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DEGRADATION OF CONGO RED USING PERIODATE, ACTIVATED BY ULTRASOUND AND IRON(II)

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Abstract. The periodate, activated by the combination of ultrasound and Fe(II), was used for oxidative degradation of an anionic diazo dye of congo red (CR). The effect of the main factors (the initial pH, the molar ratio of CR:KIO₄:FeSO₄, the amount of Fe(II), and the specific power of ultrasonic cavitation treatment) on its degradation efficiency was analyzed.

Keywords: oxidative degradation, congo red, periodate activation, ultrasound, ferrous sulfate heptahydrate.

1. Introduction

Azo dyes are toxic water-soluble compounds with potential carcinogenic and mutagenic effects¹. They are difficult to biodegrade due to their stable chemical structure. This indicates the presence of aromatic rings^{2–4}. CR is an anionic diazo dye with a pK_a value of 4.5⁵. It is used in the paper, pharmaceutical, cosmetic, textile, printing and dyeing, rubber, plastic, and chemical industries^{5,6}. CR is known to be metabolized to benzidine – a well-known carcinogen and mutagen for living organisms^{1,5}.

Adsorption methods are often used to remove CR from aqueous media. Among the adsorbents are lignocellulosic materials, which are wastes of the agro-industrial complex^{7–9} or by-products from the timber industry¹⁰, chitin suspensions after enzymolysis and sonoenzymolysis¹¹, nanomaterials – graphene oxide-CuFe₂O₄ nanohybrid material¹², iron oxide@activated carbon nanocomposite¹³ and NiO nanoparticle doped-PVA/MF polymer nanocomposites¹⁴.

The disadvantage of adsorption methods is the need for the disposal of sorbents after the sorption of CR. Other technologies for the CR removal from wastewater are photocatalysis^{6, 15–20}, catalytic ozonation²¹, thermally activated persulfate oxidation²², sonochemical degradation¹, hydrodynamic cavitation^{23, 24}, advanced oxidation processes, in particular, the Fenton process and Fenton-like processes^{25, 26}. The most promising direction to increase the efficiency of CR removal from wastewater is the combination of acoustic vibrations in the ultrasonic range and advanced oxidation processes^{27, 28}. Thus, using the sono-Fenton process, a CR degradation rate of 83 % and COD removal of 89 % were achieved within 60 min²⁸. The experimental conditions were as follows: CR initial concentration 25 mg/L, US power 80 W, pH 3.5, H₂O₂ concentration 5 mM, and FeSO₄ concentration 25 mg/L.

At present, periodate-based advanced oxidation processes have attracted much attention due to their high efficiency in the removal of certain persistent pollutants of aqueous media – dyes, chlorine- and nitrogen-containing organic compounds^{29–33}. Compared to traditional oxidizing agents such as hydrogen peroxide and persulfates, the periodates are thermally stable and more convenient for storage and transportation³². The main disadvantage of periodate oxidation is its high selectivity. This reduces the efficiency of wastewater treatment containing organic compounds of different classes. Periodates are primarily used for the oxidation of compounds with vicinal groups (-OH, -CHO. =CO. or -COOH) to aldehydes or ketones, depending on their structures³⁴. The periodates are activated to reduce the selectivity of periodate oxidation. The following methods of periodate activation are distinguished: activation by ultraviolet radiation (photolysis)^{35–37}, photocatalytic activation^{38, 39}, thermal activation^{40, 41}, activation in an US field (sonolysis)^{42, 43}, by microwaves⁴⁴, by hydrogen perox ide^{29-31} , by transition metals and their compounds $^{33, 45-47}$, by metal nanoparticles $^{48-50}$, by carbon-based materials $^{51, 52}$.

The periodate activation by transition metals and their compounds is economically advantageous due to the prevalence of transition metals and their compounds and their relatively low cost. Zong *et al.*³³ reported that the value of the oxidative degradation rate of sulfamethoxazole, carbamazepine, ciprofloxacin, acetamidophenol, 2,4,6-trichlorophenol, bisphenol A was in the range of 88.9–100 % when using the Fe(II)/IO₄⁻ system for 2 min. The main reaction species was singlet oxygen (¹O₂). Using the US to activate periodates led to the formation of highly reactive intermediates – IO₃⁻, [•]OH , IO₄⁻⁴².

