

Utilization of copper plating effluents in the degradation of the dye Sanodure Green in the presence of H_2O_2

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Oxidative degradation of metal complex dye Sanodure Green (SG) in the presence of H_2O_2 and nanostructured catalyst CuO prepared from copper plating effluents has been investigated. The activity of the CuO catalyst in the oxidative degradation reaction depended on the SG concentration, reaction time and temperature. The reaction followed a pseudo-first order kinetic model, and the rate constant was highly dependent on the increase in temperature, but only slightly on the SG concentration. Thermodynamic studies have shown that the degradation reaction of SG is endothermic. The use of copper plating effluents for the preparation of nanostructured catalyst CuO makes it possible to avoid the accumulation of difficult-to-recycle copper oxide sludge formed during effluent neutralization, and to manage copper plating and aluminum dyeing effluents more economically.

Keywords: copper plating wastewater, nanostructured catalyst, metal complex dye, oxidative degradation

INTRODUCTION

The major polluters of hazardous for environment copper (II) are such industries as smelting, surface finishing, electroplating, electrolysis, electric appliances and electric boards/circuits manufacturing as well as agriculture sector (fertilizers, pesticides) [1–3]. Copper ions in wastewater after plating operations are usually found at high concentrations. For instance, the concentration of copper in pyrophosphate copper plating wastewater is around 50 mg L^{-1} and the corresponding pH value is about 7. The direct discharge of high copper-contaminated wastewater into the water body causes serious harm to the ecological environment from the aspect of copper bioaccumulation, non-biodegradability and toxicity [4–7]. The permissi-

ble limit of copper ions stated by the World Health Organization in drinking water should not exceed 2 mg/l [6], therefore the copper-contaminated wastewater must be treated before discharging it to the environment [7]. Although many methods for copper removal from industrial wastewater including chemical precipitation, ion exchange and adsorption, membrane filtration, flotation, electrochemical treatments, coagulation/flocculation, biological treatments are created [8–12], but among them the precipitation methods of copper oxide nanostructures are more advantageous due to less energy and temperature requirements and feasible low-cost [13, 14]. However, chemical precipitation of copper oxide can produce a large amount of sludge to be treated with great difficulties [15]. It is therefore important to use the obtained copper sludge as economically as possible. One way to achieve this is to obtain $CuO/CuOH_2$

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nanostructures, which have been found to be effective as catalysts for the elimination of organic contaminants, including dyes, from wastewater [16].

Since wastewater from galvanic processes is contaminated not only with metals but may contain some organic matters including dye, methods are being developed for the removal of organic and inorganic contaminants together [17]. For example, the green and simple approach was successfully developed to prepare CuO nanosheets from simulated copper waste effluents and used as efficient Fenton-like recyclable catalyst with assistance of visible light irradiation for complete degradation of phenols [12, 17].

Coloured metal surfaces are used in a decorative application as well as for technical purposes. Organic dyes generally get into plating wastewater from the anodized metal surfaces dyeing procedure. Anodic films are most commonly applied to protect aluminum alloys [18], although processes also exist for other metals, for example, titanium [19], zinc [20], magnesium [21] and niobium [22]. The number of dye colours for anodized aluminum varies according to the base alloy. The most common colours in industry, due to them being relatively cheap, are yellow, green, blue, black, orange, purple and red. For the dyeing of aluminum mono-azo and poly-azo, metal complex dyes are used [23, 24]. When the dyeing 'activity' reaches a value of 85%, the dye bath must be replaced whereas dyes present in wastewater need additional disposal. Although coloured with organic dye anodized aluminum is considered one of the most usable in various decorative products, today the removal of dye from wastewater or spent dyeing solutions still follow the traditional textile dye removal technology. One of the decisive factors behind the process of wastewater treatment is that the metal and textile dyeing types are different [18].

