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## DECOLOURIZATION OF TARTRAZINE FROM AQUEOUS SOLUTIONS BY COUPLING ELECTROCOAGULATION WITH ZnO PHOTOCATALYST

Decolourization of tartrazine (C.I. Acid Yellow 23, AY23) in aqueous solutions has been investigated by coupling electrocoagulation and ZnO photocatalyst methods and also by a comparison between ZnO, UV, EC, UV/ZnO, UV/EC, and EC/UV/ZnO systems in the removal of AY23 as a model contaminant. Results indicated that the decolourization efficiency was in order of EC/UV/ZnO > UV/EC > EC > UV/ZnO > ZnO ≥ UV. Combining EC with UV/ZnO can trigger the Fenton or Fenton-like reaction, which accelerates the rate of decolourization. Desired operating conditions for decolourization of 40 mg·dm<sup>-3</sup> AY23 solution in EC/UV/ZnO process were [ZnO]<sub>0</sub> = 650 mg·dm<sup>-3</sup>, [NaCl] = 800 mg·dm<sup>-3</sup>, light intensity = 31/2 W·m<sup>-2</sup>, current density = 120 A·m<sup>-2</sup>, electrodes distance = 15 mm, pH = 6.29, stirring rate = 900 rpm and electrodes of steel 304/Al, which yielded 99.70% colour removal in 5 min of treatment time.

### 1. INTRODUCTION

Water is an essential natural resource for human being and for all life forms [1, 2]. One of the major challenges facing mankind today is to provide clean water to a vast majority of the population around the world. Reuse of wastewaters has become an absolute necessity. Therefore, there is an urgent need to develop innovative, more effective and inexpensive techniques for treatment of wastewater [3].

Wastewater from some industries such as textile and paper contain residual dyes, which are not readily biodegradable. One of them is tartrazine (C.I. Acid Yellow 23, AY23) which is an anionic azo dye whose presence in thousands of foods and drugs has been reported as a possible cause of asthma, urticaria, and angioedema [4, 5]. It also has phototoxic potentials [4].

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Conventional treatments of dye effluents include biological oxidation and adsorption. For instance, adsorption onto activated carbon transfers most of the contaminant from the wastewater to the solid phase. Hence, this method requires further disposal of the sludge [6, 7].

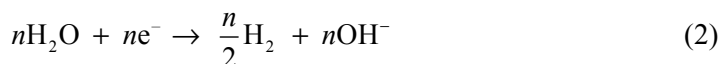
Electrocoagulation (EC) is regarded as a potentially effective method for treating textile wastewater with high decolourization efficiency and relatively little sludge formation. Several researchers reported treatments of dye wastewater based on the EC method [5–8]. EC with metallic electrodes is a technique using a current to dissolve metal such as Fe, steel or Al sacrificial anodes immersed in polluted water, giving rise for corresponding metal ions to form Fe (II) and/or Fe (III) or Al(III) species with hydroxide ions. Depending on pH, these species act as coagulants, leading the contaminants to coagulate. In general, the following processes take place during the EC treatment [9]:

1. Electrode reactions to produce metal ions from Fe or Al anodes and H<sub>2</sub> gas at the cathode [10]:

- at the anode



- at the cathode



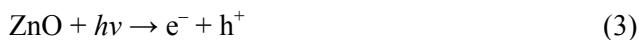
where M is the anode material and  $n$  is the number of electrons.

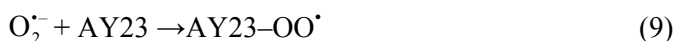
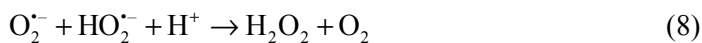
2. Formation of coagulants in the wastewater.

3. Removal of dyes with coagulants by sedimentation or by electroflotation with evolved H<sub>2</sub>.

4. Other electrochemical and chemical reactions involving reduction of organic impurities and metal ions at the cathode and coagulation of colloidal particles.

Moreover, heterogeneous photocatalysis is one of advanced oxidation processes (AOPs) which is utilized for treatment of wastewaters. In AOPs, organic pollutants are converted to short species and even to their complete mineralization products through the reaction with free radical oxidants. For example, combination of a semiconductor such as metal oxides (TiO<sub>2</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub>) and metal sulfides (CdS and ZnS) as photocatalysis with UV light can be used for degradation of a wide range of organic contaminants [2, 11].