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Considering the above, the combination of various strategies of periodate activation, in particular, US activation and activation by transition metal compounds, opens promising prospects for highly efficient oxidative degradation of resistant organic compounds. This is due to the expansion of reactive species formed both radically and non-radically.

The work is aimed to investigate the effect of experimental conditions (the initial pH value of an aqueous solution of CR, the molar ratio of reagents, and the specific power of US cavitation treatment) on the efficiency and kinetics of CR oxidative degradation using the US/KIO₄/FeSO₄ process.

2. Experimental

2.1. Reagents

Congo red (abbreviation: CR; molecular formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molar mass: 696 g/mol), potassium periodate (KIO₄), and ferrous sulfate heptahydrate (FeSO₄·7H₂O) were purchased from Merck (Germany). All used reagents were of analytical grade.

2.2. Experimental Setup

Equipment for the studies of CR oxidative degradation consisted of: a 22 kHz US magnetostrictive emitter "Ultrasonic Disintegrator UD-20" (Poland) with a variable specific power of cavitation US treatment (53.3, 68.0, and 83.3 W/L) and with a diameter of working part of the US concentrator of 15 mm and its immersion depth in the solution of 10 ± 1 mm; a CORIO C-BT5 (JULABO GmbH) thermostat for creating isothermal conditions in the reaction medium, which was equipped with an external thermostatic bath with a thermometer; a 250 mL glass reactor (reactor filling factor is 60 %), which was placed in the bath; a magnetic stirrer.

2.3. Experimental Studies of CR Oxidative Degradation

150 mL of CR aqueous solution with a concentration of 50 mg/L (71.8 μ M) was prepared using distilled water under constant stirring. The prepared solution was loaded into a glass reactor. The pH value of the CR solution (in the range from 3.00 to 9.00) was adjusted using hydrochloric acid or sodium hydroxide. The ADWA AD1200 ATC pH meter (Hungary) was used to measure pH values. Oxidation reactions were initiated by dosing of certain amounts of KIO₄ and FeSO₄·7H₂O powder into an aqueous solution of CR, followed by stirring. The specific power of US cavitation treatment varied discretely in the range from 53.3 to 83.3 W/L. Isothermal conditions of the process (temperature 20±0.5 °C, $\tau = 20$ min) were provided by thermostating the reaction medium in a glass reactor. A set of experimental studies included an analysis of the influence of the following factors on the efficiency and kinetics of CR oxidative degradation: 1) the pH value of the initial aqueous solution of CR; 2) the molar ratio of CR:KIO₄:FeSO₄, which varied from 1:5:2.5 to 1:20:10; 3) the molar ratio of KIO₄:FeSO₄, which varied from 1:0.25 to 1:1; 4) the specific power of US cavitation treatment.

2.4. Analytical Procedure

At specified time intervals, 2 mL of the reaction medium was taken and filtered under vacuum through a polyamide membrane (0.2 μ m) to remove insoluble particles of Fe (III) compounds. The filtered solution samples were analyzed using quartz cuvettes with a thickness of 1 cm by UV-Vis spectrophotometer UV-3100PC (Shanghai Mapada Instruments Co., Ltd. (China)) in the wavelength range from 200 to 1100 nm. At pH = 3.00, the maximum absorption of the solution was observed at the wavelength of 574 nm, and at pH = 5.00; 7.00; 9.00 – at the wavelength of 500 nm. The concentration of CR in its aqueous solution at different pH values was calculated using pre-constructed calibration curves.

3. Results and Discussion

3.1. The Effect of the Initial pH Value of an Aqueous Solution of CR on Its Degradation

The effect of the initial pH value of CR aqueous solution on its degradation using the US/KIO₄/FeSO₄ process is shown in Fig. 1, a.

