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DISCOLORATION OF FOOD DYES FROM AQUEOUS MEDIA BY OZONATION. CASE STUDY: BRILLIANT BLUE

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The paper presents the discoloration of a food dye (Brilliant Blue - BB) in aqueous solutions by ozonation. In order to establish the optimum parameters of this process and to reach its maximum efficiency, the influence of BB concentration, ozone dose, dye-ozone contact time and pH of aqueous solution were examined. The originality of the work consists in using low concentrations of ozone obtained from 99.5% purity oxygen. The obtained experimental data suggested that BB can be successfully discolored from aqueous solutions by ozonation.

Keywords: food dyes, discoloration, ozonation, Brilliant Blue

1. Introduction

The dyes are used in many industries, like food, textile, leather, paper, rubber, plastic, drug etc, having a significant commercial importance. Synthetic dyes have a great structural diversity (azo, anthraquinones, sulfur, triphenyl - methane, phtalocyanine, etc.), so their toxicity and environmental impact is of great importance, knowing that 10-15% of produced dyes is lost.

Many studies showed that food dyes cause diverse pathology, like allergic dermatitis and skin irritation [1]. Dye discharging and accumulation into water resource can affect aquatic life and the food chain, so the depollution of wastewater and dye removal is of acute present interest.

The paper presents the results of a study on synthetic solutions with different concentrations of Brilliant Blue FCF food dye (IUPAC name: ethyl -[4 - [ethyl -[(3 - sulfophenyl) methyl] amino] phenil]-(2- sulphophenyl) methyldene]-1 -cyclohexa-2, 5- dienylidene] - [(3 - sulfophenyl) methyl] azonium.

Brilliant Blue (BB) is a blue color food dye, used in dairy products, sweets and drinks (for example Blue Curacao liqueur). It is also used in hygiene and cosmetics applications (soap, shampoo, mouthwash, etc).

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Brilliant Blue is a weak acid organic molecule with polar and non-polar components, which may lead to a complex sorption behavior. Its negative charge stems from sulfonic acid groups as shown the structure (Fig.1) [2].

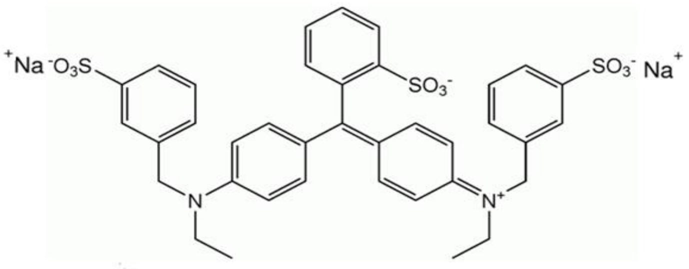

Fig. 1: The chemical structure of Brilliant Blue [2]

It is a reddish-blue powder soluble in water and slightly soluble in ethanol. UV Vis spectrophotometry studies of BB show four absorbtion peaks: 250 nm, 308 nm, 407 nm and 630 nm. [21].

Unfortunately, in large amounts BB is carcinogenic, causes reproductive and neurological disorders, severe allergies, anaphylactic reactions (rashes, swelling, breathing toubles) in human being. Even convulsion, gastrointestinal tumors, blood – lymphoma have also been described in rodents [2].

These reactions made Brilliant Blue (BB) being banned in Austria, Belgium, Denmark, France, Germany, Greece, Italy, Norway, Spain, Sweden and Switzerland. The legal limit in the EU is 150-300 mg/kg depending on type of food. Safety limit for food is 0.1 mg/day per kg body weight.

This justify the opportunity of the dye removal from industrial wastewater. A vast research and literature is dedicated to physical/(bio)chemical procedures of BB removal from waste water, in order to establish a best balance between the scientific outcome and the economical implication.

Numerous methods for BB removal have been developed:

- Physical methods - ultrasonication, ultrafiltration, micro- and nanofiltration [3-6];
- Chemical methods - oxidative processes (electrochemical oxidation, **ozonation, advanced oxidation processes AOP**), precipitation, complexation [6, 7];
- Physicochemical methods - coagulation - flocculation, sorption, ion exchange membranes, electrochemical processes [6, 8-14];
- Biological methods – aerobic/ anaerobic degradation, use of fungi, algae and microbial fuel cells [6, 14-17].