The prototype of a heterogeneous photocatalytic reaction is based on the irradiation of particles of a ZnO semiconductor in the presence of dissolved molecular oxygen. The generally accepted mechanism of heterogeneous photocatalysis includes redox reactions of adsorbed water, hydroxyl anions and oxygen molecules or other substances. Upon irradiation, valence band electrons ( $e^-$ ) are promoted to the conduction band leaving a hole ( $h^+$ ) behind (Eq. (3)). These electron-hole pairs can either recombine (Eq. (4)) or interact separately with other molecules. The holes at the ZnO valence band can oxidize adsorbed water or hydroxide ions to produce hydroxyl radicals, which are able to oxidize contaminants unselectively (Eqs. (5), (6)). Electrons of the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anions  $O_2^{\bullet -}$  (Eq. (7)). These radicals may form organic peroxides (AY23- $OO^{\bullet}$ ) or hydrogen peroxide in the presence of organic scavengers (Eqs. (8), (9)). Hydroxyl radicals are a powerful oxidizing agent, which attacks organic compounds to form intermediates (Int.). These intermediates react with hydroxyl radicals to produce final products (p) (Eq. (10)) [2, 12–16].

The principal objective of this study was to investigate the application of ZnO, UV, EC, UV/ZnO, UV/EC, and EC/UV/ZnO systems and evaluate their decolourization efficiency using tartrazine solution as a model contaminant.

## 2. MATERIALS AND METHODS

*Materials.* C.I. Acid Yellow 23 (AY23), a mono azo anionic dye was obtained from ACROS organics (USA). Its chemical structure and other characteristics are

Table 1

Characteristics of Acid Yellow 23 (AY23)

Number C.I.	$\lambda_{max}$ [nm]	Class	Colour	Ionization	$M_w$ [g/mol]
19140	428	azo	yellow	acidic	534.385

given in Table 1. ZnO was purchased from Fluka (Switzerland). Other chemicals were purchased from Merck (Germany). All chemicals were used without further treatment.

*Methods.* The experiments were performed on tartrazine solutions with concentrations of  $40 \text{ mg}\cdot\text{dm}^{-3}$ . DC power supplier (MICRO PW-3032D, 0-30 V/0-3 A) and a magnetic stirrer, flat-plate anode and cathode were employed. The electrodes (steel 304/Al) were placed inside a pyrex glass reactor with the distance of 15 mm between anode and cathode (Fig. 1). In each experiment,  $250 \text{ cm}^3$  of the dye solution was used and in 5 min process intervals, the DC power was switched off to allow precipitation for 5 min. Then, the obtained solution was centrifuged and analysed by means of a UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England). The absorbance of the dye solution at all experiments was measured at 428 nm. To maintain the conductivity and ionic strength adjustment of solution, salt was added in all EC processes [4].

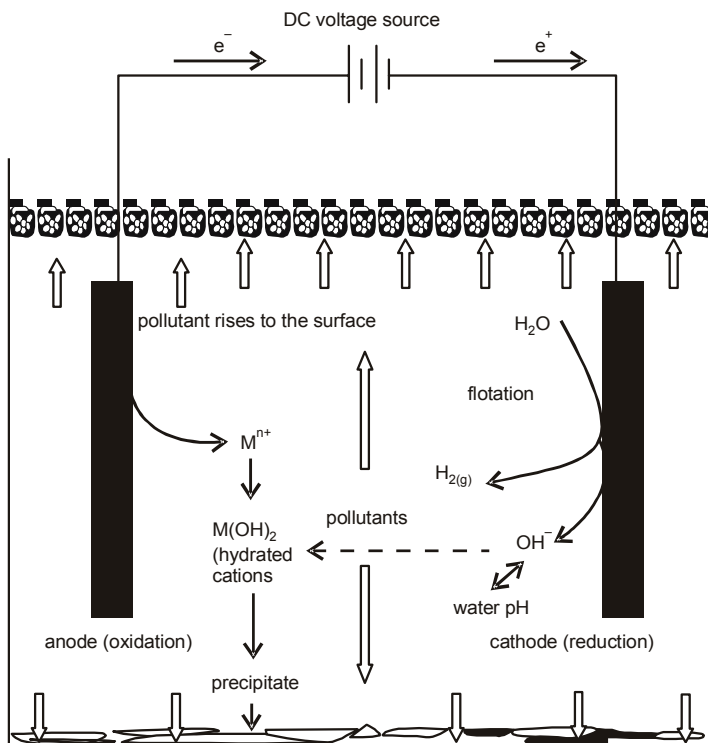


Fig. 1. Schematic diagram of the electrocoagulation cell

*UV/ZnO process.* All the experiments were carried out in a batch photoreactor. Mixing of solution was carried out by means of a magnetic stirrer. The radiation

