

# Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine

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## Abstract

The kinetics of the oxidative degradation of the indigo carmine (IC) dye (disodium salt of 3,3-dioxobi-indolin-2,2-ylidene-5,5-disulfonate) with hydrogen peroxide catalyzed with the supported metal complexes have been investigated. The complexes used are  $[\text{Cu}(\text{amm})_4]^{2+}$ ,  $[\text{Co}(\text{amm})_6]^{2+}$ ,  $[\text{Ni}(\text{amm})_6]^{2+}$ ,  $[\text{Cu}(\text{en})_2]^{2+}$ , and  $[\text{Cu}(\text{ma})_4]^{2+}$  (amm = ammonia, en = ethylenediamine, and ma = methylamine). Silica, alumina, silica-alumina (25%  $\text{Al}_2\text{O}_3$ ), and cation-exchange resins (Dowex-50W, 2 and 8% DVB) are used as supports. The reaction is first order with respect to [IC] while the order with respect to  $[\text{H}_2\text{O}_2]$  was dependent on the initial concentration and the type of the catalyst used. At lower  $[\text{H}_2\text{O}_2]_0$  the order was first, which then decreases with increasing  $[\text{H}_2\text{O}_2]_0$ , finally reaching zero. This aspect is consistent with the formation of a colored peroxo-complex on the catalysts surface. The reactivity of catalysts is dependent on the redox potential of the metal ions, the amount of complex loaded per gram of dry catalyst, the type of ligand, and the support. Moreover, the reaction rate was strongly dependent on the pH of the medium, the cationic and anionic surfactants, and the irradiation with UV-light. The reaction is enthalpy controlled as confirmed from the isokinetic relationship. A reaction mechanism was proposed with the formation of free radicals as reactive intermediates.

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## 1. Introduction

As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants such as dyes have been recently developed. Fifteen percent of the total world production of dyes is lost during the dyeing process and is released in the textile effluent [1]. The release of that colored wastewater in the ecosystem is a dramatic source of esthetic pollution, and perturbation in aquatic life. Different techniques have been used for this purpose, e.g.

adsorption, oxidation, reduction, and electrochemical reactions. The oxidation of dyes has attracted much attention in recent years [2–7]. Indigo carmine (IC) is one of the oldest dyes and still one of the most important used. Its major industrial application is the dyeing of clothes (blue jeans) and other blue denim [8]. It has also been employed as redox indicator in analytical chemistry and as a microscopic stain in biology.

Several studies have been made on the oxidation kinetics of IC using peroxydisulfate, hypohalites, and *N*-haloarenesulfonamides agents [9–11]. The oxidation of IC by  $\text{H}_2\text{O}_2$  in the presence of some sulfur compounds such as sulfide, thioacetamide, thiourea, and thiosulphate has been investigated [12]. Moreover, the homogeneous catalytic activity of transition metal

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ions for the oxidation reaction of IC and their kinetic determination has been studied [9–12].

Recent investigations revealed that reactive dyes could be decolorized by advanced oxidation processes (AOPs). These ambient temperature processes refer to the generation of highly reactive hydroxyl radical that is aggressively and almost indiscriminately attacks all types of inorganic and organic pollutants found in wastewater [13–16]. Most of the AOPs comprise combinations of UV-light with  $\text{H}_2\text{O}_2$ ,  $\text{TiO}_2$ , or  $\text{O}_3$  [17].

Hydrogen peroxide is a powerful oxidant and environmental friendly since  $\text{H}_2\text{O}$  and  $\text{O}_2$  are the products of its reduction.  $\text{H}_2\text{O}_2$  itself is a moderate oxidizing agent towards most of the organic substrate [18]. However, activation of  $\text{H}_2\text{O}_2$  with a catalyst, UV-light, ultrasound or heat, lead to oxidation and degrade many organic compounds [19–25]. The basic concept of these systems is the decomposition of  $\text{H}_2\text{O}_2$  with the formation of free radical intermediates, especially the hydroxyl radical. This radical is capable of reacting with a variety of organic compounds leading to either partial or complete degradation of these compounds to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and inorganic ions. The degradation of various organic dyes and removal of their colors from industrial wastewater effluents using  $\text{H}_2\text{O}_2$  have been investigated [26–30].

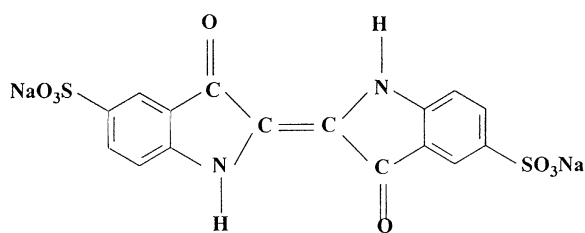
Heterogeneous catalytic systems eliminate the needs of adding soluble catalytic substances. Transition metal complexes supported on different surfaces such as metal oxides, resins, and mixed (Al-Cu) pillared clays were used as potentially active catalysts for the decomposition of  $\text{H}_2\text{O}_2$  and the oxidative degradation of organic contaminants and dyes [31–37].

The present work aims at studying the kinetics and mechanism of the oxidative degradation of IC with  $\text{H}_2\text{O}_2$  catalyzed by some supported transition metal complexes. This model system may be applicable to color removal in a textile wastewater stream.

## 2. Experimental

### 2.1. Materials

All chemicals were of high-grade quality and were used as received. Analytical grade hydrogen peroxide (30% w/v) was obtained from Merck and dilution was made as required. The initial concentration of  $\text{H}_2\text{O}_2$



Scheme 1.

was determined iodometrically using standard solution of sodium thiosulphate. IC (Scheme 1), sodium dodecyl sulphate (SDS), and cetyltrimethylammonium bromide (CTAB) were obtained from Aldrich and used as received.

Silica gel (150–230 mesh) was obtained from Baker and sieved through wire mesh sieves. The particles of the size 0.063–0.2 mm were collected and used as support. It has an estimated surface area of  $200 \text{ m}^2/\text{g}$  as determined by high-speed surface area analyzer (Shimadzu, model 2205). Alumina with particle size of 150 mesh and has surface area of  $150 \text{ m}^2/\text{g}$  was supplied from Polda Co. (Germany). Silica-alumina (25%  $\text{Al}_2\text{O}_3$ ) was supplied by Joseph Grossfield & Son Ltd. It has pore volume of  $0.80 \text{ ml/g}$ , average particle size of  $63 \mu\text{m}$ , and surface area of  $250 \text{ m}^2/\text{g}$ . Dowex-50 W cation-exchange resins with varying degrees of cross-linkage; 2 and 8% divinylbenzene (DVB) and of 20–50 and 50–100 mesh size, respectively, were used as well.

Inorganic supports were treated twice with 0.5 M HCl solution to eliminate metal ion contaminants that might present on the surface. The resins were also regenerated using 0.1 M HCl solution. Thereafter, all supports were washed several times with doubly distilled  $\text{H}_2\text{O}$  and finally the  $\text{Cl}^-$ -free samples were dried at  $100^\circ\text{C}$ . The cation-exchange capacity was determined by a batch method [38,39] and was found to be equal to 4.77 and  $4.17 \text{ meq H}^+/\text{g}$  of dry resin for 2 and 8% DVB, respectively.