Many chemical and physical methods (coagulation, precipitation, filtration, membrane separation, electrodialysis, photochemical, oxidative degradation, biodegradation and adsorption) have been used for the removal of dyes from wastewaters [25]. Nevertheless, the advanced oxidation processes (AOPs) are the most effective technology for the degradation of various organic pollutants such as aromatic compounds, dyes, pharmaceutical compounds, and pesticides present in industrial wastewater [26–29]. Usually AOPs include ozone oxidation, supercritical water oxidation, wet air oxidation, Fenton oxidation

reaction (homogeneous and heterogeneous) and catalytic oxidation. AOPs result in the production of hydroxyl radicals (HO•) in the presence of a catalyst (metal or metal oxide nanostructures), which oxidize organic pollutants to form CO₂, H₂O or some less toxic inorganic small molecules [29]. The elements with multiple redox states (iron, chromium, cerium, copper, cobalt, manganese and ruthenium) have been suggested for hydrogen peroxide (H₂O₂) activation in neutral/alkaline conditions in both homogeneous and heterogeneous reaction conditions [30]. Recently, solid wastes from various industrial processes were tested as catalysts for hydrogen peroxide activation. The iron-containing wastes from steel, goldmine as low-cost catalyst instead of iron salts reduce the cost of wastewater with methyl orange treatment keeping reasonable efficiency [31–33].

In conclusion, it is still important to study and improve known methods and to develop combined methods using industrial wastes for the removal of organic and inorganic pollutants in order to avoid serious environmental problems, including secondary pollution. The purpose of this study was to prepare the nanostructured catalyst from simulated copper plating effluent and evaluate their efficiency in the oxidative degradation of organic pollutant, the hazardous metal complex Sanodure green LWN dye (SG).

2. EXPERIMENTAL

Materials and methods

Analytical grade copper sulphate (CuSO₄ · 5H₂O), sodium hydroxide (NaOH), hydrochloric acid (HCl), citric acid and H₂O₂ (35 wt%) were supplied from Thermo Fisher GmbH (Alfa Aesar, Germany).

Sanodure green LWN (SG) dye for anodized aluminum ascribable to the chemical family of azo dyestuff/chromium complex anionic dye (RSO₃⁻) was obtained from Clariant International Ltd., Switzerland.

The SG dye has been characterized according to the FTIR spectrum (Fig. 1). The small peak at 737 cm⁻¹ shows Cr–O group, which is inherent by chromium complex compounds; the band at 3307 is due to O–H stretching; the bands at 1145 and 1026 belong to stretching vibrations of sulfonate groups; the bands due to the aromatic ring absorption appear at 1472, 1579 and 1617 cm⁻¹; azo bond (N=N) stretching vibrations appear at a range of 1511–1550 cm⁻¹ and at 1390 cm⁻¹; bands at 825 and

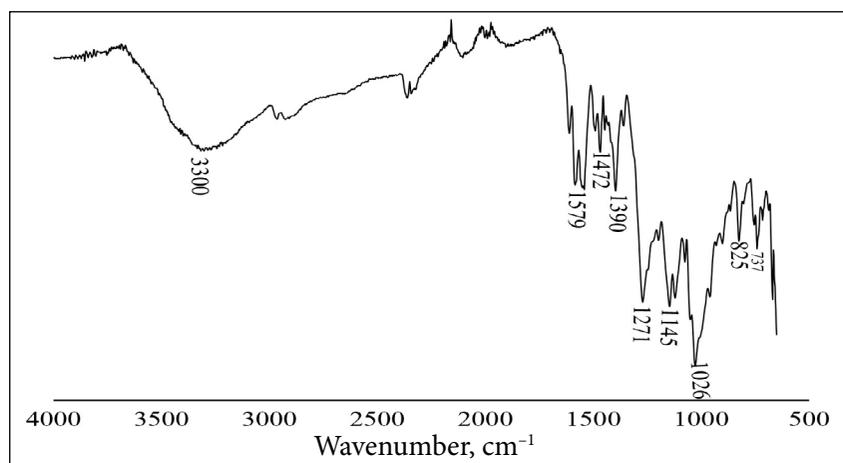


Fig. 1. FTIR spectrum of SG dye

737 can be assigned to C–H out-of-plane bending on an aromatic ring [34–36].

The preparation of a CuO catalyst from the simulated spent acid copper plating electrolyte or wastewater was performed by adding 0.2 ml portions of a 1 M NaOH solution to a 200 ml mixture of 0.1 M CuSO_4 and 0.1 M citric acid solution with vigorous stirring to $\text{pH} \geq 12$ until the $\text{Cu}(\text{OH})_2$ precipitate has been formed [37]. The precipitate obtained was washed 3 times with 40 ml deionized water to remove possible by-ions present in the final products and dried. The obtained product was kept at 500°C for 3 h in a muffle furnace to get the final product of CuO nanostructures.