source was a UV lamp (30 W, UV-C,  $\lambda_{\max} = 254$  nm, manufactured by Philips, Holland) which was situated above a Pyrex reactor. The light intensity in the centre of the photoreactor was measured by means of a Lux-UV-IR meter (Leybold Co.). For the photocatalytic degradation of AY23, a solution of known concentration of the dye and ZnO was prepared and allowed to equilibrate for 30 min in the darkness, afterward, 250 cm<sup>3</sup> of the prepared suspension was transferred into the reactor, then the lamp was switched on to initiate the reaction. During irradiation, the glass reactor mounted on a magnetic stirrer to keep the suspension homogenous and at 15 min reaction intervals, 5 cm<sup>3</sup> of the sample was withdrawn, centrifuged, and the dye concentration was analyzed with a UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 428 nm.

*EC/UV/ZnO process.* The experiments were performed with tartrazine solutions of the concentrations of 40 mg·dm<sup>-3</sup>. All experiments were carried out in a batch photoreactor with the radiation source of a UV lamp (30 W, UV-C,  $\lambda_{\max} = 254$  nm, manufactured by Philips, Holland) which was situated above a Pyrex 250 cm<sup>3</sup> reactor.

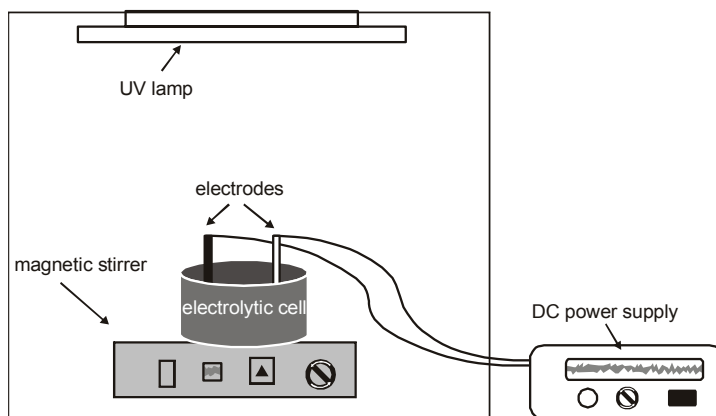


Fig. 2. Schematic diagram of EC/UV/ZnO process

NaCl salt as an electrolyte was added to the solution to adjust its ionic strength (Fig. 2). The catalyst was added to the reactor and the solution was allowed to equilibrate for 30 min in darkness then the flat-plate electrodes (steel 304/Al) were immersed in the reactor at the distance of 15 mm. The total submerged surface area of each electrode was 18 cm<sup>2</sup>. Electrodes were connected to a DC power supplier (MICRO PW-3032D, 0-30 V/0-3 A). In each experiment, 250 cm<sup>3</sup> of the dye solution was used and in 5 min process intervals, the DC power and UV lamp were switched off to allow precipitation for 5 min. Then, the obtained solution was centrifuged and analysed by a UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England). The absorbance of the dye solution at all experiments was measured at 428 nm.

The solution was mixed with a magnetic stirrer at 900 rpm. The process was carried out in a combined form and the treatment time was 5 min with NaCl concentration of  $800 \text{ mg}\cdot\text{dm}^{-3}$ . The initial concentration of AY23 was  $40 \text{ mg}\cdot\text{dm}^{-3}$ .

The colour removal efficiency (*CR*) after electrocoagulation was calculated from the following formula:

$$CR = \frac{C_0 - C}{C_0} \times 100 \quad [\%] \quad (11)$$

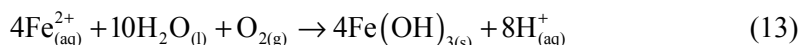
The chemical oxygen demand (COD) of the dye solution was measured by the standard methods for the examination of water and wastewater (open reflux method, 5220B) [17].

### 3. RESULTS AND DISCUSSION

#### 3.1. DECOLOURIZATION EFFICIENCY OF THE ELECTROCOAGULATION PROCESS

The decolourization of AY23 solution by electrocoagulation depends on the current density (CD), time of electrolysis, electrodes distance and material, electrolyte type and concentration. Series of experiments were conducted in order to establish the optimum values of these parameters for  $40 \text{ mg}\cdot\text{dm}^{-3}$  of dye solution.  $[\text{NaCl}] = 400 \text{ mg}\cdot\text{dm}^{-3}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ , electrode distance = 15 mm, pH = 5.44, stirring rate = 900 rpm, electrodes of steel 304/Al yielded 99.72% colour removal in 60 min of treatment time. During electrolysis, the following equations occur on the electrodes [4, 5]:

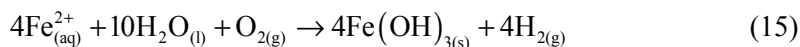
• Anode:



• Cathode:



• Taken as a whole:



Anodic oxidation of Fe generates ionic species such as  $\text{Fe}(\text{OH})^{2+}$ ,  $[\text{Fe}(\text{OH})_2]^+$ ,  $[\text{Fe}(\text{OH})_2]^{4+}$ ,  $[\text{Fe}(\text{OH})_4]^-$ ,  $[\text{Fe}(\text{H}_2\text{O})_2]^+$ ,  $[\text{Fe}(\text{H}_2\text{O})_3\text{OH}]^{2+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ , and  $[\text{Fe}(\text{H}_2\text{O})_6(\text{OH})_4]^{2+}$ , which are converted to  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ , eventually. The

colour removal efficiency depends directly on the concentration of ions produced by the electrodes. Upon increasing the treatment time, the concentration of ions and their hydroxide flocs increase as well. Accordingly, as shown in Fig. 3, an increase in the time of treatment from 5 to 60 min yields an increase in the colour removal from 69.28% to 99.72% [4].

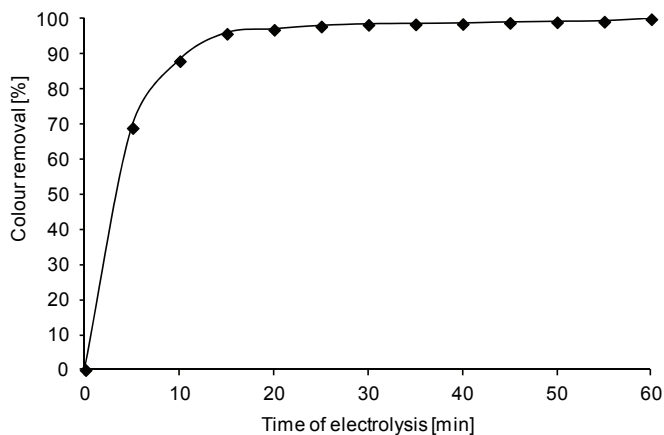


Fig. 3. Decolourization efficiency of electrocoagulation process,  $[AY23]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{NaCl}] = 400 \text{ mg}\cdot\text{dm}^{-3}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  $d = 15 \text{ mm}$ ,  $\text{pH} = 5.44$ , stirring rate =  $900 \text{ rpm}$ ,  $t_{\text{elec}} = 5 \text{ min}$  and electrodes of steel 304/Al

### 3.2. DECOLOURIZATION EFFICIENCY OF UV/ZnO PROCESS

Similarly as in the EC process, it is necessary to find desired process parameters through the laboratory tests [18]. Optimum operating conditions of the UV/ZnO process

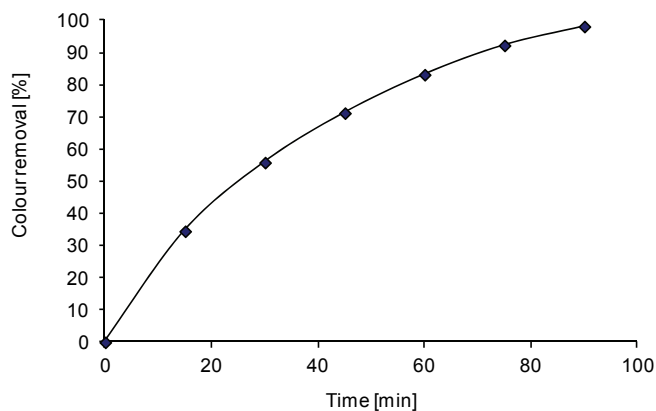


Fig. 4. Decolourization efficiency of UV/ZnO process;  $[AY23]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{ZnO}] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ ,  $\text{pH} = 7.53$  and stirring rate =  $900 \text{ rpm}$

for  $40 \text{ mg}\cdot\text{dm}^{-3}$  dye solution (photocatalyst concentration  $650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ ,  $\text{pH} = 7.53$  and stirring rate = 900 rpm) yielded 98.14% colour removal in 90 min of the treatment time. When the treatment time increased, an increase in the colour removal was visible [11]. The colour removal efficiency by the UV/ZnO process depends directly on the concentration of active radicals like hydroxyl and superoxide which increase during the process time. When the treatment time increases, the concentration of hydroxyl and superoxide radicals increases [12, 14, 15].

