Supplementary material to

Fenton-like oxidative degradation of Orange G dye and binary dye mixtures using Oxone® activated with cobalt-doped alumina catalysts

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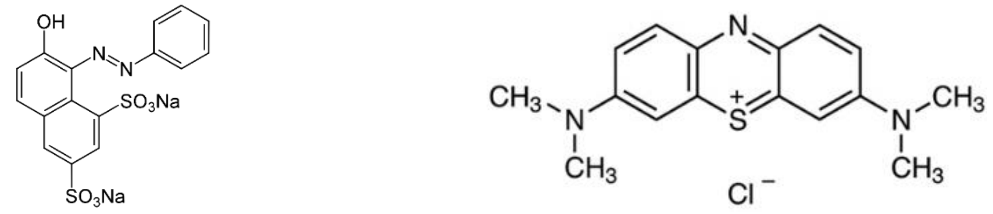
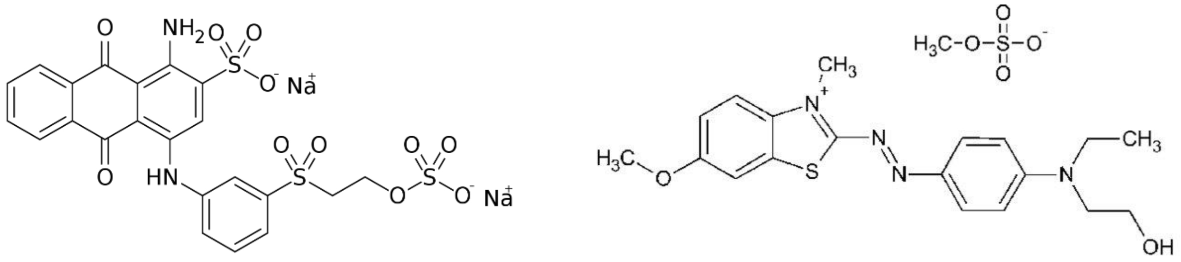
S1 Structural formulas of investigated dyes



Orange G

Methylene blue



Remazol brilliant blue R

Basic blue 41

Figure S1. Structural formulas of investigated dyes

S2 Kinetic models

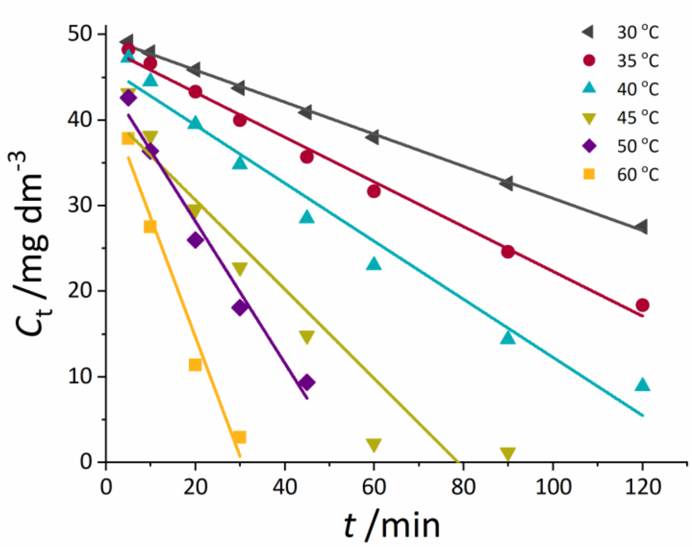


Figure S2. Zero kinetic model for OG degradation at different temperatures for CoA-1000

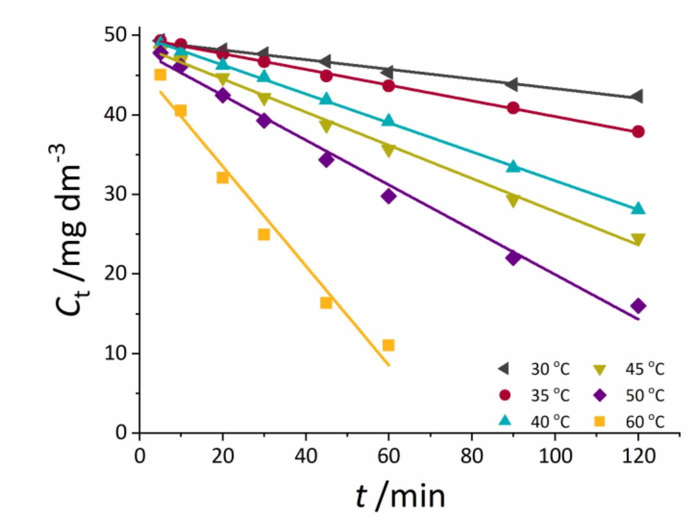


Figure S3. Zero kinetic model for OG degradation at different temperatures for CoA-1100