Using the US/KIO₄/FeSO₄ process for the oxidative degradation of CR at the initial pH value of its aqueous solution of 3.00 for 600 s led to a decrease in the concentration of CR from 71.8 to 2.0 μ M. This corresponded to the CR degradation degree of 97.2 %. During the same time, at the initial pH values of CR aqueous solution of 5.00, 7.00, and 9.00, the oxidative degradation degree of CR was 76.1, 69.3, and 50.1 %, respectively. An increase in the duration of the combined US and reagent treatment to 1200 s led to an increase in the degradation degree to 94.3, 90.5, and 75.1 %, respectively. So, with an increase in the initial pH of CR aqueous solution, the efficiency of dye degradation significantly decreased. Lee *et al.*⁴² also reported a decrease in the efficiency of sonochemical degradation of perfluorooctanoic acid using periodate from 62.4 to 56.7 % with increasing pH from 3.9 to 10.1. The conditions of the experimental studies were as follows: initial concentration of perfluorooctanoic acid in its

> 80 70 60 50 C (JuM) 40 30 20 10 0 0 200 400 600 800 1000 1200 τ (s) pH=3.00 pH=5.00 pH=7.00 pH=9.00 а 40000 $= 2.401 \cdot 10^2 x$ 35000 $R^2 = 0.939$ 30000 25000 20000 15000 10000 5000 0 90 0 30 60 120 150 τ(s) ◆ pH=3.00 ■ pH=5.00 ▲ pH=7.00 • pH=9.00 с

I/C - I/C₀ (M⁻¹)

Different types of I^{VII} can coexist in an aqueous solution. At pH < 8, the dehydrated form (IO_4^-) dominates; at pH > 8, the dominant form is the dimerized form $(H_2I_2O_{10}^{4-})^{32, 53}$. Under acidic conditions, the IO_3^{\bullet} radicals can be formed as a result of acid catalysis (Scheme 1), and they participate in the decomposition and oxidation reactions of organic pollutants.

$$IO_4^- + H^+ \xrightarrow{US})))IO_3^\bullet + H_2O.$$
 (1)

Under alkaline conditions, the dimerized form $(H_2I_2O_{10}^{4-})$ generates the following reaction species: I(V) (such as IO_3^{\bullet}), ${}^{\bullet}OH$ and IO_4^{\bullet} (Scheme 2, Eq. 3)⁴²:

$$H_{2}I_{2}O_{10}^{4-}(I(VII)) \xrightarrow{US}))) I(V(IO_{3}^{\bullet}, etc.)) + {}^{\bullet}OH, (2)$$

$$^{\bullet}\mathrm{OH} + \mathrm{IO}_{4}^{\bullet} \to \mathrm{OH}^{\bullet} + \mathrm{IO}_{4}^{\bullet}. \tag{3}$$

aqueous solution 170.1 μ M, volume of the solution 300 mL, periodate concentration 4.5 mM, temperature of the reaction medium 25±1 °C, US power 150 W, US frequency 40 kHz, and treatment time 120 min.

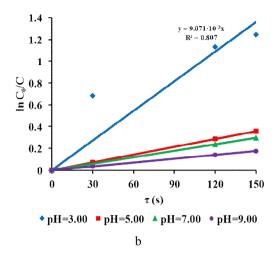


Fig. 1. The effect of the initial pH value of an aqueous solution of CR on (a) its degradation, (b) pseudo-first-order kinetic plots of CR dye degradation, and (c) second-order kinetic plots of CR dye degradation (conditions: $V = 150\pm1$ mL, $C_0(CR) = 71.8 \ \mu\text{M}$, the temperature is $20\pm0.5 \ ^\circ\text{C}$, the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5, the specific power of US cavitation treatment is 68.0 W/L)

The IO_3^{\bullet} radicals have a greater oxidizing power compared to IO_4^{\bullet} radicals. Since more iodyl radicals (IO_3^{\bullet}) are formed under acidic conditions, and periodate acts as an absorber for hydroxyl radicals ($^{\bullet}OH$) under alkaline conditions (Scheme 2, Eq. 3), the efficiency of oxidative degradation of organic pollutants in the ultrasonic field under acidic conditions is higher.

