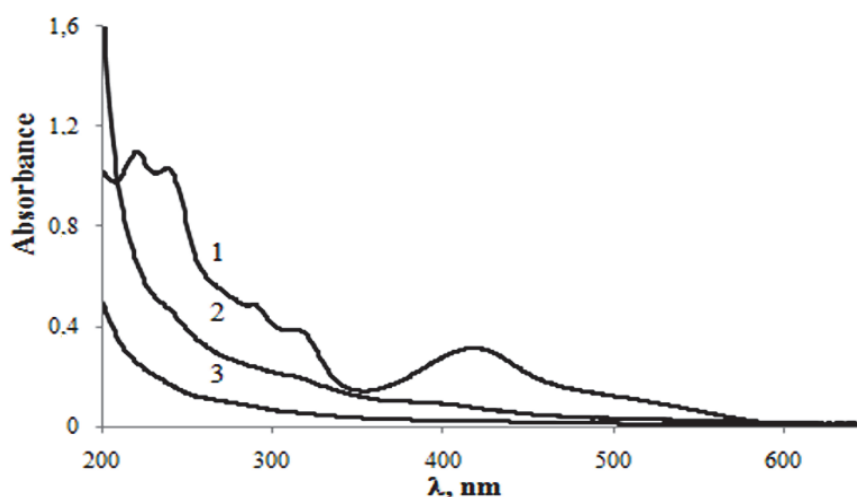
Fig. 3. UV-Vis spectra of Acid Yellow (**1**) after treatment by GC/H₂O₂ (**2**) and GC/H₂O₂/UV (**3**)
$C_0(H_2O_2) = 100$ mg L^{-1}, pH 6.2, τ = 15 min

The dissolved iron content at GC (where iron ions formed *in situ*) is appropriate for the treatment with Fenton processes, in which H_2O_2 is added directly. Using Acid Yellow as a model dye, it was observed that the decolorization efficiency increased to 40% when GC/H_2O_2 combination was used as compared to GC alone. The additional UV treatment increased the efficiency of the GC/H_2O_2 system.

The enhancement of the decolorization rate of Acid Yellow could be attributed to the generation of additional •OH during photodisproportionation of H_2O_2, the cleavage of iron complexes (hydroxy-, oxalate and similar) present in the system, and the reduction of Fe^{3+} to Fe^{2+}. The dye removal is attributed to both the oxidation by the photo-Fenton process and following coagulation.

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