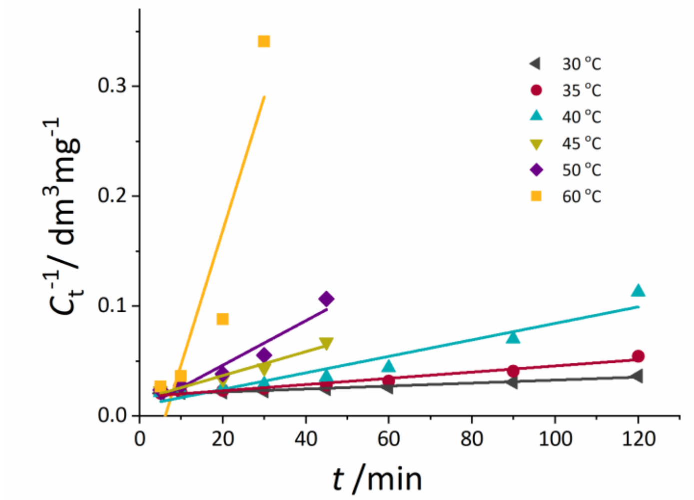


Figure S4. PSO kinetic model for OG degradation at different temperatures for CoA-1000

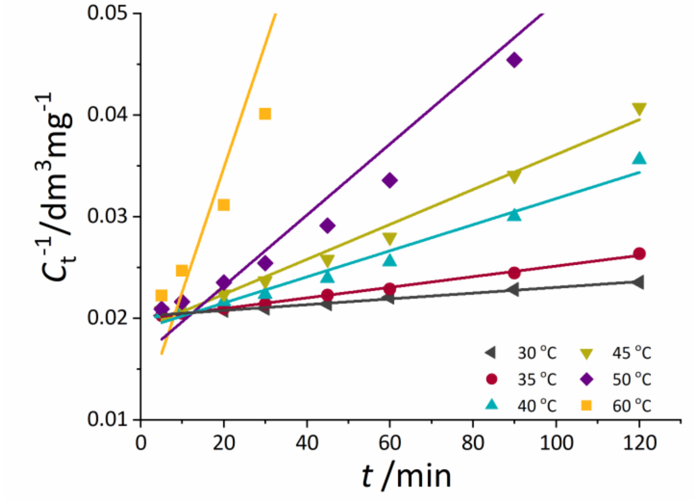


Figure S5. PSO kinetic model for OG degradation at different temperatures for CoA-1100

Table S1. Pseudo-first-order kinetic model parameters obtained by non-linear fitting of the experimental data

Catalyst		Temperature, °C					
		30	35	40	45	50	60
CoA-1000	$k_1 \times 10^2$ / min^{-1}	0.5	0.8	1.5	2.8	3.8	10.2
	R^2	0.9984	0.9975	0.9972	0.9968	0.9953	0.9802
CoA-1100	$k_1 \times 10^2$ / min^{-1}	0.1	0.2	0.5	0.6	1.0	2.6
	R^2	0.9930	0.9991	0.9923	0.9987	0.9970	0.9985

S3. Proposed reaction mechanism

It is known from the literature that transition metal oxide catalysts usually produce radical-dominated reactive oxygen species [1]. Sulphate anion radicals are commonly generated from persulfate or peroxymonosulfate (PMS) through different activation methods. Mixed salt Oxone® ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) contains potassium peroxymonosulfate as an active component. In our previous work [2], where a similar reaction system was employed, the presence of $SO_4^{\cdot -}$ and $HO^{\cdot}$ radicals was confirmed using EPR. The signal designated to $SO_4^{\cdot -}$ was more pronounced in comparison to signal originating from $HO^{\cdot}$ radicals, indicating a higher concentration of $SO_4^{\cdot -}$ radicals in the investigated reaction. The conclusion was that sulphate anion radicals were the dominant reactive oxygen species [2]. Similar results were obtained by other authors [3,4].