In order to streamline colour removal many combined methods showed their efficacy. Thus, ozonation and photocatalytic oxidation, ozonation and ultrafiltration, complexing/sorption and ozonation, complexing – flotation – ozonation, etc. were described and used with better results.

The ozonation process – as an alternative method of dye removal from aqueous systems - involves the reaction of O_3 with the dye by oxidation [18]. The ozone will act by direct mechanism (by itself – molecular ozone), indirect (by other strong oxidizing agents, like hydroxyl (HO·) free radicals), or rather by both mechanism. The ozone and the hydroxyl radical are very strong oxidants, their oxidation potentials being 2.07 respectively 2.80 V [21].

Whereas ozone is a very selective oxidant, acting on organic compounds that contain double bonds - C = C -, - N = N -, activated aromatic rings, functional groups and on amines, hydroxyl radicals react fast and non-selective with many dissolved compounds and the water matrix.[21].

Ozonation will act by oxidation on chromophore group of the dye, thus causing the formation of simplier, intermediate structures that are no longer colored, easily biodegradable in post-oxidation step.

Ozone application in color removal of aqueous systems requires knowledge of physical and chemical properties of ozone to explain its mechanism of reaction, process efficiency, color removal yield, consumption of reagents during the process. The oxidation of the dye by ozone will remove the colour but will not act to a complete mineralisation[19]. Consequently it is of great importance to estimate the quality of the effluent expressed by sum parameters like COD(Chemical Oxygen Demand), TOC((Total Organic Carbon) and also the amount of effluent toxicity and biodegradability. Several studies were described the oxidation by-products being more toxic than the initial dye solution[20]. Those by-products will depend on the dye concentration, ozone flow, contact time, the presence of other substances, etc. Usually the dye ozonation process will generate a mixture of substances, wich identification is complicated, generally carbonyl, hydroxyl compounds, aromatic amines, etc. [Zhu et al – 2015, Vaiano et al - 2015]

2. Matherials, Equipments and Methods

The dye Briliant Blue (analytical grade, Sigma Aldrich, Cas Number 3844-45-9) - Initial dye concentration (the dye stock) was set at 1000 mg/L by dissolving into distilled water. Working concentrations were in the range of 5 – 50 mg/L. The working volume was, each time, of 0.1L.

The ozone was obtained by OZONOSAN ALPHA-PLUS Generator utilizing 99.5% oxygen gas feed (oxygen of medical use). The ozone generator is equipped with UV-Photometer for continuous measurement of ozone concentration (in the range of 1 – 130 mg O_3/L gaseous mixture), high flow 1-10 L/min. The 99.5 % O2 purity in the cylinder was the oxygen supply for corona discharge ozone generator. Under a constant oxygen flow rate (measured by the generator mass flow controller), the ozone dose was constant.

The contact time of dye ozone was in the range of 0-900sec, and specific measurements were done at different time of contact (60,120,300 sec). The experiment was done at the room temperature.

The batch experiments were carried out using HEILDORPH VIBRAMAX 100 orbital shaker (stirring speed=200 rpm).

The pH of the solutions was adjusted by adding H_2SO_4 0.1M or NaOH 0.1M. The pH values were measured with ORION 290A pH-meter.

The BB final concentrations of aqueous samples were analyzed by CINTRA 404 UV/VIS Spectrometer. The quantitative assessment of discoloration was done at 407 and 630 nm short wavelength with the same analytical results. 407 nm was chosen to be used in the quantitative assessment because it is the band that it assumed to correspond to the prototropic equilibrium state of the dye solution [23].

The experiment to evaluate the discoloration efficiency by ozonation in term of yield (% R_{BB}) was conducted at room temperature:

- using increasing BB solutions (5-50 mg/L);
- adding increasing doses of ozone (100 – 250 mg/L $_{\text{gaseous mixture}}$) at each BB concentration;
- at different contact time (60-300 s);
- in two variants (with and without continuously stirring 200 rpm).
- the experiment was fulfilled mostly at pH of BB solution (pH = 7.03), excepted those where the influence of pH was evaluated; those tests were done at a pH = 4.0-8.0.

Ozonation of dye samples was carried out using glass recipients equipped with a diffuser. Each time a working volume of 0.1 L of dye solution with different concentrations was added into the glass recipient.

Ozone gas was supplied at various doses ranging 100 – 250 mg O_3/ L $_{\text{gaseous mixture}}$ followed by aeration for 300 sec to remove residual ozone.