Catalytic experiments

The dye Sanodure green (SG) was chosen to investigate the catalytic activity of CuO catalysts. To a 10 mL aqueous solution of dye (5 or 10 mg/L) of

50 or 25°C temperature 1 mL of H_2O_2 (35 wt%) was added keeping $\text{pH} = 6$. Immediately, 3 mg of the catalyst was added and as the reaction proceeded, the colour of the solution faded. The entire mixture was stirred during the reaction period. The supernatant was then transferred to a quartz cuvette for UV–visible spectral measurement. After the spectrum was measured, the solution was transferred back to the previous reaction vessel while stirring. The process was repeated and UV–visible spectra were recorded consecutively, to check the progress of the reaction. Blank experiments were also conducted to confirm that the reactions did not proceed with the catalyst in the absence of H_2O_2 , or without the catalyst in the presence of H_2O_2 . When the colour no longer changes, the solution is filtered and the remaining CuO is used again in the catalytic experiment. The scheme of CuO behaviour as Fenton-like catalyst is presented in Fig. 2.

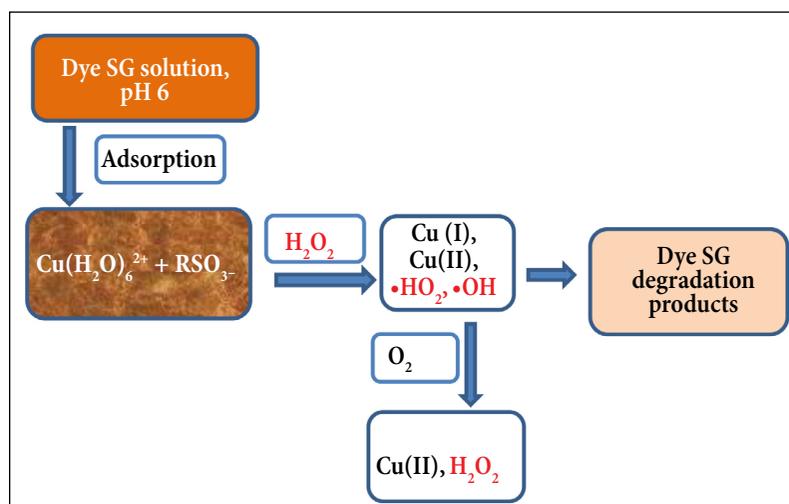


Fig. 2. Scheme of CuO behaviour as Fenton-active catalyst

UV-visible spectra were measured using a Varian Cary 50 spectrometer from Agilent Technologies (USA).

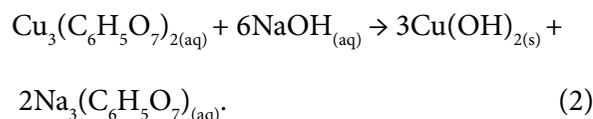
Based on UV-absorbance data at the previous determined wavelength 630 nm, the SG dye degradation rates were calculated according to Eq. (1):

$$\text{Degradation rate, \%} = \frac{(A_0 - A_t)}{A_0} \cdot 100. \quad (1)$$

Here A_0 is the absorbance at $t = 0$, whereas A_t is the absorbance at the same wavelength 630 nm at a given reaction time t for dye solutions.

RESULTS AND DISCUSSION

The addition of the NaOH into mixture of CuSO_4 with citric acid, a copper (II) citrate complex – $\text{Cu}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ (Fig. 3) – is formed. A sparingly soluble $\text{Cu}(\text{OH})_2$ precipitate forms on addition of more NaOH solution. This process can be represented by Eq. (2) [37]:



It is known that citric acid and other organic acids (oxalic, amino acids) used in the synthesis of nanoparticles determine the shape and size of the crystals formed. Upon potentiometric titration of the citrate solution with 1 M NaOH data, the pH changes abruptly from 6.87 to 9.72.