### 2.2. Preparation of the catalysts

The ligands used were ammonia (amm), ethylenediamine (en), and methylamine (ma) while the metal ions used were Cu(II), Co(II), and Ni(II). The complex solutions were prepared from mixing 0.01 M aqueous metal chloride and 0.1 M aqueous solutions of the

Table 1

The color and pH changes of the different catalysts during the catalyzed oxidative reaction of IC using H<sub>2</sub>O<sub>2</sub>

Catalyst	Color and pH changes during the oxidation reaction				Complex (mmol/g)
	Color		pH		
	Before	After	Before	After	
S-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	Blue	Brown	7.0	5.73	4.0
S-[Ni(amm) <sub>6</sub> ] <sup>2+</sup>	Faint green	Faint green	7.37	6.59	46.0
S-[Co(amm) <sub>6</sub> ] <sup>2+</sup>	Pale violet	Brownish	7.40	6.68	0.96
S-[Cu(ma) <sub>4</sub> ] <sup>2+</sup>	Blue	Brown	7.75	6.92	4.50
R-[Ni(amm) <sub>6</sub> ] <sup>2+</sup>	Faint green	Faint green	7.25	6.98	41.4
R-[Co(amm) <sub>6</sub> ] <sup>2+</sup>	Blood red	Orange	6.70	6.53	3.80
R-[Cu(amm) <sub>6</sub> ] <sup>2+</sup>	Deep blue	Deep brown	7.21	6.86	38.5
S-[Cu(en) <sub>2</sub> ] <sup>2+</sup>	Faint violet	Brown	6.80	5.78	3.30
S-A-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	Faint blue	Brownish	7.41	6.67	39.5
A-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	Faint blue	Brownish	7.05	5.77	56.1

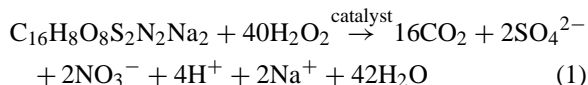
Abbreviations—S: silica, A: alumina, S-A: silica-alumina, R: resin (8% DVB, 50–100 mesh).

appropriate ligands. The catalysts were prepared from the addition of 5 g of dry support to an excess amount of known concentration of the metal complex solution prepared with the stoichiometry shown in Table 1. After equilibration, stirring for about 4 h, the catalyst was filtered, washed, and the excess amount of complex in the supernatant was determined spectrophotometrically at  $\lambda_{\max} = 600, 617.5, 570, 628,$  and  $510$  nm with extinction coefficient,  $\epsilon$ , equals 50, 50.5, 50.5, 10.8, and 780 l/mol cm for [Cu(amm)<sub>4</sub>]<sup>2+</sup>, [Cu(ma)<sub>4</sub>]<sup>2+</sup>, [Cu(en)<sub>2</sub>]<sup>2+</sup>, [Ni(amm)<sub>6</sub>]<sup>2+</sup>, and [Co(amm)<sub>6</sub>]<sup>2+</sup>, respectively. Thus, the amount of complex per gram of dry support was determined and is shown in Table 1.

### 2.3. Stoichiometry

In CO<sub>2</sub>-free doubly distilled H<sub>2</sub>O, 10<sup>-3</sup> M of IC was allowed to react with 0.5 M of H<sub>2</sub>O<sub>2</sub> in the presence of 1.0 g of catalyst. After complete color removal, the mixture was filtered and the unreacted H<sub>2</sub>O<sub>2</sub> was determined iodometrically. The complete oxidative degradation of IC has been established by Herrmann and co-workers. [40] and led to the conversion of the organic carbon into gaseous CO<sub>2</sub>, whereas nitrogen and sulfur heteroatoms are converted into inorganic ions such as nitrate/or ammonium and sulfate ions. In our system, the amount of CO<sub>2</sub> evolved from the reaction was captured by an aqueous solution of barium hydroxide and determined gravimetrically as precipitated barium carbonate and the amount of CO<sub>2</sub> was calculated as mentioned elsewhere [26,32]. The

results revealed that 60% of the dye carbon atoms are degraded and transformed to CO<sub>2</sub>. The difference between the observed and the expected quantities of CO<sub>2</sub> is probably due to the persistence of some intermediate products and to loss of volatile ones. The sulfate ions were determined gravimetrically by precipitating it as BaSO<sub>4</sub> using BaCl<sub>2</sub> solution [41]. The quantity of sulfate ions was lower than that expected from stoichiometry, which can be explained by adsorption of SO<sub>4</sub><sup>2-</sup> on the catalyst surface as previously indicated [40,42]. The total acid concentration in the mixture was determined by titration with sodium hydroxide and the concentration of HNO<sub>3</sub> was estimated by difference. Therefore, the stoichiometric equation can be written as:



### 2.4. Kinetic measurements

The kinetic measurements were performed with a Shimadzu UV-2100S spectrophotometer operating via a Shimadzu data acquisition system. The cell holder temperature of the spectrophotometer was held constant electronically with the aid of an attached Shimadzu temperature controller. For pH measurements, a Crison pH-meter digit-501 that had been calibrated prior to the measurements was used. The UV-lamp (Vilber Lourmat, 2 × 6 W, 254 nm tube) was used as a UV-light source.

In typical kinetic experiment a number of flasks (volume  $100\text{ cm}^3$ ) containing a definite quantity of catalyst together with  $17\text{ cm}^3$  of doubly distilled  $\text{H}_2\text{O}$  were placed in shaker water thermostat for 30 min. To each flask,  $3\text{ cm}^3$  of IC/ $\text{H}_2\text{O}_2$  mixture was added within about 3 s by micropipette and zero time was noted at half the addition point. At regular time intervals aliquot was withdrawn and the absorbance was recorded at  $\lambda_{\text{max}} = 610\text{ nm}$ ,  $\varepsilon = 16,365.1 \pm 150\text{ l/mol cm}$ . The absorbance of IC/ $\text{H}_2\text{O}_2$  solution was stable for several hours without any observable changes, which indicates that no reaction take place between IC and  $\text{H}_2\text{O}_2$  in the absence of the catalyst.

### 3. Results and discussion

An exhaustive kinetic study has been conducted on the oxidative degradation of IC by  $\text{H}_2\text{O}_2$  catalyzed by supported transition metal complexes. Before addition of the reactants (IC/ $\text{H}_2\text{O}_2$  mixture) to the catalyst, the pH of the medium containing catalyst/ $\text{H}_2\text{O}$  showed no remarkable changes with the transition metal complex or the support as shown in Table 1. However, with a given transition metal complex, a slight decrease in the pH of the medium was observed when the reaction comes to completion. This decrease in pH may

be attributed to the ionizing character of  $\text{H}_2\text{O}_2$  or the evolution of some acidic reaction products as can be seen in the stoichiometric equation. Similar changes in pH were reported earlier for the oxidative degradation of some azo dyes to  $\text{CO}_2$  and small fragments as final products [26,33,43] and for the decomposition reaction of  $\text{H}_2\text{O}_2$  in the presence of supported metal complexes [39,47]. Table 1 also shows the observed changes of the color of each catalyst during the course of reaction. These changes of the color may be ascribed to the formation of a peroxo-complex resulting from the reaction of  $\text{H}_2\text{O}_2$  with the supported metal complex as has been reported elsewhere [33,39,44,46]. This color persists as long as any residual amount of  $\text{H}_2\text{O}_2$  remained undecomposed.