The ozone/oxygen gaseous mixture (g,m.) was introduced through a glass tube from top to the bottom of a glass recipient with the dye sample solution. Ozone mass transfer was achieved through micro bubble generation through the diffuser. The experiments were fulfilled using low doses of ozone for economic and toxicological reasons. The choice of ozone concentrations was related to the intention of obtaining an efficient discoloration with low doses of ozone, in order to have low energy requirements and low operation costs.

3. Results and discussions

In order to establish the optimal parameters of the BB discolorating process in aqueous media by ozonation and to obtain an improved bleaching efficiency, the following factors were investigated: various concentrations of the dye and of the ozone, the dye-ozone contact time, the stirring influence, and various values of the test solution pH.

It was obvious that ozone, under specific conditions, led to rapid discoloration, by attacking the chromophore group of the dye, breaking it and leading to the formation of colorless by-products. [24]

The efficiency of the BB removal, expressed in the yield (%R_{BB}) of the reaction is:

$$\%R_{BB} = (1-C_{iBB}/C_{tBB}) \times 100$$

Where: C_{iBB} = the initial dye concentration at time t=0

C_{tBB} = the dye concentration at time t

The following graphs (Figs. 1-4) are showing the discoloration efficiency, expressed in terms of chemical yield (%R), of different BB solution concentration (5 mg/L, 10 mg/L, 20 mg/L, 50 mg/L) by ozonation with increasing O_3 dose (100 mg O_3/L g.m., 150 mg O_3/L g.m., 200 mg O_3/L g.m., 250 mg O_3/L g.m.), ensuring different contact time (0-900 sec), with and without stirring.

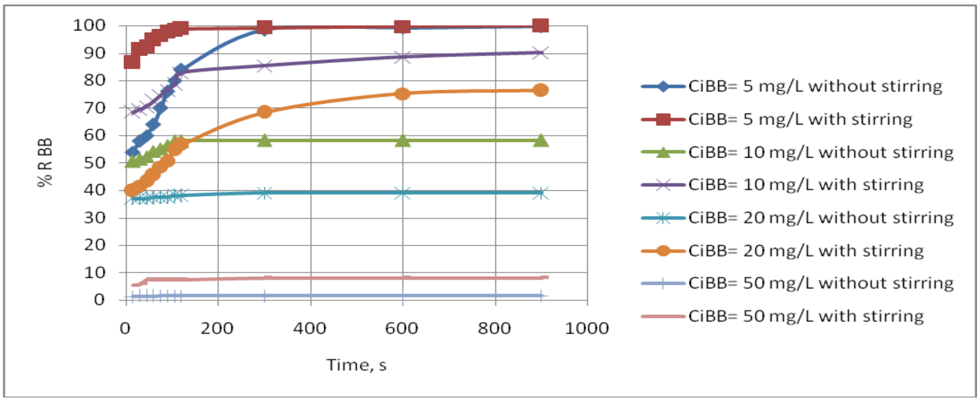

Fig. 1: %R_{BB} = f(t) at 100 mg O_3/L g.m. applied dose in aqueous solutions with different BB concentrations in two variants: with stirring and without stirring

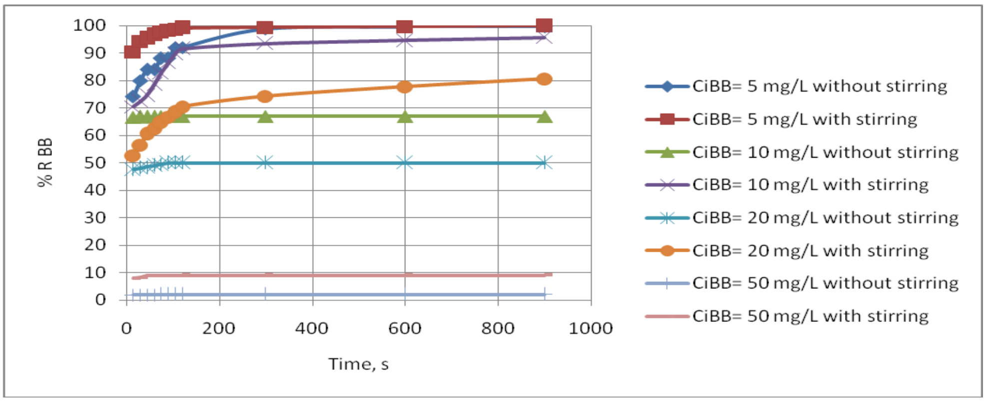

Fig. 2: %R_{BB} = f(t) at 150 mg O_3/L g.m. applied dose in aqueous solutions with different BB concentrations in two variants: with stirring and without stirring