Under alkaline conditions, free radicals (in particular [•]OH and $O_2^{\bullet-}$) are formed as a result of the water sonolysis (Eq. 4)⁵³ and the activation of periodates by Fe²⁺ ions (Scheme 5)^{45, 50}, as well as the interaction of Fe²⁺ with oxygen dissolved in water (Eq. 6)⁴⁵:

$$H_2O \xrightarrow{US})))H^{\bullet} + {}^{\bullet}OH,$$
 (4)

$$\operatorname{Fe}^{2+} + \operatorname{IO}_{4}^{-} + \operatorname{H}_{2}O \rightleftharpoons \operatorname{Fe}^{3+} + \operatorname{IO}_{3}^{-} + \operatorname{O}_{2}^{\bullet-} + \operatorname{H}^{+}, \qquad (5)$$

$$\operatorname{Fe}^{2^{+}} + \operatorname{O}_{2} \to \operatorname{Fe}^{3^{+}} + \operatorname{O}_{2}^{\bullet^{-}}.$$
 (6)

The **•**OH and $O_2^{\bullet^-}$ free radicals are absorbed by HCO₃⁻ or CO₃²⁻ ions, which can be formed from CO₂ that dissolves in water as a product of CR mineralization³¹. This leads to the formation of CO₃^{•-}, which is a much weaker oxidizing agent compared to **•**OH and O₂^{•-}. The O₂^{•-} is a precursor of singlet oxygen (Eqs. 7, 8), which plays an important role in the degradation of organic pollutants in aqueous media⁴⁶:

$$2O_2^{\bullet-} + 2H_2O \rightleftharpoons {}^{1}O_2 + H_2O_2 + 2OH^{-}, \qquad (7)$$

$$IO_4^- + 2O_2^{\bullet-} + H_2O \rightleftharpoons IO_3^- + 2^1O_2 + 2OH^-.$$
 (8)

The results shown in Fig. 1, b and Fig. 1, c indicate that CR degradation using the US/KIO₄/FeSO₄ process is more accurately described (with a higher value of the determination coefficient R^2) by a second-order reaction kinetic equation. With an increase in the initial pH value of an aqueous solution from 3.00 to 5.00, the CR degradation rate constant decreases by 6.1 times – from 2.401×10^{2} to $0.393 \times 10^2 \text{ M}^{-1} \text{s}^{-1}$. In the case of the neutral pH, the CR degradation rate constant is 0.314×10^2 M⁻¹s⁻¹, and at pH = 9.00 it is $0.175 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$. So, the CR degradation using the US/KIO₄/FeSO₄ process proceeds much more intensively (by 13.7 times) in acidic conditions (pH = 3.00) compared to alkaline ones (pH = 9.00). Wang et al.⁴⁵ reported that the degradation rate constant of bisphenol \overrightarrow{AF} by the FeS (mackinawite)/ IO_4^- system at pH = 3.00 was 1.305×10^{-3} s⁻¹. The concentration of dissolved Fe^{2+} , which is involved in the periodate activation, was the highest (1.23 mg/L) at pH = 3.00. With an increase in the pH value to 10, it decreased to 0.3 mg/L.

3.2. The Effect of the Molar Ratio of CR:KIO₄:FeSO₄ on the Degradation of CR

The effect of the CR:KIO₄:FeSO₄ molar ratio on the CR degradation is shown in Fig. 2, *a*. It was found that for 600 s of the combined US and reagent treatment, when the amount of reagents (KIO₄ and FeSO₄·7H₂O) is increased by 2 times (which is equivalent to an increase in the CR:KIO₄:FeSO₄ molar ratio from 1:5:2.5 to 1:10:5), the oxidative degradation degree of CR increased from 86.5 to 97.2 %. A further increase in the molar ratio to 1:20:10 led only to a slight increase (by 2.2 %) in the CR degradation degree to 99.4 %. At a high concentration of periodate, the probability of free radicals (*OH and IO₃) quenching by an excess of IO₄⁻ increases (Eqs. 3, 9)³⁷. In this case, periodyl radicals (IO₄[•]) with a lower oxidizing ability are formed:

$$\mathrm{IO}_{3}^{\bullet} + \mathrm{IO}_{4}^{\bullet} \to \mathrm{IO}_{3}^{\bullet} + \mathrm{IO}_{4}^{\bullet}. \tag{9}$$