When the solution of IC was mixed with  $\text{H}_2\text{O}_2$ , no observable change on the color was noticed. However, when the catalyst was introduced, the oxidative reaction was started and a gradual loss of the absorbance of IC was observed as shown in Fig. 1. The kinetic measurements were carried out under pseudo-first-order conditions with respect to [IC]. The observed rate constant,  $k_0$ , was determined from first-order kinetics plot,  $\ln A_t = \ln A_0 - k_0 w t$ , as shown in Fig. 2, where  $A_t$  is the absorbance at time =  $t$ ,  $A_0$  is the absorbance at  $t = 0$ , and  $w$  is the amount of the catalyst used. The  $k_0$  value per g of dry catalyst (pgdr) was determined

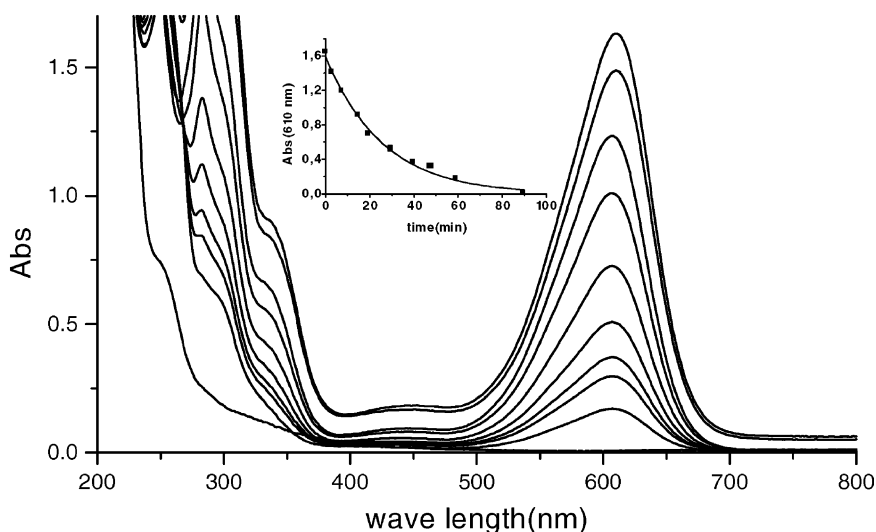


Fig. 1. The time-resolved absorption spectra during the reaction of  $10^{-4}\text{ mol/l}$  of IC with  $0.007\text{ mol/l}$  of  $\text{H}_2\text{O}_2$  in the presence of  $0.01\text{ g}$  of  $\text{S}[\text{Cu}(\text{amm})_4]^{2+}$  at  $30^\circ\text{C}$ .

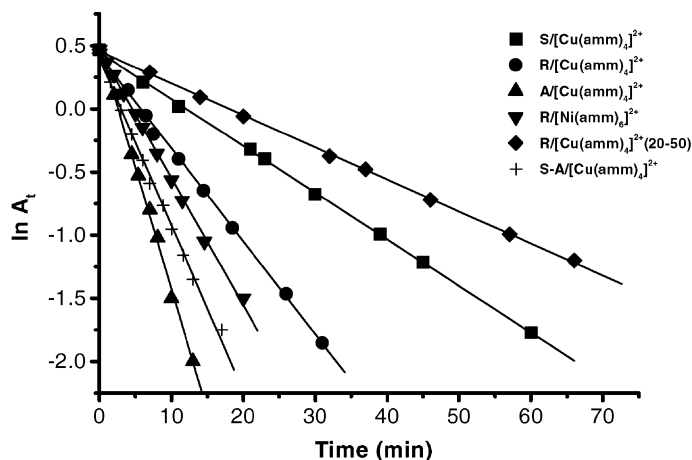


Fig. 2. First-order plot for the reaction of  $10^{-4}$  mol/l of IC with 0.007 mol/l of  $\text{H}_2\text{O}_2$  in the presence of 0.01 g of different catalysts at  $30^\circ\text{C}$ .

for all catalysts at different temperatures and used to estimate the activation parameters (Table 2). It is clear that the reaction of higher rate constant is associated with lower activation energy. This indicates that the IC was easily attacked by oxidizing agent. Table 2 also reveals that the activation process is enthalpy controlled since the enthalpy change is greater for the slower reaction. The same has been reported elsewhere [44,45]. Furthermore, the isokinetic relationship between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for all types of catalysts is depicted in Fig. 3. The slope “isokinetic temperature” was found to be

equal to 322 K, which is higher than the average experimental value, 305.5 K. This confirms our conclusion that the reaction is enthalpy controlled. The linear relation of Fig. 3. is also an evidence that the oxidative degradation of IC by  $\text{H}_2\text{O}_2$  in the presence of all catalysts followed the same reaction mechanism [48].

The kinetic experiments carried out at different initial concentrations of hydrogen peroxide,  $[\text{H}_2\text{O}_2]_0$ , revealed that the initial rate increased with increasing  $[\text{H}_2\text{O}_2]_0$ . As shown in Fig. 4, the rate of reaction has a first-order dependence on  $[\text{H}_2\text{O}_2]_0$  at lower

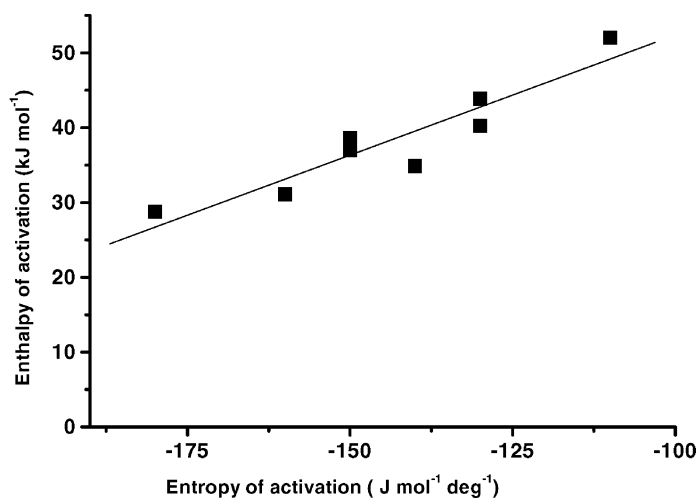


Fig. 3. Isokinetic relationship for the oxidative degradation of IC by  $\text{H}_2\text{O}_2$  catalyzed by supported transition metal complexes.