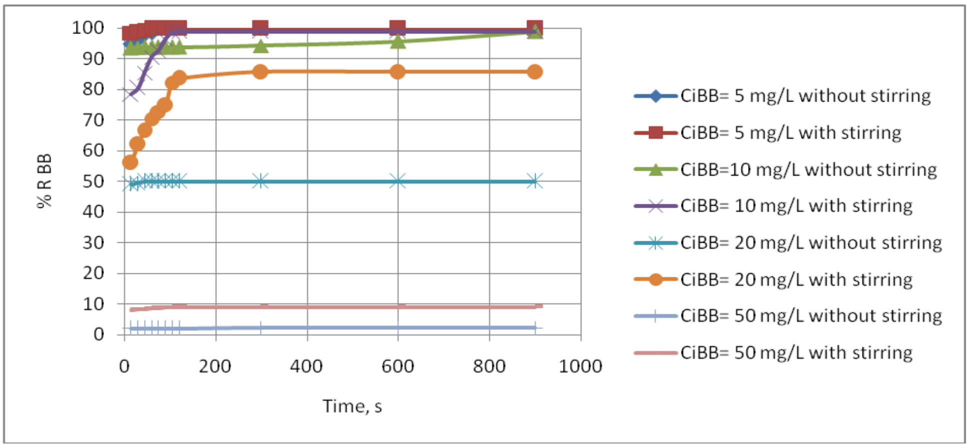

Fig. 3: %R_{BB} = f(t) at 200 O_3/L g.m. applied dose in aqueous solutions with different BB concentrations in two variants: with stirring and without stirring

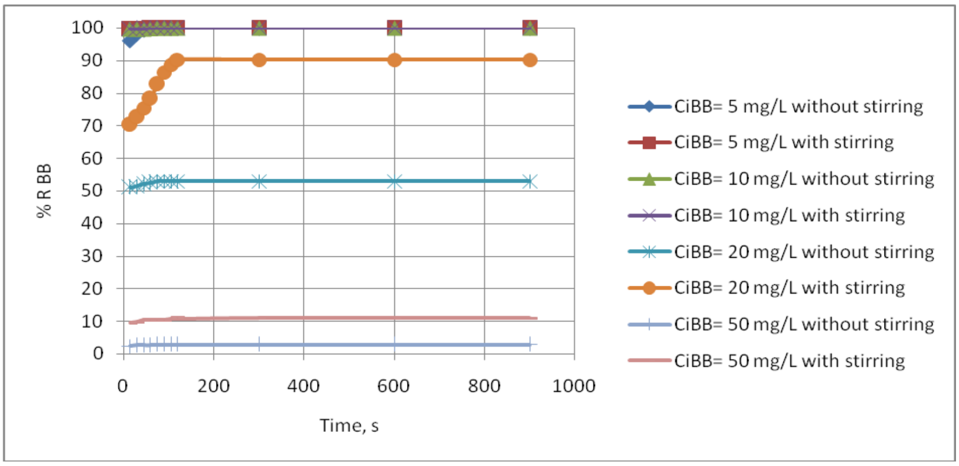

Fig. 4: %R_{BB} = f(t) at 250 O_3/L g.m. applied dose in aqueous solutions with different BB concentrations in two variants: with stirring and without stirring

The discoloration efficiency (%R) is directly proportional with the ozone concentration for each BB concentration of the studied domain. With the increasing O_3 doses, the necessary contact-time is shorter.

For exemple, for a chosen initial BB concentration, at the same contact-time (200 sec) the bleaching efficacy increased from %R = 99.2 at O_3 dose of 100 mg O_3/L g.m., to %R = 99.9, at O_3 dose of 250 mg O_3/ L g.m. It is obvious that increasing ozone concentration more than 200 mg O_3/L g.m. has not economic justification since the discoloration yield is increasing unsatisfactory. As expected, the discoloration efficiency (%R) is strongly related to the initial BB concentration (C_{iBB}):

- for a diluted BB solution (5 mg/L) the %R will be 99.9, with a O_3 dose of 200 mg O_3/ L g.m and a contact-time of 200 sec;
- for a BB solution of 10 mg/L - the %R will be 98.8 (under the same physical/chemical conditions);
- for a BB solution of 20 mg/L - the %R will be 85.6 (under the same physical/chemical conditions);
- for a BB solution of 50 mg/L - the %R will be 9.0 (under the same physical/chemical conditions).