Accordingly, as shown in Fig. 4, an increase in the treatment time from 15 to 90 min yields an enhancement in the colour removal efficiency from 34.55% to 98.14%.

### 3.3. THE EFFECT OF OPERATIONAL PARAMETERS ON EC/UV/ZNO PROCESS

*Effect of the photocatalyst concentration.* With an increase of the catalyst loading from  $150$  to  $650 \text{ mg}\cdot\text{dm}^{-3}$ , the decolourization percent increased from 37.14 to 99.70 after 5 min of the treatment time. After that the increase in the catalyst loading did not affect the decolourization. Thus, the catalyst loading for maximum decolourization of  $40 \text{ mg}\cdot\text{dm}^{-3}$  of AY23 was  $650 \text{ mg}\cdot\text{dm}^{-3}$  under the experimental conditions (Fig. 5).

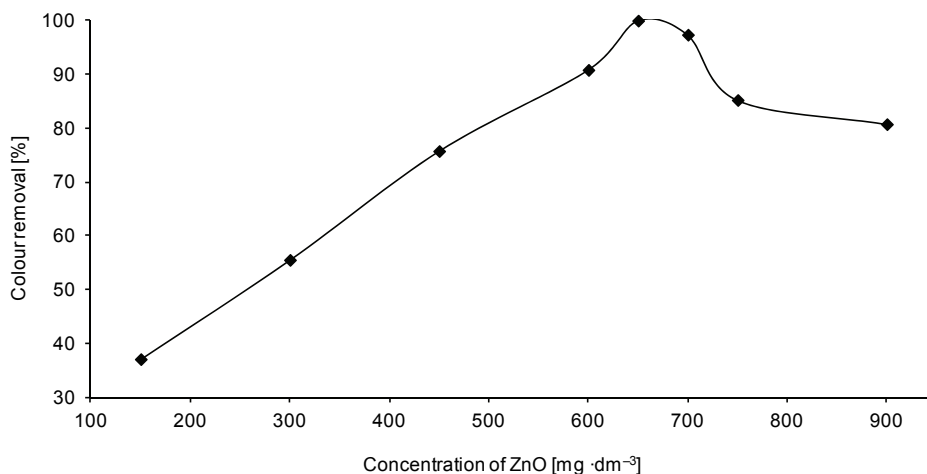


Fig. 5. Effect of the photocatalyst concentration on the degradation efficiency of AY23 [ $\text{AY23}]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{NaCl}] = 800 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 39 \text{ W}\cdot\text{m}^{-2}$ ,  $\text{pH} = 7.57$ ,  $d = 15 \text{ mm}$ , stirring rate = 900 rpm, current density =  $120 \text{ A}\cdot\text{m}^{-2}$  and steel 304/Al was used as electrodes

An increase in the amount of catalyst increased the number of active sites on its surface, which in turn increased the number of hydroxyl and superoxide radicals. When the concentration of ZnO catalyst increased above the optimum value, the removal rate decreased due to more turbidity of the suspension and less UV light penetrating the solution as a result of further scattering effect [4, 11].



*Effect of the light intensity.* The influence of light intensity on the decolourization has been examined at constant dye concentration ( $40 \text{ mg}\cdot\text{dm}^{-3}$ ) and catalyst loading ( $650 \text{ mg}\cdot\text{dm}^{-3}$ ). It is evident that the percentage of decolourization increased upon increasing the light intensity (Fig. 6). UV irradiation generated photons required for the electron transfer from the valence band to the conduction band of the semiconductor photocatalyst. The energy of a photon is related to its wavelength and the overall energy input to a photocatalytic process is dependent on light intensity. The rate of decolourization increased when more radiation fell on the catalyst surface and hence more hydroxyl radicals were generated [11].

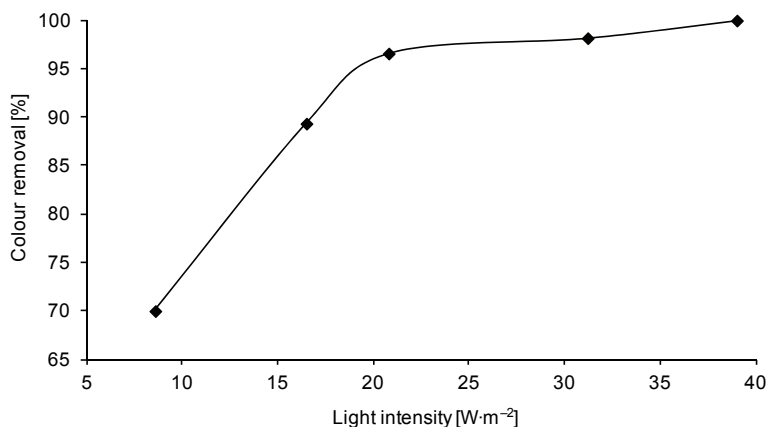


Fig. 6. Effect of the light intensity on photocatalytic degradation of AY23  
 $[\text{AY23}]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{ZnO}] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{NaCl}] = 800 \text{ mg}\cdot\text{dm}^{-3}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  
 $d = 15 \text{ mm}$ ,  $\text{pH} = 7.57$ , stirring rate =  $900 \text{ rpm}$  and electrodes of steel 304/Al