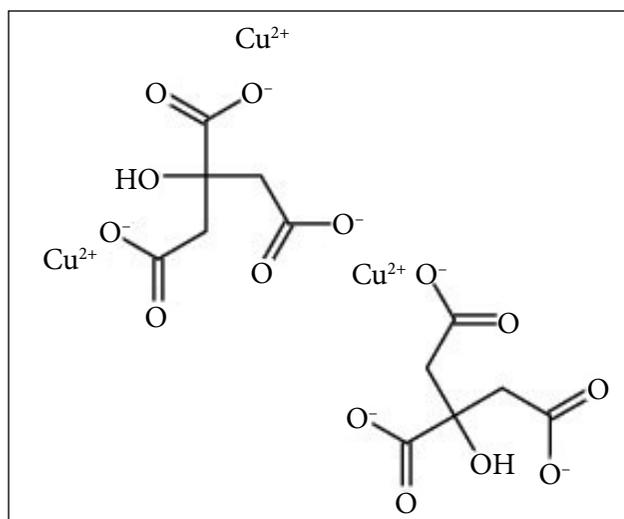
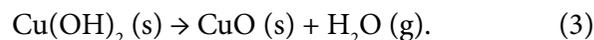


Fig. 3. Cu(II) citrate complex ($\text{C}_{12}\text{H}_{10}\text{Cu}_3\text{O}_{14}$) [<http://www.chemspider.com/Chemical-Structure.4953985.html>]

However, no $\text{Cu}(\text{OH})_2$ precipitate is yet formed. In this pH range, only the decomposition of the citrate complex occurs and the onset of $\text{Cu}(\text{OH})_2$ precipitation begins. At the solution of pH 12, the amount of precipitate increased significantly. The thermal decomposition reaction took place by heating the $\text{Cu}(\text{OH})_2$ precipitate at 500°C :



The black, powdery precipitate obtained by heating was visually similar to the copper (II) oxide of the reagent.

In a previous paper, it was shown that the morphology of the obtained catalyst CuO nanostructures consists of small, approximately 70 nm in diameter, spherical nanocrystallites and interconnected ultra-fine particles forming agglomerates [38]. XDR patterns of the synthesized CuO confirmed the identity to CuO standards (tenorite, Card No. 04-007-0518) and commercial CuO.

The classical homogeneous Fenton process used widely in wastewater treatment for degradation of organic pollutants to non-toxic carbon dioxide and water (the advanced oxidation processes (AOPs)) has such shortcomings as the limited operation condition (pH 2–3) and iron sludge generated during the reaction, causing secondary pollution. To solve the above problems, copper catalyst, both monovalent (Cu^+) and divalent (Cu^{2+}), is proposed because it shows similar redox properties and reacts easily with H_2O_2 by analogy with the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ reaction systems [25, 39, 40].

In an aqueous solution, the CuO surface is covered with -OH functional groups formed by dissociative chemisorption of water molecules and it is like a Bronsted–Lowry base behaving as a proton acceptor. These protons are in the form of a hydrogen (H^+) ion [41]:



Thus SG dye anions (RSO_3^-) are electrostatically attracted on the positive catalyst surface (physical adsorption), where the dye degradation process in the presence of H_2O_2 occurs. Herewith, the hydrolyzed complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ generated OH^\bullet and behaviours as Fenton-active catalyst are predominant in neutral pH conditions. The dye

degradation proceeds when the hydroxyl radicals react in well-known ways with organic compounds, principally by abstracting H from C–H, N–H, or O–H bonds, adding to C=C bonds, or adding to aromatic rings [34–36].

The SG dye degradation at pH 6 was observed by measurement of UV–vis absorbance at a wavelength of 630 nm. Time dependent UV–vis absorbance of the SG dye before and during the degrada-

tion reaction of SG with H_2O_2 and CuO catalyst is presented in Fig. 4. As the degradation reaction proceeded, the characteristic peak gradually tumbled when reaction time increased.