The influence of stirring on the discoloration process (Fig 1-4 and 5-6) is significant in the sense that the bleaching efficiency is favored by this mechanical parameter.

- at BB low concentration (5 - 10 mg/L) and at 200 sec contact-time a remarcable efficiency ($\%R_{BB}$ = 94.2 without stirring and $\%R_{BB}$ = 98.8 with stirring) can be observed ;
- at higher BB concentrations (20 - 50 mg/L) much less discoloration yield is seen ($\%R_{BB}$ = 2.0 without stirring and $\%R_{BB}$ = 9.0 with stirring).

In order to determine the optimal contact-time applicable in the bleaching process by ozonation the chosen BB concentrations were tested at different values of contact-time (60, 120 and 300 sec) (Fig 5a, 5b). The experiment was revealing that the major part of the discoloration process is unfolding in the first 0 - 300 sec (see also in fig 1-4). It was remarkable bleaching efficiency (%R=98.8) of a BB solution (C_{iBB}=10 mg/L) ozonated with 200 mg O_3/L g.m. at time range of 0 - 200 sec. After this interval of contact-time the efficiency graph become flat (plateau shape of the %R curve).

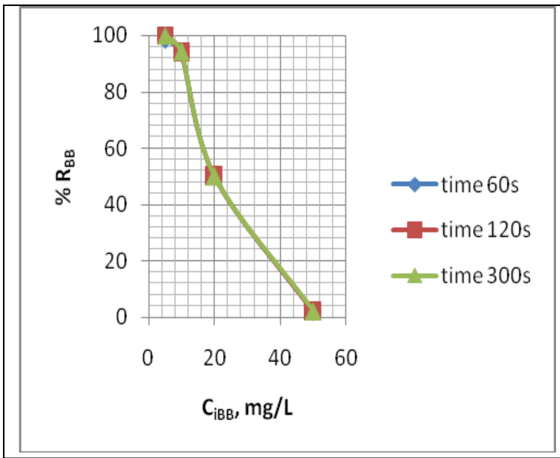

Fig. 5a: % $R_{BB} = f(C_{i\,BB})$ without stirring, $C_{i\,O3}$ = 200 mg O_3/L g.m.

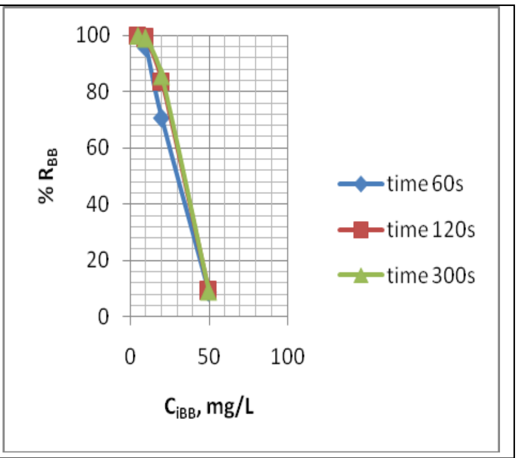

Fig. 5b: % $R_{BB} = f(C_{i\,BB})$ with stirring, $C_{i\,O3}$ = 200 mg O_3/L g.m.

Also, the influence of the stirring is mentioned above and a bleaching efficiency greater than 90% in the BB concentration range 5 - 10 mg/L with a contact time = 300s. can be noted.

Recognizing the BB concentration of 10 mg/L as the one that responds best to ozonation the discoloration efficiency at different ozone concentrations was plotted (fig 6a and 6b). At one particular time of reaction (300sec) good yields are observed at ozone concentration = 200 mg/L.