Table 2

The rate constant and the activation parameters for the oxidative degradation of IC by H<sub>2</sub>O<sub>2</sub> of 0.007 mol/l in the presence of 0.01 g of dry catalysts

Catalyst	Temperature (°C)	$k \times 10^2$ (s <sup>-1</sup> )	$E$ (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta G^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol K)
S-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	25	4.30				
	30	6.00	39.49	36.99	81.01	-150.0
	35	7.80				
	40	9.30				
<sup>a</sup> S-[Co(amm) <sub>6</sub> ] <sup>2+</sup>	25	8.66				
	30	14.1	42.84	40.3	79.86	-130.0
	35	16.2				
	40	20.7				
<sup>a</sup> S-[Ni(amm) <sub>6</sub> ] <sup>2+</sup>	25	6.60				
	30	9.12	46.46	43.92	80.66	-130.0
	35	11.6				
	40	16.5				
A-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	20	24.3				
	22	26.5	33.62	31.14	75.96	-160.0
	25	30.3				
	30	38.2				
S-A-[Co(amm) <sub>6</sub> ] <sup>2+</sup>	25	8.78				
	30	13.8	37.42	34.88	76.90	-140.0
	35	19.8				
	40	26.8				
R-[Cu(amm) <sub>4</sub> ] <sup>2+</sup>	25	10.4				
	30	13.0	41.24	38.66	82.39	-150.0
	35	16.3				
	40	22.9				
R-[Ni(amm) <sub>6</sub> ] <sup>2+</sup>	30	14.1				
	35	17.4	31.34	28.76	81.78	-180.0
	40	21.4				
	45	25.2				
R-[Co(amm) <sub>6</sub> ] <sup>2+</sup>	30	2.93				
	35	4.39	54.64	52.06	85.24	-110.0
	40	5.72				
	45	8.35				

<sup>a</sup> [H<sub>2</sub>O<sub>2</sub>] = 0.05 mol/l.

concentrations, while at higher [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> the order is decreased, reaching almost zero. This decreases of the order was consistent with the changes of the color of catalysts as seen in Table 1. The formation of these colors (peroxo-complex) was testified when H<sub>2</sub>O<sub>2</sub> was allowed to react with the catalysts in the absence of IC. This result is in good agreement with that reported elsewhere for the decomposition of H<sub>2</sub>O<sub>2</sub> using the supported transition metal complexes as a catalyst [34,46,47]. Furthermore, it has been reported that the formation of such colored species had an inhibi-

ing effect on the reaction rate of H<sub>2</sub>O<sub>2</sub> decomposition [46,47]. This inhibition was increased as the intensity of this color increased. The conclusion can be drawn from these discussion that the inhibiting effect of such color (peroxo-complex) is also extended to the oxidative reaction rate of IC. Therefore, the oxidation mechanism of IC should involved firstly an interaction between H<sub>2</sub>O<sub>2</sub> and the catalyst and an active species are formed and used as an oxidant for IC.

The dependence of the reaction rate on the initial concentration of IC, [IC]<sub>0</sub>, was investigated. As shown

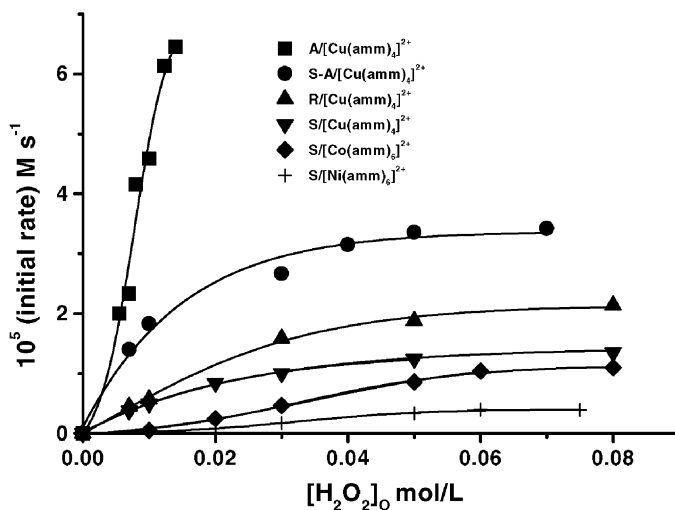


Fig. 4. Dependence of the initial reaction rate on the initial concentrations of  $\text{H}_2\text{O}_2$ , for their reaction with  $10^{-4}$  mol/l of IC in the presence of 0.01 g of different catalyst at  $30^\circ\text{C}$ .

in Fig. 5, the initial rate has a first-order dependence on  $[\text{IC}]_0$  at lower concentrations. However, with increases of  $[\text{IC}]_0$  the order of reaction decreases and almost a limiting rate was reached at higher concentrations. The reaction rate increased with increasing the amount of catalysts.

As can be seen in Figs. 2 and 4, the reaction rate is strongly dependent on the type of metal ion, lig-

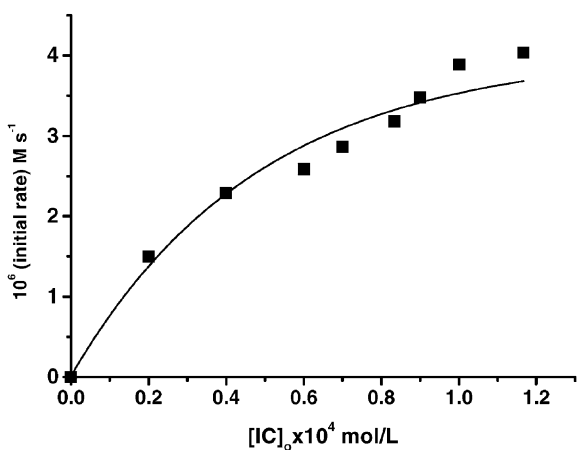


Fig. 5. Dependence of the initial reaction rate on the initial concentration of IC,  $[\text{IC}]_0$ , for its reaction with 0.007 mol/l of  $\text{H}_2\text{O}_2$  in the presence of 0.01 g of  $\text{S}-[\text{Cu}(\text{amm})_4]^{2+}$  catalyst at  $30^\circ\text{C}$ .

and, and the support. The effect of metal ions on the reaction rate followed the order:  $\text{S}-[\text{Cu}(\text{amm})_4]^{2+} > \text{S}-[\text{Co}(\text{amm})_6]^{2+} > \text{S}-[\text{Ni}(\text{amm})_6]^{2+}$  with rate constant of 0.06, 0.026, and  $0.014 \text{ s}^{-1}$  (pgdr), respectively. This order of rate constant can be ascribed to the following effects: (i) the difference in the redox potential of these metal ions, which has the value, +0.337, -0.277, and -0.257 V for Cu(II), Co(II), and Ni(II), respectively. The catalytic activity of these complexes towards  $\text{H}_2\text{O}_2$  decomposition was found to follow the same order [49,50]; (ii) the formation constant of these complexes, which has the value,  $1.1 \times 10^{13}$ ,  $5.5 \times 10^8$ , and  $1.3 \times 10^5$  for  $[\text{Cu}(\text{amm})_4]^{2+}$ ,  $[\text{Ni}(\text{amm})_6]^{2+}$ , and  $[\text{Co}(\text{amm})_6]^{2+}$ , respectively [51]; and (iii) the amount of complex loaded per gram of catalyst, which has the order:  $[\text{Ni}(\text{amm})_6]^{2+} > [\text{Cu}(\text{amm})_4]^{2+} > [\text{Co}(\text{amm})_6]^{2+}$  as seen in Table 1. Therefore, it is clear that the order of the former one is in good agreement with the order of the rate constants of these complexes, which means that the redox potential of metal ions is the key factor of the catalytic activity of these complexes towards the oxidation of IC. On the other hand, when the support was changed to the cation-exchange resin (8% DVB, 50–100 mesh), the reactivity of the complexes followed the order:  $\text{R}-[\text{Ni}(\text{amm})_4]^{2+} > \text{R}-[\text{Cu}(\text{amm})_4]^{2+} > \text{R}-[\text{Co}(\text{amm})_4]^{2+}$  with rate constant of 0.146, 0.130, and  $0.03 \text{ s}^{-1}$  (pgdc), respec-