The mechanism of PMS activation by using Co^{2+} was explained by many researchers [5,6,7]. This mechanism is rather complicated, but the rate-limiting step is the formation of $CoOH^+$ (Eq. (1)) which is the most effective specie to activate PMS. In the reaction of $CoOH^+$ with HSO_5^-, reactive oxygen species, sulphate anion radical, is formed (Eq. (2)). In the next step the reduction of Co^{3+} to Co^{2+} is happening providing regeneration of Co^{2+} (Eq. (4)):

$$Co^{2+} + H_2O \rightarrow CoOH^+ + H^+ \quad (1)$$

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4^{\cdot -} + H_2O \quad (2)$$

$$CoO^+ + 2H^+ \rightarrow Co^{3+} + H_2O \quad (3)$$

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{\cdot -} + H_2O \quad (4)$$

Orange G is an azo dye and as other azo dyes, it contains –N=N– bond which is easily dissociated to form a naphthalene ring [8]. The degradation mechanism of the OG dye by sulphate anion radicals is very complex thus only a few studies have attempted to find an explanation. Certain reaction products are subsequently converted to another products step by step. The UV-Vis spectrum of OG shows three distinctive bands: the major band with a maximum adsorption at 478 nm, the major band in the visible region, with a shoulder at 405 nm, due to azo-hydrazone tautomerization of the azo (–N=N–) bond. Two other bands at approx. 329 nm and 248 nm are associated with naphthalene and benzene rings, respectively.

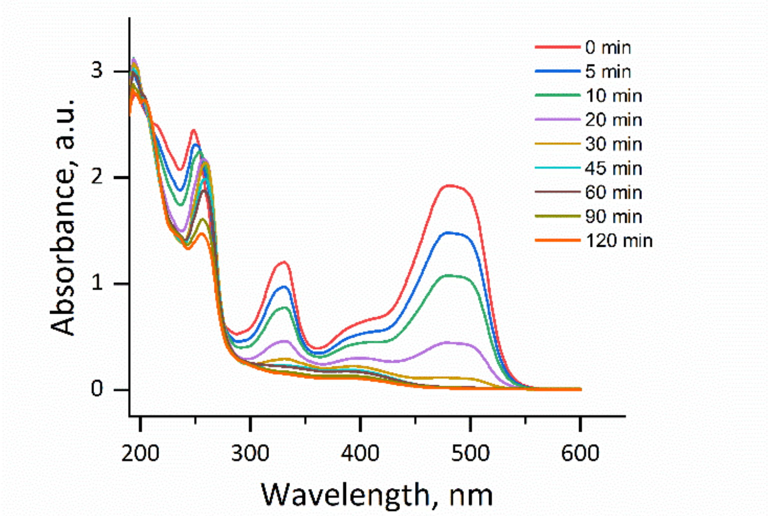


Figure S6. UV-Vis spectra for catalytic degradation of OG using CoA-1000 catalyst ($C_{0,OG}$ = 50 mg dm^{-3}; $V_{OG\ solution}$ = 200 cm^3; $m_{Oxone®}$ = 40 mg; $m_{CoA\text{-}1000}$ = 10 mg; θ = 60 °C)

In Figure S6 UV-Vis spectra for catalytic degradation of OG at 60 °C, using CoA-1000 catalyst are presented. The temperature of 60 °C was chosen because at this temperature complete disappearance of the peak at 478 nm was observed, and the decay of other peaks is clearly visible.

The cleavage of –N=N– bond in the OG molecule is responsible for the decolorization of the reaction solution. This step is proposed as the first step in OG degradation. From Figure S6 it is noticeable that complete decolorization is achieved for the investigated reaction period (both, the peak at 478 nm and the shoulder at 405 nm disappeared). The peak associated with the naphthalene ring disappeared at the same time, indicating that its degradation was happening simultaneously with the decolorization process. On the other hand, the peak at 248 declined slowly, and the new peak at about 258 nm appeared indicating that the aromatic rings were still present in the system after the investigated reaction time at the selected reaction conditions.

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