The degradation rate of dye (SG) in the presence of H_2O_2 and catalyst CuO presented in Fig. 5 shows that at temperature 50°C degradation is rapid when within 15 min. SG degraded by about 40% and in 70 min a maximum degradation equal

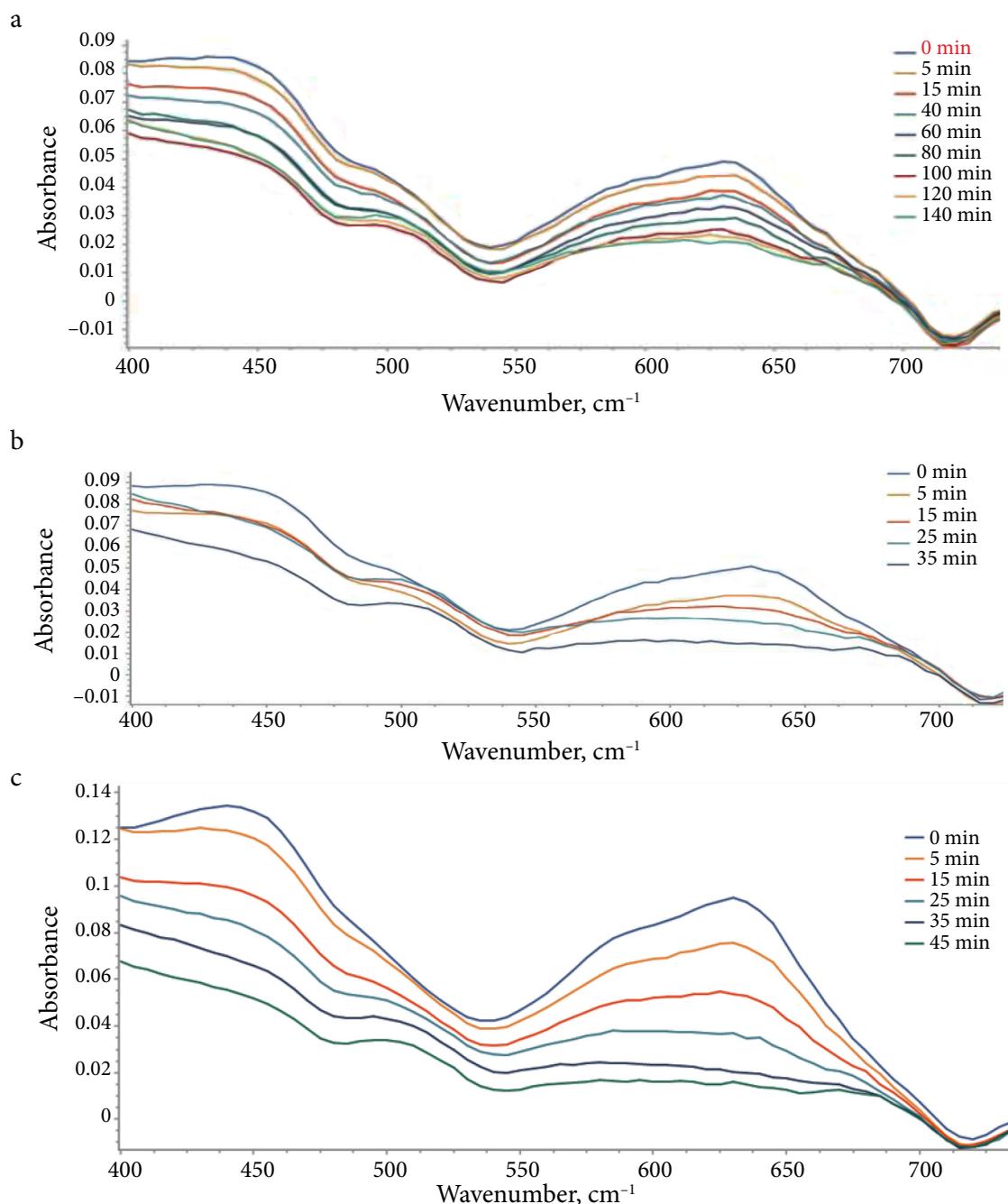


Fig. 4. Time dependent UV–vis absorbance of the SG dye before and during the degradation reaction of SG mixtures with H_2O_2 and catalyst CuO: (a) 5 mg/L SG, $T = 20^\circ\text{C}$; (b) 5 mg/L SG, $T = 50^\circ\text{C}$; (c) 10 mg/L SG, $T = 50^\circ\text{C}$. Conditions: 10 mL SG solution (concentration SG 5 mg/L or 10 mg/L), 1 mL H_2O_2 , catalyst 3 mg CuO