tively. This order is consistent with the amount of the loaded complex of 41.4, 38.53, 3.8 mmol/g, respectively. The change of the rate constant with changing the support indicates that the type of surface play a role in the catalytic activity of the complex. Accordingly, the higher rate constant obtained with the cation-exchange resin clearly indicates that it is more preferable than the inorganic supports. This can be ascribed to its capability to adsorb higher amount of complex or to their organic matrix. But from the application point of view, it is recommended to use the inorganic supports due to their higher thermal stability. Furthermore, the effect of cross-linkage and the mesh size of resins have been investigated. It was found that the smaller the mesh size, the lower was the reaction rate. The values of 0.13 and  $0.042\text{ s}^{-1}$  (pgdc) have been obtained for R-[Cu(amm)<sub>4</sub>]<sup>2+</sup>, 8% DVB of 50–100 mesh and 20–50 mesh, respectively. Moreover, when the cross-linkage of resins was varied from 8% DVB to 2% DVB the higher rate constant is obtained.

The effect of the surface type was also investigated using [Cu(amm)<sub>4</sub>]<sup>2+</sup> complex supported on alumina, silica-alumina (25% Al<sub>2</sub>O<sub>3</sub>), and silica. The dependence of the reaction rate on the supporting surface followed the order: alumina > silica-alumina > silica. This order may be ascribed to the difference in the amount of the complex loaded per g of support, which has the value; 56.07, 39.53, and 4.0 mmol/g, respectively. In general, the amount of adsorbent on the various solids has been correlated with the point of zero charge (pzc) of the surface, which is equals 9.1, 8.5, and 1.9 for alumina, silica-alumina, and silica, respectively [40]. This reveals that the adsorption of the complex requires an electrostatic interaction between the complex and the hydroxyl groups on the supporting surface. Therefore, the difference in the adsorption mode of the surface produce changes in the amount of the complex.

Since the reactivity of transition metal complex depends on the nature and the specific chemical properties of the metal ion and the ligand. The dependence of the reaction rate on the type of ligand followed the order: S-[Cu(ma)<sub>4</sub>]<sup>2+</sup> > S-[Cu(amm)<sub>4</sub>]<sup>2+</sup> > S-[Cu(en)<sub>2</sub>]<sup>2+</sup> with rate constant of 0.225, 0.164, and  $0.048\text{ s}^{-1}$ , respectively. This order agrees with the amount of complex (pgdc) and the pH of the medium before introducing IC as shown in Table 1.

### 3.1. Effect of pH

The effect of pH on the reaction rate was studied using phosphate buffer (0.067 mol/l) of 5.5–11 range and a few drops of NaOH were added to obtain higher pH values. The pK<sub>a</sub> value of IC was determined from the pH dependence of electronic absorption spectra of dilute IC solution and was equal to 12.3. The pK<sub>a</sub> of H<sub>2</sub>O<sub>2</sub> known from literature and equal to 11.6 [52]. The reaction rate exhibited a slow and almost constant rate in acidic and neutral mediums while in strong alkaline medium a sharp increase and finally attained limiting value is obtained (Fig. 6). This trend of reaction rate can be explained as follows: (i) The deprotonation of H<sub>2</sub>O<sub>2</sub> in highly alkaline medium, which should increased the decomposition rate of H<sub>2</sub>O<sub>2</sub> since the formation of the peroxy-complex is more facile [35,53,54]. Thus, the rate of the formation of the oxidizing species required for the oxidation of IC increased. (ii) The deprotonation of imine groups of IC. The effect of the former seems to be more pronounced when the pK<sub>a</sub> values of H<sub>2</sub>O<sub>2</sub> and IC are compared.

### 3.2. Effect of surfactants

The effect of both the anionic and cationic surfactants in the reaction rate was investigated using SDS and CTAB. In the presence of SDS no changes in the absorbance at 610 nm was observed even above the critical micelle concentration (cmc) ( $8 \times 10^{-3}$  mol/l). This indicates that there is no interaction between IC and SDS, which may be ascribed to that both IC and SDS have the sulfonate groups. Fig. 7 shows the decrease of the reaction rate with increasing [SDS]. This decrease may be attributed to: (i) the blocking of the positively active sites of the catalyst by the adsorbed anionic SDS aggregates [33] and (ii) the increases of the viscosity of reaction medium coming along with the formation of micelles. The former may reduce the rate of the interaction between H<sub>2</sub>O<sub>2</sub> and the catalyst, reducing the formation of active species responsible for the oxidation of IC, while the latter may diminish the diffusion rate and the efficiency of the reactants. Eventually, both factors should decrease the oxidative rate of IC.

The addition of the cationic surfactant, CTAB, showed two effects: (i) below cmc ( $9 \times 10^{-4}$  mol/l) the absorbance of IC was shifted to  $\lambda_{\text{max}} = 566\text{ nm}$  and



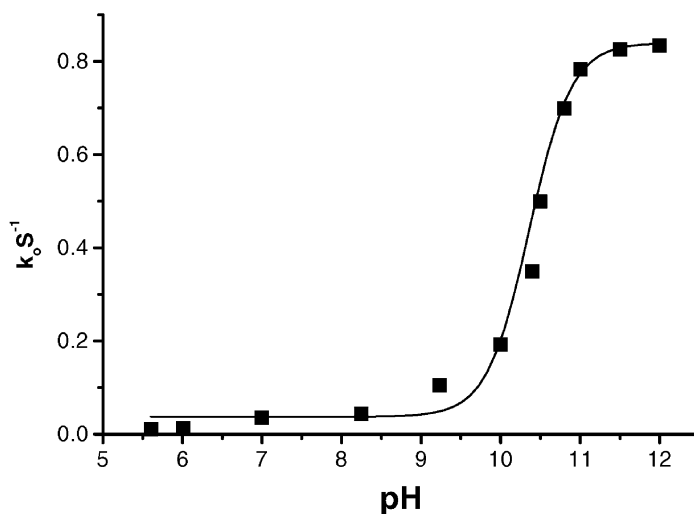


Fig. 6. Variation of the rate constant with pH for the reaction of  $10^{-4}$  mol/l of IC with 0.007 mol/l of  $\text{H}_2\text{O}_2$  in the presence of 0.01 g of  $\text{S-}[\text{Cu}(\text{amm})_4]^{2+}$  at  $30^\circ\text{C}$ .