*Effect of NaCl concentration.* As shown in Fig. 7, the decolourization in EC/UV/ZnO process increases with the increasing NaCl concentration. When the concentration of NaCl in solution increases, its conductivity and current density are increased and the necessary voltage for reaching a certain current density will be reduced, thus the consumption of electrical energy is decreased. For lower concentrations of NaCl due to insufficient concentration of ions, electric resistance of the solution would decrease the efficiency of the process [5, 7, 19].

$$V = E_C - E_a - |\varepsilon_A| - |\varepsilon_C| - IR_{\text{cell}} - IR_{\text{circuit}} \quad (16)$$

Where  $V$ ,  $E_c$ ,  $E_a$ ,  $\varepsilon_A$ ,  $\varepsilon_C$ ,  $IR_{\text{cell}}$  and  $IR_{\text{circuit}}$  are potential difference, cathodic potential, anodic potential, anodic overpotential, cathodic overpotential, cell ohmic drop and circuit ohmic drop, respectively.

Chlorine molecules ( $\text{Cl}_2$ ) and hypochlorite ions (ions), being strong oxidants, can be produced in wastewaters containing chloride ions [5]:

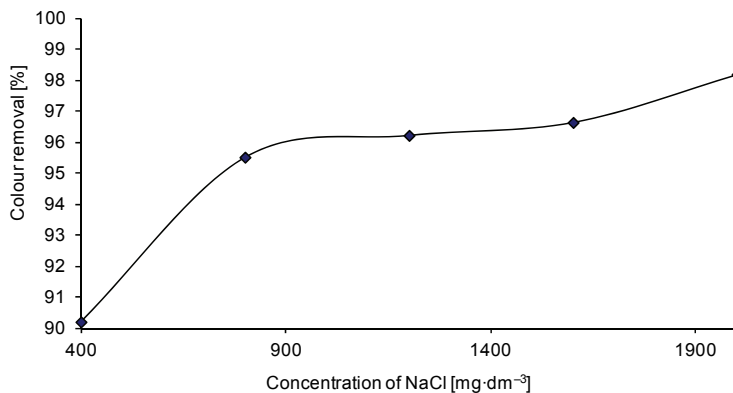


Fig. 7. Effect of NaCl concentration on the degradation efficiency of AY23;  $[\text{AY23}]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{ZnO}] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  $d = 15 \text{ mm}$ ,  $\text{pH} = 7.57$ , stirring rate = 900 rpm and electrodes of steel 304/Al

*Effect of  $\text{Na}_2\text{SO}_4$  concentration.* Colour removal of tartrazine in the EC/UV/ZnO process upon increasing  $\text{Na}_2\text{SO}_4$  concentration is demonstrated in Fig. 8.

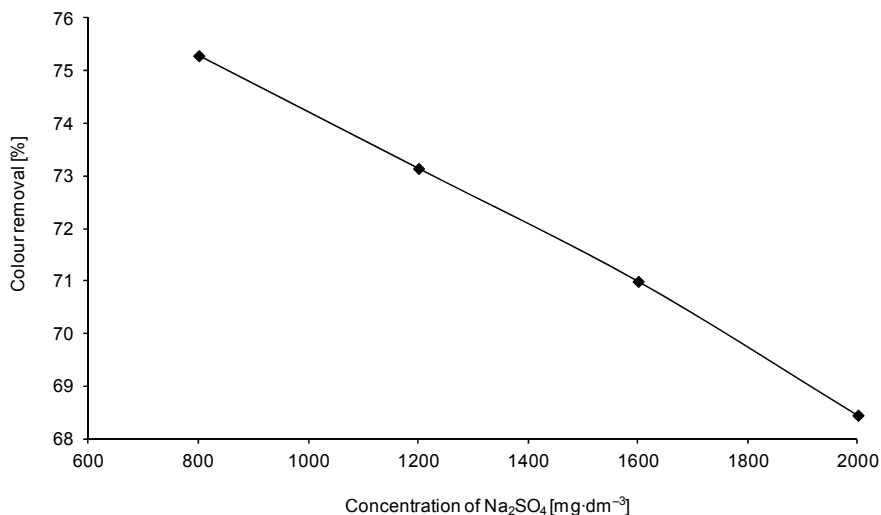
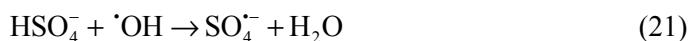