Another factor of the low increase in the degradation rate of CR (with increasing concentration of periodate) are competing reactions – recombination of radicals (Eqs. 10-12) and their interaction with dye molecules:

$$2^{\bullet} OH \rightarrow H_2 O_2, \tag{10}$$

$$2\mathrm{IO}_{3}^{\bullet} \to \mathrm{I}_{2}\mathrm{O}_{6}, \tag{11}$$

$$2\mathrm{IO}_{4}^{\bullet} \to \mathrm{I}_{2}\mathrm{O}_{8}. \tag{12}$$

Thus, Hamdaoui and Merouani⁴³ noted that at a high periodate concentration the rate of radicals recombination was higher compared to the rate of their interaction with Brilliant blue R dye molecules.

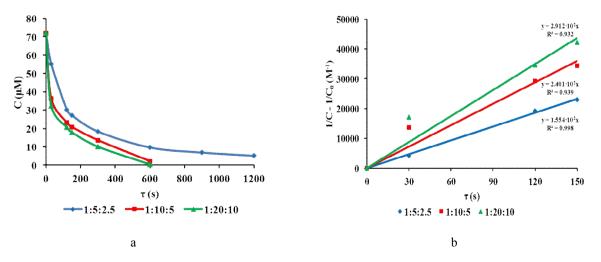


Fig. 2. The effect of the CR:KIO₄:FeSO₄ molar ratio on (a) the degradation of CR, and (b) second-order kinetic plots of CR dye degradation (conditions: V = 150 ± 1 mL, C₀(CR) = 71.8μ M, the temperature is $20\pm0.5 \circ$ C, pH = 3.00 ± 0.01 , the specific power of US cavitation treatment is 68.0 W/L)

With an increase in the CR:KIO₄:FeSO₄ molar ratio from 1:5:2.5 to 1:10:5, the CR degradation rate constant increased by 54.5 % – from 1.554×10^2 to 2.401×10^2 M⁻¹s⁻¹ (Fig. 2, *b*). A further increase in the reagents amount (up to the CR:KIO₄:FeSO₄ = 1:20:10) had a less significant effect on the degradation rate constant of CR. It increased by 21.3 % – from 2.401×10^2 to 2.912×10^2 M⁻¹s⁻¹.

Considering the above, it is expedient to carry out the oxidative degradation of CR at the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5 to reduce the cost of purification of aqueous media containing this dye.

3.3. The Effect of the Molar Ratio of KIO₄:FeSO₄ on the Degradation of CR

With an increase in the amount of Fe^{2+} ions in the reaction medium by 2 times (which is equivalent to an increase in the molar ratio of KIO₄:FeSO₄ from 1:0.25 to 1:0.5), the CR degradation rate constant increased by 8.3 % – from 2.218×10^2 to 2.401×10^2 M⁻¹s⁻¹ (Fig. 3). As a result of increasing the KIO₄:FeSO₄ molar ratio from 1:0.5 to 1:1, the CR degradation rate constant increased by 62.1 % – from 2.401×10^2 to 3.892×10^2 M⁻¹s⁻¹. Such character of the change in the degradation rate constant of CR confirms the function of Fe²⁺ ions as activators for the periodate decomposition.