(ii) above cmc the  $\lambda_{\text{max}}$  of IC does not change but the  $\epsilon$  value decreased to 9717 l/mol cm. The association process of dye-surfactant was attributed to the following three steps: (i) The formation of  $(\text{DS})^0$  species at low surfactant concentrations, which is mainly governed by electrostatic long-range and dispersive short-range attractive forces. (ii) With increasing surfactant concentration a free surfactant ion binds to a neutral associate, forming a  $(\text{DS}_2)^+$  species, where hydrophobic interactions may play an important role. (iii) The formation of more complex species such

as  $(\text{DS}_3)^{2+}$  at higher surfactant concentration. The same has been reported for the association of acid orange dye and cetylpyridinium chloride [55,56]. Thus, based on these discussion the red shift of  $\lambda_{\text{max}}$  below the cmc can be ascribed to the formation of a neutral species,  $[\text{IC}(\text{CTAB})_2]^0$ , taking into account that each molecule of IC contains two sulfonate groups that need two molecules of CTAB to be neutralized. The decrease in the  $\epsilon$  value may also attributed to the formation of  $[\text{IC}(\text{CTAB})_3]^+$  species. Fig. 8 shows the

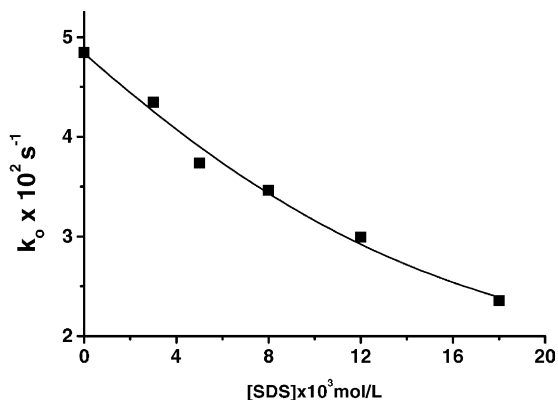


Fig. 7. Variation of rate constant with  $[\text{SDS}]$  for the reaction of  $10^{-4}$  mol/l of IC with 0.007 mol/l of  $\text{H}_2\text{O}_2$  in the presence of 0.01 g of  $\text{S-}[\text{Cu}(\text{amm})_4]^{2+}$  at  $30^\circ\text{C}$ .

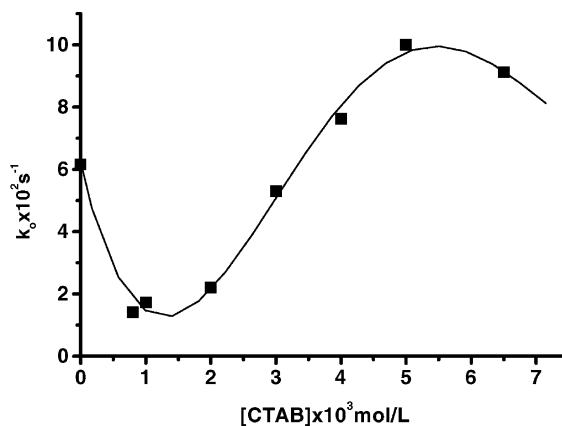


Fig. 8. Variation of rate constant with  $[\text{CTAB}]$  for the reaction of  $10^{-4}$  mol/l of IC with 0.007 mol/l of  $\text{H}_2\text{O}_2$  in the presence of 0.01 g of  $\text{S-}[\text{Cu}(\text{amm})_4]^{2+}$  at  $30^\circ\text{C}$ .

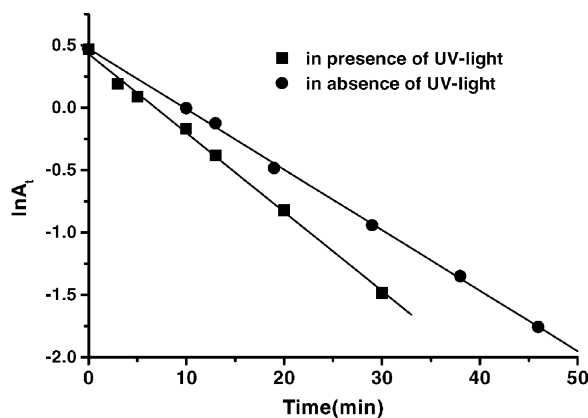


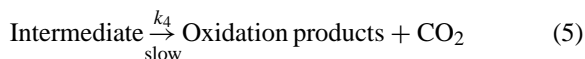
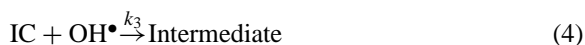
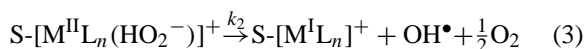
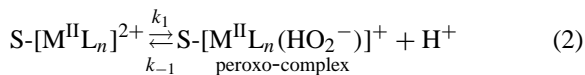
Fig. 9. The effect of irradiation,  $\lambda = 254$  nm, on the reaction between IC of  $10^{-4}$  mol/l and  $\text{H}_2\text{O}_2$  of 0.007 mol/l in the presence of 0.01 g of  $\text{S}[\text{Cu}(\text{amm})_4]^{2+}$  at  $30^\circ\text{C}$ .

dependence of the reaction rate on the [CTAB]. The reaction rate showed minimum value at cmc, then reaching a maximum at almost  $5 \times 10^{-3}$  mol/l. This behavior could be explained in term of the formation of the aforementioned neutral and charged associated species. The neutral species has an inhibiting effect on the reaction rate while the formation of charged species results in an enhancement. These results are in good agreement with that found for the oxidation of *p*-aminodiphenylamine with peroxodisulfate ion [57].

### 3.3. Reaction mechanism

The involvement of free radical species in the reaction mechanism of  $\text{H}_2\text{O}_2$  with transition metal complexes was confirmed earlier by ESR spectroscopy using spin trapping [58,59]. Furthermore, the radical scavengers, *tert*-butanol and chromogen, 2,2-azino-bis(3-ethylbenzthiazoline)-6-sulfate diammonium salt were used as probe, confirming the generation of the radical species [44–46]. It is well established that the irradiation of  $\text{H}_2\text{O}_2$  by UV-light source leads to the formation of  $\text{OH}^\bullet$  radical [60–63]. Therefore, when our reaction mixture was exposed to the UV-light of  $\lambda = 254$  nm, an enhancement of ca. 20% in the reaction rate was observed (Fig. 9). The conclusion can be drawn that the irradiation of reaction increased the amount of radical species and thus increased the reaction rate.