Fig. 8. Effect of  $\text{Na}_2\text{SO}_4$  concentration on the degradation efficiency of AY23;  $[\text{AY23}]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{ZnO}] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  $d = 15 \text{ mm}$ ,  $\text{pH} = 7.57$ , stirring rate = 900 rpm and electrodes of steel 304/Al

As can be observed, upon increasing the concentration of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  the decolourization percent decreases. This inhibition is undoubtedly due to their ability to act as scavengers of hydroxyl radicals in the following reactions [11]:



These ions may also block active sites on the ZnO surface thus deactivating the catalyst towards the AY23 and intermediates. Although the generated sulphate radical anions can act as oxidants but its oxidation potential is less positive than that of hydroxyl radicals. Furthermore, electrode potential of sulfate and hydrogen sulfate anions are higher than water, they are reduced in cathode instead of water, hence the removal efficiency decreases [5, 11].

*Effect of the initial pH.* Initial pH of the sample was adjusted to a desired amount using NaOH or  $\text{HNO}_3$ . Figure 9 demonstrates the decolourization of tartrazine in function of pH.

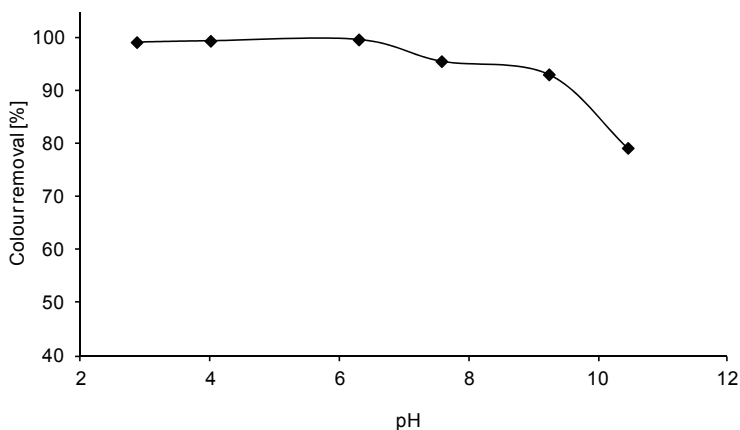


Fig. 9. Effect of the initial pH on the degradation efficiency of AY23,  $[\text{AY23}]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ;  $[\text{ZnO}] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[\text{NaCl}] = 800 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  $d = 15 \text{ mm}$ , stirring rate = 900 rpm and electrodes of steel 304/Al

The maximum decolourization of tartrazine was observed at pH ca. 6.3. When pH is increased above this value, the amount of hydroxide ions in solution increases, consequently some of the hydroxide ions are probably oxidized at the anode. This action prevents the production of the same proportion of iron ions and therefore the removal efficiency of tartrazine decreases [5, 19].

### 3.4. DECOLOURIZATION EFFICIENCY OF ZNO, UV, EC, UV/ZNO, UV/EC, AND EC/UV/ZNO SYSTEMS

Table 2 presents the decolourization efficiency of ZnO, UV, EC, UV/ZnO, UV/EC, and EC/UV/ZnO systems under the following conditions:  $[AY23]_0 = 40 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[ZnO] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[NaCl] = 800 \text{ mg}\cdot\text{dm}^{-3}$ ,  $I_0 = 31.2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,  $d = 15 \text{ mm}$ ,  $\text{pH} = 7.57$ , stirring rate = 900 rpm, electrodes of steel 304/Al. Results indicated that the decolourization efficiency was in order of  $\text{EC/UV/ZnO} > \text{UV/EC} > \text{EC} > \text{UV/ZnO} > \text{ZnO} \geq \text{UV}$ . These experiments demonstrated that both UV light and a photocatalyst were needed for the effective destruction of AY23. It has been established that the photocatalytic process in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an electron-hole pair on the surface of the catalyst (Eq. (3)) [4]. According to EC process,  $\text{Fe}(\text{OH})_3$  can remove dye by the complexation, electrostatic attraction and coagulation.