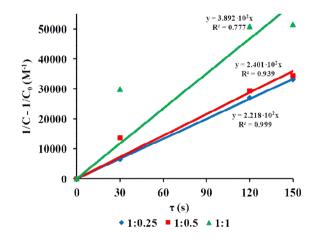


Fig. 3. Second-order kinetic plots of CR dye degradation the effect of KIO₄:FeSO₄ molar ratio) (conditions: $V = 150\pm1$ mL, C₀(CR) = 71.8 µM, C₀ (KIO₄) = 0.718 mM, the temperature is 20\pm0.5 °C, pH = 3.00\pm0.01, the specific power of US cavitation treatment is 68.0 W/L)

The proceeding of the US/KIO₄/FeSO₄ process for 600 s allowed us to achieve the CR degradation degree of 79.5 % (at KIO₄:FeSO₄ = 1:0.25), 97.2 % (at KIO₄:FeSO₄ = 1:0.5), and 80.0 % (at KIO₄:FeSO₄ = 1:1). The extreme character of the dependence of the oxidative degradation

degree of CR on the FeSO₄ consumption (the amount of Fe²⁺ ions) was due to the shift of the chemical equilibrium in Scheme 5 to the right – towards the formation of Fe³⁺ ions. At the molar ratio of KIO₄:FeSO₄ = 1:1, the rate of reaching the value of solubility product for Fe(OH)₃ (Eq. 15)⁵⁰ was maximum in the reaction medium:

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2,$$
 (13)

$$\mathrm{H}_{2}\mathrm{O}_{2} + 2\mathrm{e}^{-} \to 2\mathrm{OH}^{-}, \qquad (14)$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3.$$
 (15)

And the passage probability of Eq. 16 with the same initial amount of periodate was the minimum

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}. \tag{16}$$

Therefore, the duration of the "active stay" of Fe³⁺ ions in the reaction medium at KIO_4 :FeSO₄ = 1:1 was minimal. This leads to anomalous decrease in the oxidative degradation degree of CR. Also, an excess of Fe²⁺ ions can scavenge hydroxyl radicals (Eq. 17)⁴⁹

$$\operatorname{Fe}^{2+} + \operatorname{^{\bullet}OH} \to \operatorname{Fe}^{3+} + \operatorname{OH}^{-}.$$
 (17)

3.4. The effect of the specific power of US cavitation treatment on the degradation of CR

The effect of the specific power of US cavitation treatment on the CR degradation is shown in Fig. 4, *a*.

It was found that with an increase in the specific power of US cavitation treatment from 53.3 to 68.0 W/L, the degradation degree of CR increased from 75.7 to 97.2 % due to the use of the US/KIO₄/FeSO₄ process for 600 s. A further increase in the specific power of US cavitation treatment to 83.3 W/L had almost no effect on the oxidative degradation degree of CR. It increased by 1.0 % (up to 98.2 %). Hamdaoui and Merouani⁴³ noted that higher radical production can be achieved with higher US power. A higher rate of radical generation at higher US power results in higher radical concentrations. This can lead to the predominance of radical recombination reactions (Eqs. 10–12) over reactions of their interaction with dye molecules and, accordingly, to a decrease in the increase in the degradation degree.

The increase in the specific power of US cavitation treatment from 53.3 to 83.3 W/L led to a linear increase (Fig. 4, *b*) in the oxidative degradation rate constant of CR from 1.310×10^2 to 4.308×10^2 M⁻¹s⁻¹.

It is advisable to carry out the oxidative degradation of the dye at the specific power of US cavitation treatment of 68.0 W/L to reduce the energy consumption of purification of aqueous media containing CR.

The degradation degrees of CR were 4.1, 66.6, and 97.2 % using only the US action or only the reagent treatment ($KIO_4/FeSO_4$) or the combined process ($US/KIO_4/FeSO_4$), respectively, for 600 s (Fig. 5, *a*). The

degradation rate constants of CR were 0.033×10^2 , 0.578×10^2 , and 2.401×10^2 M⁻¹s⁻¹ using only the US action or only the reagent treatment (KIO₄/FeSO₄) or the combined process (US/KIO₄/FeSO₄), respectively (Fig. 5, *b*). A significant increase in the degradation degree and the degradation rate constant of CR for the combined process, compared to the individual ones, indicates a synergistic effect.