Based on the these experimental results and discussion the following mechanism is proposed and implies an interaction between  $\text{H}_2\text{O}_2$  and the supported transition metal ion complexes with the formation of highly energetic and reactive oxidizing agent, hydroxyl radicals. The latter attacks the IC forming active intermediate, which then decomposes in the rate-determining step giving the final oxidation products as follows:



From Eq. (2) the concentration of the peroxo-complex is given by:

$$[\text{S}[\text{M}^{\text{II}}\text{L}_n(\text{HO}_2^-)]^+] = K_1 \frac{[\text{S}[\text{M}^{\text{II}}\text{L}_n]^{2+}][\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad (8)$$

where  $K_1 = k_1/k_{-1}$

Applying steady-state approximation to the determination of  $[\text{OH}^\bullet]$  and  $[\text{Intermediate}]$ :

$$\begin{aligned} \frac{d[\text{HO}^\bullet]}{dt} &= k_2[\text{S}[\text{M}^{\text{II}}\text{L}_n(\text{HO}_2^-)]^+] - k_3[\text{IC}][\text{HO}^\bullet] \\ &\quad - k_5[\text{S}[\text{M}^{\text{I}}\text{L}_n]^+][\text{HO}^\bullet] = 0 \end{aligned} \quad (9)$$

Assuming that  $\text{S}[\text{M}^{\text{II}}\text{L}_n(\text{HO}_2^-)]^+ = \text{S}[\text{M}^{\text{I}}\text{L}_n]^+$ , and by substituting from Eq. (8) in Eq. (9), we get:

$$[\text{OH}^\bullet] = \frac{k_2 K_1 [\text{S}[\text{M}^{\text{II}}\text{L}_n]^{2+}][\text{H}_2\text{O}_2]}{k_3 [\text{IC}][\text{H}^+] + k_5 K_1 [\text{S}[\text{M}^{\text{II}}\text{L}_n]^{2+}][\text{H}_2\text{O}_2]} \quad (10)$$

and:

$$\begin{aligned} \frac{d[\text{Intermediate}]}{dt} &= k_3 [\text{IC}][\text{OH}^\bullet] - k_4 [\text{Intermediate}] \\ &= 0 \end{aligned} \quad (11)$$

Thus, by substituting from Eq. (10) in Eq. (11) we get:

$$\begin{aligned} & \text{[Intermediate]} \\ &= \frac{k_2 k_3 K_1 [\text{IC}] [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]}{k_3 k_4 [\text{IC}] [\text{H}^+] + k_4 k_5 K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]} \end{aligned} \quad (12)$$

The rate-determining step, Eq. (5), expresses the rate equation and is given by:

$$\text{Rate} = k_4 [\text{Intermediate}] \quad (13)$$

Thus, by substitution from Eq. (12) in Eq. (13) we get:

$$\text{Rate} = \frac{k_2 k_3 K_1 [\text{IC}] [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]}{k_3 [\text{IC}] [\text{H}^+] + k_5 K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]} \quad (14)$$

Expressing the initial concentration of both reactants,  $[\text{H}_2\text{O}_2]_0$  and  $[\text{IC}]_0$ :

$$[\text{H}_2\text{O}_2]_0 = [\text{H}_2\text{O}_2] + [\text{S}-[\text{M}^{\text{II}}\text{L}_n(\text{HO}_2^-)]^+] + [\text{OH}^\bullet] \quad (15)$$

Thus, substituting from Eq. (8) and Eq. (10) and assuming that:

$$\begin{aligned} k_3 [\text{IC}] [\text{H}^+] &\ll k_5 K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2] \\ [\text{H}_2\text{O}_2] &= \frac{[\text{H}^+] \{k_5 [\text{H}_2\text{O}_2]_0 - k_2\}}{k_5 [\text{H}^+] + k_5 K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}]} \end{aligned} \quad (16)$$

Also,

$$[\text{IC}]_0 = [\text{IC}] + [\text{Intermediate}] \quad (17)$$

Substituting Eq. (12) and assuming that:

$$\begin{aligned} k_3 k_4 [\text{IC}] [\text{H}^+] &\ll k_4 k_5 K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2] \\ [\text{IC}] &= \frac{[\text{IC}]_0 k_4 k_5}{k_4 k_5 + k_2 k_3} \end{aligned} \quad (18)$$

From Eqs. (14), (16) and (18), the rate is given by:

$$\begin{aligned} \text{Rate} &= \frac{k_2 k_3 k_4 k_5 K_1 [\text{IC}]_0 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]_0}{k_3 k_4 k_5 [\text{IC}]_0 \{[\text{H}^+] + K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}]\} + K_1 k_5} \\ &\quad \times [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]_0 \{K_1 k_5 k_4 + k_2 k_3\} \end{aligned}$$

By assuming that  $k_4 k_5 K_1 \gg k_2 k_3$ , we get:

$$\text{Rate} = \frac{k_2 k_3 K_1 [\text{IC}]_0 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]_0}{k_3 [\text{IC}]_0 \{[\text{H}^+] + K_1 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}]\} + K_1^2 k_5 [\text{S}-[\text{M}^{\text{II}}\text{L}_n]^{2+}] [\text{H}_2\text{O}_2]_0} \quad (19)$$

Eq. (19) shows that at lower  $[\text{IC}]_0$ , the first term in the denominator becomes very small compared to the second and can be neglected. Therefore, the rate attains a first-order dependence on  $[\text{IC}]_0$ . However, with increasing  $[\text{IC}]_0$ , the rate decreases and reaches a limiting rate at higher concentrations. This equation also predicts that reaction rate is a first-order dependence on  $[\text{H}_2\text{O}_2]_0$  at low concentrations. With increasing concentration of  $\text{H}_2\text{O}_2$ , the rate decreases and attains a limiting value at high concentrations (Fig. 4). The equation also explains the pH dependence shown in Fig. 6. At higher pH,  $[\text{H}^+]$  can be omitted from the denominator and the rate becomes independent on pH.

#### 4. Conclusions

The heterogeneous catalytic degradation of indigo carmine with  $\text{H}_2\text{O}_2$  catalyzed by supported transition metal complexes has been successfully demonstrated. These catalysts are simple, inexpensive, and easily prepared. In addition to a prompt removal of the color, catalytic oxidation leads simultaneously to the degradation of the dye with almost complete mineralization of carbon, nitrogen, and sulfur heteroatoms. The catalytic activity of supported complexes depended on certain factors such as the redox potential of metal ions, ligand, the amount of complex loaded per g of catalyst, and the supporting surface. All these factors are working and the net effect depends on which factor is the more pronounced. The ensemble of these results clearly suggests that this heterogeneous catalytic reaction may be envisaged as a method for treatment of colored wastewater in textile industries using a simple and inexpensive system.

#### References

- [1] H. Zollinger, Color Chemistry. Synthesis, Properties and Applications of Organic Dyes and Pigments, 2nd revised ed. VCH, New York, 1991.
- [2] K. Bredereck, C. Schumacher, Dyes and Pigments 94 (1993) 45.
- [3] T. Omura, Y. Kayane, Y. Tezuka, Dyes and Pigments 20 (1992) 227.
- [4] R. Ohura, A. Katayama, T. Takagishi, Textile Res. J. 61 (1991) 242.
- [5] J. Oakes, P. Gratton, R. Clark, I. Wilkes, J. Chem. Soc. Perkin Trans 2 (1998) 2569.