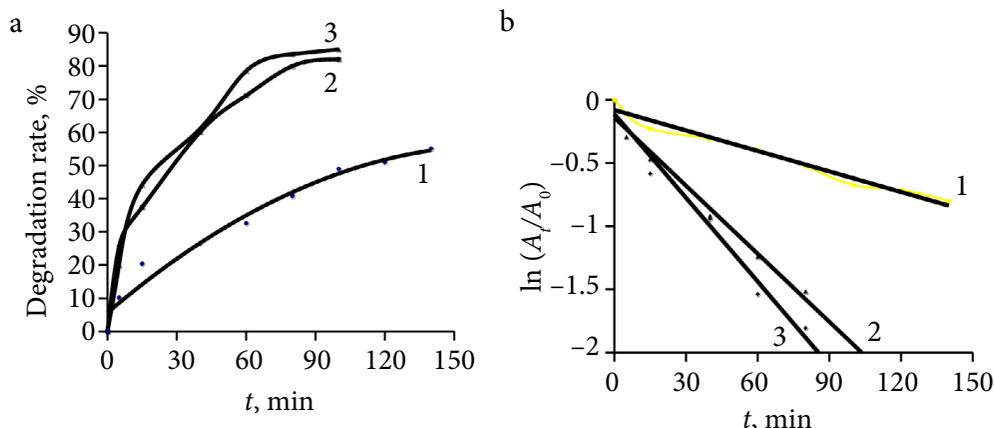


Fig. 5. Degradation rate of dye Sanodure green LWN (SG) in mixture with H_2O_2 and catalyst CuO(a) and the corresponding first order kinetic results (b) depending on dye concentration and temperature: 1) 5 mg/L SG, $T = 20^\circ\text{C}$; 2) 5 mg/L SG, $T = 50^\circ\text{C}$; 3) 10 mg/L SG, $T = 50^\circ\text{C}$. Conditions: 10 ml of SG solution, 1 mL H_2O_2 , catalyst 3 mg CuO

to 80% is reached (Fig. 5a, curves 2 and 3). That is possible due to diminishing non-degraded dye concentration in the solution and the release of catalysts active centers. The increase of the degradation rate of SG with increase in temperature indicates not only the mobility of the dye molecule but also the velocity of the degradation reaction. The rate constant k of the SG degradation reaction was determined using the pseudo-first order kinetic equation (Eq. (5)) form presented in [43, 44]

$$\ln \frac{C_t}{C_0} \text{ or } \ln \left(\frac{A_t}{A_0} \right) = -kt, \quad (5)$$

where k is the reaction rate constant, A_0 is the initial absorbance of the dye solution, and A_t is the absorbance of the dye solution after time t . The well-behaved linear fitting with the correlation factor $R \geq 0.98$ showed that SG degradation proceeded in accordance with pseudo-first-order kinetics. The rate constant k at two temperatures was calculated from the slope of the linear fitted lines for catalysts CuO (Fig. 5b). Whereas the rate constants calculated at two temperatures showed that when the reaction temperature was raised

from 20 to 50°C , the SG dye degradation reaction rate increased by 13.3 times (Table 1).

Furthermore, the rate constant for catalytic degradation of SG dye in the presence of H_2O_2 and catalyst CuO is highly dependent on the increase in temperature but not very much on the concentration (Table 1). Comparing the results with those presented in our previous article [38] it can be seen that the SG dye with the more complex metal complex structure degrades significantly more slowly than the less complex structure methyl orange dye, and the rate constants k are 0.018 and 0.029, respectively.

The variation of the temperature in a range of 293.15–323.15 K increases the rate of degradation of SG dye, because the higher temperature increased the reaction rate between hydrogen peroxide and the catalyst, thus increasing the rate of generation $\text{OH}\cdot$ radical [45, 46]. The values of the thermodynamic parameters for SG degradation reaction in the presence of H_2O_2 and catalyst CuO nanostructures were determined from the temperature dependence of the rate constant k according to the Eyring equation that is a theoretical construct, based on the transition state model [45]:

Table 1. The rate constants for the catalytic oxidation of SG dye in the presence of H_2O_2 and catalyst CuO at pH 6

SG concentration, mg/L	Temperature, $^\circ\text{C}$	The rate constant k (min^{-1})
5	20	0.0054 ($R^2 = 0.9753$)
5	50	0.018 ($R^2 = 0.9794$)
10	50	0.0221 ($R^2 = 0.9805$)

Conditions: 10 ml of 5 or 10 mg/L SG solution, 1 mL H_2O_2 , 3 mg CuO.