The synergistic coefficient (f) for the combined process (US/KIO₄/FeSO₄) was calculated based on the rate constants:

$$f_{\rm US/KIO_4/FeSO_4} = \frac{k_{\rm US/KIO_4/FeSO_4}}{k_{\rm US} + k_{\rm KIO_4/FeSO_4}} = \frac{2.401 \times 10^2}{0.033 \times 10^2 + 0.578 \times 10^2} = 3.93.$$
(18)

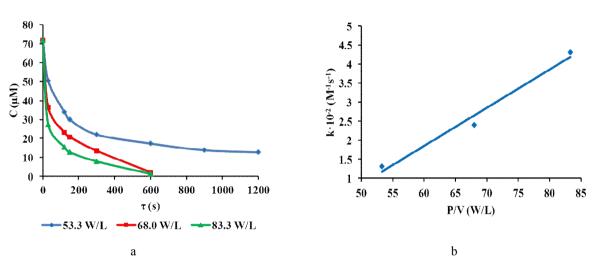


Fig. 4. The effect of the specific power of US cavitation treatment on (a) CR degradation, and (b) the degradation rate constant of CR (conditions: $V = 150\pm1$ mL, $C_0(CR) = 71.8 \mu$ M, the temperature is 20 ± 0.5 °C, the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5, pH = 3.00\pm0.01)

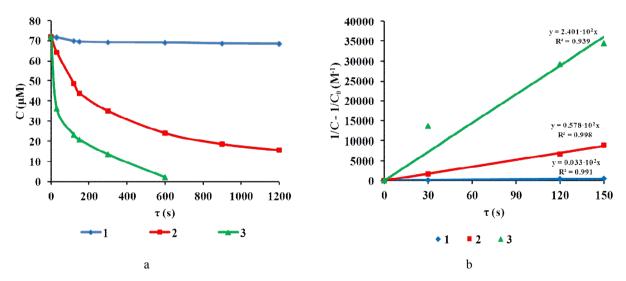


Fig. 5. (a) The dependence of CR concentration on the treatment duration, and (b) second-order kinetic plots of CR dye degradation using: 1 - US; $2 - \text{KIO}_4/\text{FeSO}_4$; $3 - \text{US/KIO}_4/\text{FeSO}_4$ (conditions: $V = 150 \pm 1 \text{ mL}$, $C_0(\text{CR}) = 71.8 \mu\text{M}$, the temperature is $20 \pm 0.5 \text{ °C}$, the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5, pH = 3.00\pm0.01, the specific power of US cavitation treatment is 68.0 W/L)

The synergism between US and reagent (using FeSO₄) activation of periodates was due to the formation of the complex of powerful oxidants (${}^{1}O_{2}$, IO_{3}^{\bullet} , ${}^{\bullet}OH$, IO_{4}^{\bullet})^{31,42}. Fig. 6 shows a photographic interpretation of the

CR color intensity before (*a*) and after (*b*, *c*) using the US/KIO₄/FeSO₄ process. The figures unambiguously confirm the effectiveness of the oxidative degradation of CR, which was shown in the decolorization of its aqueous solution.

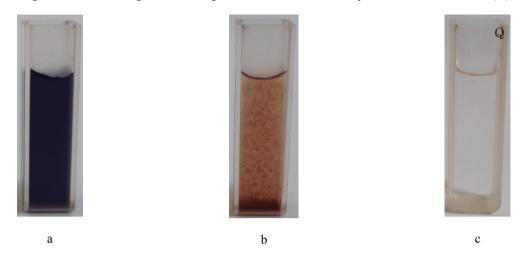


Fig. 6. Comparison of CR color before (a) and after (b, c) using the US/KIO₄/FeSO₄ process: a – aqueous solution of CR at pH = 3.00; b – unfiltered sample of the solution containing insoluble particles of Fe (III) compounds; c – filtered sample of the solution (conditions: V = 150 ± 1 mL, C₀(CR) = 71.8μ M, the temperature is $20\pm0.5 \,^{\circ}$ C, the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5, pH = 3.00 ± 0.01 , the specific power of US cavitation treatment is 68.0 W/L)

Fig. 7 shows the UV/Vis spectra of CR during its degradation using the US/KIO₄/FeSO₄ process. The absorption spectrum of the original CR solution with a concentration of 71.8 μ M ($\tau = 0$ s) was characterized by one main band in the visible region with an absorption peak at 574 nm and two bands located in the ultraviolet region at 237 nm and 336 nm.