Table 2

Decolourization efficiency of AY23

System	Colour removal [%]	
	for 5 min	for 10 min
EC/UV/ZnO	99.70	99.96
EC /UV	76.32	93.32
EC	69.28	88.44
UV/ZnO	10.31	22.67
ZnO	0.75	1.93
UV	0.04	0.07

The following reaction can be conducted [4, 20].



$\text{Fe}(\text{OH})^{2+}$  is the predominant  $\text{Fe}^{3+}$  hydroxy species in solution at pH 2.5–5.5. It easily absorbs light (300–400 nm) to generate hydroxyl radicals [20]:



Other  $\text{Fe}^{3+}$  complexes such as  $\text{Fe}(\text{OH})_2^+$  which dominate at  $\text{pH} > 5.5$ , are less photoreactive. Moreover,  $\text{Fe}^{2+}$  does not absorb light above 300 nm and thus it is not expected to undergo photolysis under the experimental conditions used herein [10, 20]. During the reaction, pH increases from 6.1 to 7.4 in the UV/EC system. This may be due to the formation of  $\text{Fe}(\text{OH})_2^+$ . Hence, the enhancement of UV in UV/EC

system is very limited and proves the result  $UV/EC > EC$  [10]. Behnajady et al. [12] summarized the degradation of dye in UV/ZnO according to Eqs. (3)–(10).

Chen et al. [21] further suggested the following mechanism of the UV/ZnO process:



where hydroxyl radicals ( $\cdot OH$ ), superoxide radical anions ( $O_2^{\cdot-}$ ), hydrodioxyl radicals ( $HO_2^{\cdot}$ ) and photogenerated holes ( $h_{VB}^+$ ) are the primary oxidizing species in the UV/ZnO system. Furthermore,  $H_2O_2$  was generated in an UV/ZnO reaction (Eqs. (8), (24)).  $Fe^{2+}$  and  $Fe^{3+}$  are generated in the EC system (Es. (12), (22)), thus combining UV/ZnO with EC may cause a Fenton or Fenton-like reaction and accelerate decolourization [10].

Chen et al. [21] stated that  $H_2O_2$  plays an important role in reducing electron/hole recombination and promoting the photocatalytic activity of ZnO. The presence of  $Fe^{2+}$  and  $Fe^{3+}$  may increase photocatalytic activity, either by scavenging electrons, reducing the recombination of charges, favouring the formation of hydroxyl radicals, or by intermediate Fenton reactions. Hence, UV/ZnO and EC combination is a more powerful method than UV/ZnO or EC for wastewater treatment.

### 3.5. COD MEASUREMENTS

To investigate the mineralization of the dye solution in EC/UV/ZnO, which was the most effective process for the decolourization of AY23, COD measurements were carried out by the open reflux method and repeated for three times [17]. Results indicated that 79% and 92% of COD was eliminated after 5 and 10 min in optimum conditions ( $[ZnO]_0 = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[NaCl] = 800 \text{ mg}\cdot\text{dm}^{-3}$ , light intensity =  $31/2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ , electrodes distance = 15 mm, pH = 6.29, stirring rate = 900 rpm and electrodes of steel 304/Al) for dye concentration of  $40 \text{ mg}\cdot\text{dm}^{-3}$ .

## 4. CONCLUSIONS

Decolourization efficiency of AY23 has been investigated by ZnO, UV, EC, UV/ZnO, UV/EC, and EC/UV/ZnO systems. Results indicated that the decolourization efficiency was in order of  $EC/UV/ZnO > UV/EC > EC > UV/ZnO > ZnO \geq UV$ . Additionally, it could be promoted by combining UV with EC, UV with ZnO and EC with UV/ZnO. This study reveals that combining EC with UV/ZnO may induce a Fenton or Fenton-like reaction and accelerate decolourization. At desired operating conditions of the EC/UV/ZnO process for  $40 \text{ mg}\cdot\text{dm}^{-3}$  of the dye solution ( $[ZnO] = 650 \text{ mg}\cdot\text{dm}^{-3}$ ,  $[NaCl] = 800 \text{ mg}\cdot\text{dm}^{-3}$ , light intensity =  $31/2 \text{ W}\cdot\text{m}^{-2}$ , current density =  $120 \text{ A}\cdot\text{m}^{-2}$ ,

$d = 15$  mm, pH = 7.57, stirring rate = 900 rpm and electrodes of steel 304/Al) yielded 99.70% colour removal in 5 min of the treatment time. While in UV/EC, EC, UV/ZnO, ZnO and UV processes under the same operating conditions yielded 76.32%, 69.28%, 10.31%, 0.75% and 0.04% colour removal in 5 min of the treatment time, respectively.

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