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{K_B}{h}\right) - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R} \quad (6)$$

Here k is the rate constant of the reaction, K_B = Boltzmann's constant ($1.381 \cdot 10^{-23}$ J K⁻¹), T = absolute temperature in degrees Kelvin, h = Plank constant ($6.626 \cdot 10^{-34}$ J s), R = universal gas constant 8.314472 , J K⁻¹ mol⁻¹, ΔH^\ddagger is activation enthalpy (J mol⁻¹), and ΔS^\ddagger is activation entropy (J mol⁻¹ K⁻¹).

The changes in activation enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) were determined from the slope and intercept of plot $\ln(k/T)$ versus $1/T$ of (Eq. (6)), respectively. The free energy of activation (ΔG^\ddagger) was determined from Eq. (7):

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

Activation energies E_a was determined from the slopes of the linear fitting of the plots $\ln k$ versus $1/T$ from Eq. (8) [42]:

$$\ln k = \ln A - E_a/RT \quad (8)$$

The values of the thermodynamic parameters obtained for the SG dye degradation reaction in the presence of catalyst CuO nanostructures are presented in Table 2. The reaction activation energy (31.48 kJ mol⁻¹) is relatively low and the positive value of activation enthalpy ΔH^\ddagger indicated the endothermic nature of the SG degradation reaction. While the obtained ΔH^\ddagger value was higher than ΔS^\ddagger that suggested that the degradation reaction is controlled by the enthalpy of activation. Meanwhile, the negative value of ΔS reflects decreasing in the dispersal of energy at the catalyst CuO/solution interface during reaction [42, 46]. However, the decoloured wastewater may be rich in organic substance, therefore it is more correct to refer to the degradation using COD and TOC parameters [47]. We plan to carry out research in the future, given that there are more other organic pollutants in plating wastewater.

CONCLUSIONS

The nanostructures of CuO prepared from a simulated plating effluent are effective catalysts in the Fenton-like oxidation of metal complex dye Sanodure green LWN in the presence of H₂O₂ leading to decolouration wastewater from the anodized aluminum dyeing process. The dye degradation reaction takes place without an energy source (at visible light), is endothermic and controlled by the enthalpy of activation.

The results of this study suggest that the preparation of catalyst from highly copper contaminated plating effluents may not only solve a serious environmental problem associated with the disposal of coloured effluents, but also provide an opportunity to reuse the spent copper electrolyte.

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Table 2. The activation parameters for the degradation of SG dye using CuO nanostructures in the presence of H₂O₂ at different temperatures

SG concentration, mg/L	Temperature, °C	E_a , kJ mol ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , kJ mol ⁻¹	ΔG^\ddagger , kJ mol ⁻¹
5	20	31.48	29.21	-0.19	84.9
5	50				90.6

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VARIO DENGIMO NUOTEKŲ UTILIZAVIMAS SKAIDANT DAŽIKLĮ SANODURE GREEN ESANT H₂O₂

Santrauka

Ištirtas metalo kompleksinio dažiklio „Sanodure Green“ (SG) skaidymas oksidaciniu būdu esant H₂O₂ ir iš vario dengimo nuotekų pagamintam nanostruktūruotam katalizatoriui CuO. Paruošto CuO katalizatoriaus aktyvumas skaidant SG dažiklį priklausė nuo SG koncentracijos, reakcijos trukmės ir temperatūros. SG skilimo reakcija vyko pagal pseudopirmosios eilės kinetinį modelį, greičio konstanta itin priklausė nuo temperatūros didėjimo ir šiek tiek nuo SG koncentracijos. Termodinaminiai tyrimai parodė, kad SG skilimo reakcija yra endoterminio pobūdžio.

Vario dengimo nuotekų naudojimas nanostruktūruotam katalizatoriui CuO paruošti suteikia galimybę išvengti sunkiai perdirbamo vario oksido dumblo kaupimosi neutralizuojant nuotekas ir ekonomiškiau tvarkyti vario dengimo ir aliuminio dažymo nuotekas.