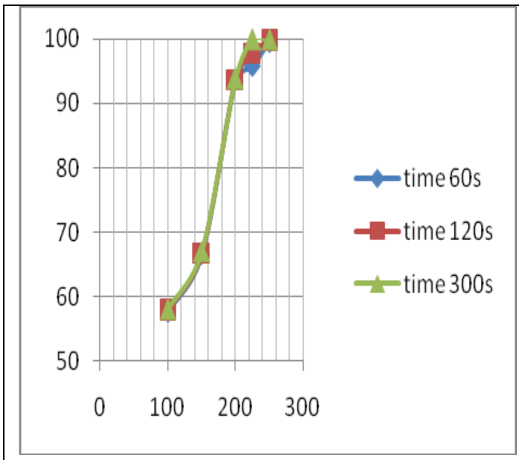

Fig. 6a. %$R_{BB} = f(C_{i\,O3})$ without stirring, $C_{i\,BB}$ = 10 mg/L

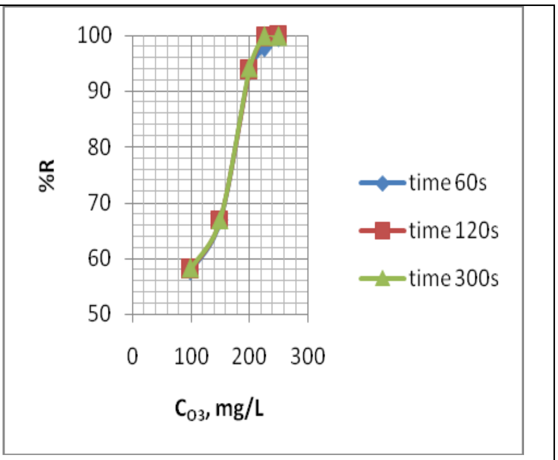

Fig. 6b. %$R_{BB} = f(C_{i\,O3})$ with stirring, $C_{i\,BB}$ = 10 mg/L

The results of this experiment indicated a good discoloration efficiency at low concentration of BB solution (%R= 99.9 at 10 mg/L). This low concentration of the dye would be of limited practical application, vue that in real systems (industrial/medical wastewater, etc.) the dyes are found in variable major concentrations.

On the other hand, at pH=7 the BB solution of 50 mg/L concentration suffered practically no discoloration (%R=9) independently of the contact-time.

Thus, it was important to study the influence that other parameters would exercise on the bleaching process (e.g. pH), considering BB which is an anionic azo dye with terminal sulphonic groups.

Therefore, discoloration of the 50 mg/L BB solution at constant O_3 concentration have been done, with variable pH values (4-8) and with different contact-time values (60,120,300 sec) - See Table 1.

Table 1

%R = f(pH)

Working conditions	**pH**	**Contact time, s**	**%R_{BB}**
$C_{i\,BB}$ = 50 mg/L, $C_{i\,O_3}$ = 200 mg O_3/L g.m, with stirring	**7.00**	**300**	**9.0**
	6.00	300	66.7
	5.00	120	87.5
	4.00	**60**	**99.9**
	8.00	> 300	0.2

One may observe that at pH greater than 7 (pH=8) no discoloration occurred, while at more acidic pH, respectively at pH=4 a maximum bleaching efficiency (%R=99.9) with a shorter contact-time (60sec) was observed.

These notifications seem to be in compliance with specially literature information which explain this behavior by differential ionization of dye according to the acid/alkaline medium [25, 26]. In aqueous solution, BB dye molecule is found in acid-base forms which are in dynamic equilibrium depending on pH values [23, 26].

Several other studies have highlighted that in the dye discoloration process by ozonation, the oxidation mechanism depends on the pH of the medium, and hence the predominant oxidant will be either the molecular ozone at low pH or hydroxyl radical at higher pH. Even the hydroxyl radical has significantly higher oxidation ability than ozone, the direction of the discoloration process will be determined by the electrochemical nature of the dye and by the pH condition [27, 28].

4. Conclusions

The ozonation of Brilliant Blue dye led to a rapid and effective discoloration of the respective dye aqueous solutions. The oxidation process (by ozone alone or in AOPs) appeared to be a promising alternative for the dye removal, resulting in more that 90% discoloration under specific physical/chemical conditions. The discoloration efficiency was maximized by using low BB concentration (10 mg/L), ozone of 200 mg O_3/L g.m., under adequate stirring condition (200 rpm), to a neutral/slightly acidic pH (pH=7.03). At decreased pH (4.0) the bleaching efficiency was improved even with higher concentration of BB (50 mg/L) and with a shorter contact-time (60 sec). The research has emphasis in particular the influence of high-purity ozone obtained by pure (99.5%) oxygen in the oxidation process. Thus, the efficiency of the ozonation (even in very low dose) was significantly high.

The results of the described experiment will act like premises for further research on dye ozonation, and especially on by-products evaluation regarding their toxicity and the impact to the environment.

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