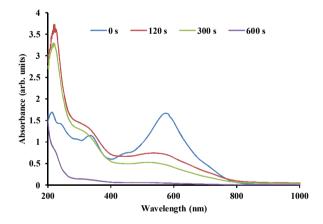


Fig. 7. The UV/Vis spectra of CR during its degradation using the US/KIO₄/FeSO₄ process (conditions: V = 150±1 mL, C₀(CR) = 71.8 μM, the temperature is 20±0.5 °C, the molar ratio of CR:KIO₄:FeSO₄ = 1:10:5, pH = 3.00±0.01, the specific power of US cavitation treatment is 68.0 W/L)

The absorption peak in the visible region (at 574 nm) was attributed to the azo bonds of the CR molecule and the absorption peaks in the ultraviolet region (at 237 nm and 336 nm) were attributed to the structures of the benzene and naphthalene rings, respectively⁵⁴. A sharp increase in absorption intensity in the range of 200– 250 nm ($\tau = 120$ s; 300 s) was due to the addition of an oxidant (potassium periodate)³⁷ to the CR solution.

Degradation of CR can consist of the following steps⁵⁵: I) cleavage of benzene and naphthalene rings; II) cleavage of the C–S bond between the aromatic ring and the sulfonate groups by hydroxyl and iodyl radicals attack; III) cleavage of C–N, and C–C bonds of the chromophore group; IV) cleavage of azo bonds. Such steps are confirmed by the hypochromic effect ($\tau = 600$ s), *i.e.* a significant decrease in absorption intensity in the wavelength ranges of 500–574 nm (indicates the cleavage of azo bonds) and 230–350 nm (indicates the destruction of the aromatic structure). Therefore, changes in the UV/Vis spectra indicate the mineralization of CR diazo dye.

4. Conclusions

In this study, the periodate, activated by US and Fe(II), was used for the oxidative degradation of the diazo dve of CR. Based on the analysis of the main factors' effect (the initial pH of the CR aqueous solution, the molar ratio of CR:KIO₄:FeSO₄, the Fe (II) amount, the specific power of US cavitation treatment) on the degradation efficiency of CR, the best conditions for oxidative degradation were determined: pH = 3.00, the molar ratio of $CR:KIO_4:FeSO_4 = 1:10:5$, the molar ratio of KIO_4 :FeSO₄ = 1:0.5, the specific power of US cavitation treatment is 68.0 W/L. Under such conditions, the degradation degree of CR was 97.2 %, the degradation rate constant was 2.401×10^2 M⁻¹s⁻¹, and the synergistic coefficient of the US/KIO₄/FeSO₄ process was 3.93. So, the combination of various periodate activation strategies, in particular, US activation and activation by transition metal

compounds, can become the basis of a highly efficient, high-intensity, environmentally friendly, energy- and resource-saving technology for the oxidative degradation of resistant organic compounds, such as azo dyes.

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ДЕГРАДАЦІЯ КОНГО ЧЕРВОНОГО З ВИКОРИСТАННЯМ ПЕРЙОДАТУ, АКТИВОВАНОГО УЛЬТРАЗВУКОМ І ЗАЛІЗОМ(II)

Анотація. Перйодат, активований комбінацією ультразвуку та Fe(II), використано для окиснювальної деградації аніонного діазобарвника конго червоного (КЧ). Проаналізовано вплив основних факторів (початкового рН, мольного співвідношення KЧ:KIO₄:FeSO₄, кількості Fe(II), питомої потужності ультразвукового кавітаційного оброблення) на ефективність його деградації.

Ключові слова: окиснювальна деградація, конго червоний, активація перйодату, ультразвук, заліза сульфат гептагідрат.