- [6] G.R. Hodges, J.R.L. Smith, J. Oakes, *J. Chem. Soc. Perkin Trans 2* (1999) 1943.
- [7] J. Oakes, P. Gratton, *J. Chem. Soc. Perkin Trans 2* (1998) 1857.
- [8] F.J. Green (Ed.), *The Sigma Aldrich Handbook of Stains, Dyes and Indicators* Aldrich Chemical, Milwaukee, WI, 1990, pp. 403–406.
- [9] P.V. Subba Rao, P.S.N. Murty, R.V.S. Murty, B.A.N. Murty, *J. Indian Chem. Soc.* LV (1978) 1280.
- [10] Puttaswamy, D.S. Mahadevappa, N.M.M. Gowad, *Inter. J. Chem. Kinet.* 23 (1991) 27.
- [11] Puttaswamy, D.S. Mahadevappa, K.S. Rangappa, *Bull. Chem. Soc. Jpn.* 62 (1989) 3343.
- [12] H. Weisz, S. Pantel, J. Marquardt, *Anal. Chim. Acta* 143 (1982) 177.
- [13] M.S. Bahorsky, *Textiles Water Environ. Res.* 69 (1997) 658.
- [14] A.M. Marechal, Y.M. Slokar, T. Taufer, *Dyes Pigments* 33 (1997) 281.
- [15] I. Arslan, I.A. Balcioglu, D.W. Bahnemann, *Appl. Catal. B: Environ.* 26 (3) (2000) 193.
- [16] I. Arslan, I.A. Balcioglu, *Dyes Pigments* 43 (1999) 95.
- [17] W.H. Glaze, J.W. Kang, D.H. Chapin, *Oz. Sci. Eng.* 9 (1987) 335.
- [18] P. Forlano, J.A. Olable, J.F. Magallans, M.A. Blesa, *Can. J. Chem.* 75 (1997) 9.
- [19] V.I. Parvulescu, D. Dumitru D, G. Poncelet, *J. Mol. Catal. A* 140 (1999) 91.
- [20] O.P. Pestunova, G.L. Elizarova, V.N. Parmon, *Russ. J. Appl. Chem.* 72 (1999) 1209.
- [21] D.D. Dionysiou, M. Suidan, E. Bekou, I. Baudin, J.M. Laine, *Appl. Catal. B: Environ.* 26 (2000) 153.
- [22] D. Drijvers, H.V. Langenhove, M. Beckers, *Water Res.* 33 (1999) 1187.
- [23] G. Centi, S. Perathoner, T. Torre, M.G. Verduna, *Catal. Today* 55 (2000) 61.
- [24] J.T. Spadaro, M.H. Gold, V. Renganathan, *Appl. Environ. Microbiol.* 58 (1992) 2397.
- [25] A. Paszezynski, M.B. Pasti-Grigsby, S. Goszczynski, R.L. Crawford, D.L. Crawford, *Appl. Environ. Microbiol.* 58 (1992) 3598.
- [26] J.T. Spadaro, L. Isabelle, V. Renganathan, *Environ. Sci. Technol.* 28 (1994) 1389.
- [27] M.H. Robbins, R.S. Drago, *J. Catal.* 170 (1997) 295.
- [28] S.T. Chen, D.K. Steven, G.Y. Kang, *Water Res.* 33 (1999) 3657.
- [29] C. Galindo, A. Kalt, *Dyes and Pigments* 42 (1999) 199.
- [30] C.S. Poon, Q. Huang, P.C. Fung, *Chemosphere* 38 (1999) 1005.
- [31] J. Barrault, C. Bouchoule, K. Echachoui, N. Frinsrasra, J. Trabelsi, F. Bergaya, *Appl. Catal. B: Environ.* 15 (1998) 269.
- [32] I.A. Salem, *Appl. Catal. B: Environ.* 28 (2000) 153.
- [33] I.A. Salem, M.S. El-Maazawi, *Chemosphere* 41 (2000) 1173.
- [34] I.A. Salem, *Chemosphere* 44 (2001) 1109.
- [35] I.A. Salem, *Trans. Met. Chem.* 25 (2000) 599.
- [36] R.L. Valentine, H.C.A. Wang, *J. Environ. Eng.* 124 (1998) 305.
- [37] M. Bressan, N.D. Alessandro, L. Liberatore, *Proceedings of the First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Italy, Environ. Abstr.* 98-13078 (1998) 433.
- [38] M.Y. El-Sheikh, F.M. Ashmawy, I.A. Salem, A.B. Zaki, *Z. Phys. Chem. (Leipzig)* 268 (1987) 595.
- [39] M.A. Salem, I.A. Salem, A.H. Gemeay, *Inter. J. Chem. Kinet.* 26 (1994) 1055.
- [40] M. Vautier, C. Guillard, J.M. Herrmann, *J. Catal.* 201 (2001) 46.
- [41] G.H. Jeffergam, J. Bassett, J. Mendham, R.G. Denney, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th ed., 1989, pp. 490–493.
- [42] J.M. Herrmann, C. Guillard, M. Arguello, A. Agüera, A. Tejedor, L. Piedra, A. Fernandez-Alba, *Catal. Today* 54 (1999) 353.
- [43] A. Mills, R.H. Davies, D. Worsly, *Chem. Soc. Rev.* 22 (1993) 417.
- [44] I.A. Salem, *Inter. J. Chem. Kinet.* 26 (1994) 341.
- [45] M.A. Salem, A.H. Gemeay, *Monat. Für Chemie.* 131 (2000) 117.
- [46] A.H. Gemeay, M.A. Salem, I.A. Salem, *Collo. and Surf. A* 117 (1996) 245.
- [47] A.H. Gemeay, *Collo. and Surf. A* 116 (1996) 277.
- [48] R.G. Wilkins, *The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes*, Allyn and Bacon, Boston, MA, 1974, p. 101.
- [49] M.Y. El-Sheikh, A.M. Habib, A.H. Gemeay, A.B. Zaki, J. Bargon, *J. Chim. Phys.* 89 (1992) 2057.
- [50] M.Y. El-Sheikh, F.M. Ashmawy, I.A. Salem, A.B. Zaki, *Z. Phys. Chem. (Leipzig)* 269 (1988) 126.
- [51] H.R. Petrucci, W.S. Harwood, *General Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1997, pp. D-3, A27.
- [52] I.I. Moiseev, *J. Mol. Catal. A* 127 (1997) 1.
- [53] F.M. Ashmawy, M.Y. El-Sheikh, I.A. Salem, A.B. Zaki, *Trans. Met. Chem.* 12 (1987) 51.
- [54] I.A. Salem, R.I. Elhag, K.M.S. Khalil, *Trans. Met. Chem.* 25 (2000) 260.
- [55] B. Simoncic, *J. Span, Dyes and Pigments* 46 (2000) 1.
- [56] A.H. Gemeay, *Dyes and Pigments* 54 (3) (2002) 1102.
- [57] M.Y. El-Sheikh, M.A. Salem, A.A. Ismail, A.B. Zaki, *J. Phys. Org. Chem.* 6 (1993) 609.
- [58] T. Ozawa, A. Hanaki, *J. Chem. Soc. Chem. Commun.* (1991) 330.
- [59] T. Ozawa, F. Takazawa, H. Goto, A. Hanaki, *Nippon Kagaku Zasshi* (1988) 459.
- [60] P.C. Selvaraj, V. Mahadevan, *J. Mol. Catal. A* 120 (1997) 47.
- [61] E. Finkelstein, G.M. Rosen, E.J. Rauckman, *J. Am. Chem. Soc.* 102 (1980) 4994.
- [62] I.A. Alaton, I.A. Balcioglu, D.W. Bahneman, *Water Res.* 36 (2002) 1143.
- [63] D. Georgiou, P. Melids, A. Aivasidis, K. Gimouhopoulos, *Dyes and Pigments* 54 (2002) 69.