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Sponge-like europium oxide from hollow carbon sphere as a template for an anode material for Reactive Blue 52 electrochemical degradation

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Abstract

The textile industry is one of the major pollutants of waterbodies with effluents high in biochemical and chemical oxygen demand values, high values of total dissolved solids, total suspended solids, and low dissolved oxygen values along with strong color. The existence of a successful method for its decontamination would be beneficial. In this work, we synthesized sponge-like europium oxide (Eu₂O₃) using a template-directed route from carbon hollow spheres, obtained from glucose as a carbon source. The material synthesis method was done in an aqueous environment, without using any organic solvents. Electrochemical properties of the synthesized material were investigated using cyclic voltammetry and electrical impedance spectroscopy, while morphological characterization was done using scanning electron microscopy and X-ray powder diffraction analysis. Eu₂O₃ were successfully immobilized at the surface of a screen-printed carbon electrode (Eu₂O₃/SPCE) using the drop-casting method. Finally, the prepared electrodes were tested toward the removal of Reactive Blue 52 (RB52) using electrochemical advanced oxidation processes (EAOPs). Important parameters, that is, the supporting electrolyte, its concentration, pH value, and the applied voltage, were optimized for RB52 degradation. The rate of removal was monitored spectrophotometrically and by high-performance liquid chromatography with a diode array detector (HPLC-DAD). It was found that the proposed approach reaches complete decolorization of the RB52 solution after a 60-minute treatment, at pH 5.6 of KCl supporting

electrolyte at a concentration of 0.05 M. Under optimal parameters, after 3 h of treatment, total organic carbon (TOC) was lowered by ~40%. The obtained results indicate that the proposed method may find potential application in EAOPs, considering electrode stability, durability, and efficiency and simplicity of the method.

Keywords: electrochemical advanced oxidation process, modified screen-printed carbon electrode, decolorization, azo dyes, hollow structures

Introduction

The chemical industry processes over 10000 tons of synthetic dyes per year. One of the most used dyes is Reactive Blue 52 (RB52), predominantly used for nylon, wool, leather, and silk dyeing, due to its bright color and excellent solubility [1–3]. Azo dyes, a class of industrial reactive dyes, have one or more azo groups in their structure, with aromatic rings substituted by sulfonate or other groups. The mechanism of their action is based on their structure – they form covalent bonds with hydroxyl or amino groups present on the fiber [4,5].

Today, the removal of organic pollutants is one of the burning problems in environmental chemistry. Effective, low-cost, and easily manipulated processes are mandatory in this field. Electrochemical advanced oxidation processes (EAOP) nowadays present a very attractive approach for this purpose, due to their environmental compatibility, versatility, and easy operation [6–8]. Several research groups, including ours, are extensively dealing with the development of novel materials for this application, based on new nanomaterials and composites as anodes. Belal et al developed a working electrode based on IrO₂/Ti-meshed electrode for the removal of Basic Yellow 28 textile dye in various electrolytes [9] with a removal rate of 93.3%. Shetti et al used a graphene-modified electrode for the degradation of Congo red together with the submicromolar detection [10]. Khan and co-workers proposed the degradation of phenolic azo dyes using gold nanoparticles as electrode material, with more than 90% of dye removal after 40 min of treatment [11]. Pencil graphite electrode showed excellent performances for the removal of Novacron Deep Red C-D and Novacron Orange C-RN azo dyes with 99% and 97% decolorization rates, respectively [12]. Ognjanović and his team investigated the application of differently shaped iron

oxide materials in combination with graphene for the degradation of reactive dye with the full removal rate for 51 min of electrolysis [5,13]. Similarly, Shao and co-workers applied magnetically assembled electrode architecture for azo dyes and phenol removal [14]. A boron-doped diamond electrode was introduced in this field by several research groups with promising results for the removal of various textile dyes [15–21].

Europium oxide, like a rare earth metal oxide, showed excellent electrochemical properties. Therefore, various applications have been reported, especially when it is in the form of nanoparticles carried on adequate support. Teker and Aslanoglu reported a sensitive voltammetric platform for terbutaline detection, based on europium oxide and carbon nanotube coated glassy carbon electrode. The linear response range of the optimized composite material was almost two orders of magnitude, while they achieved a terbutaline detection limit of 3.7 nM. [22] Moreover, Rajaji and colleagues fabricated a graphene oxide decorated with Eu_2O_3 , improved by microwave treatment, to detect chloramphenicol. They applied screen-printed carbon electrodes for detection of this commonly used antibiotic in honey and milk samples at fascinating 1.3 nM. [23] Other than sensing, Eu was involved as photocatalytic material for organic compounds degradation. Rhodamine B and tetracycline were used as model compounds for photocatalytic testing of Eu-doped graphitic carbon nitrides. The hollow lantern-like photocatalyst with an optimal amount of Eu degraded almost 100% of rhodamine B and over 95% of tetracycline under 50 minutes of irradiation. [24] Similarly, Guo and colleagues tested boron- and europium-codoped graphitic carbon nitrides and accomplished over 90% of tetracycline degradation, also under 50 minutes. [25] Europium oxide was also described as a promising material for pseudocapacitors, for its unique redox properties and excellent electrode stability, but owing to its poor conductivity it is usually coupled with other materials (graphene oxide, conductive polymers, mixed oxides, doping, etc.). [26–28] Based on the above-mentioned examples, this material can be an encouraging alternative for the EAOP application.

Hollow micro- or nanostructures are reported to be beneficial for various applications, due to their large surface area and low density. Furthermore, it seems that the extent of the use of hollow structures in diverse shapes still has not been thoroughly exploited. Lately, researchers have shown an increased interest in the template-based synthesis of organic and inorganic hollow structures, because they provide uniform products with well-controlled morphology at micro- and nano-scale.

[29] Resulting hollow structures, often with templates being removed prior to use, have found numerous applications, such as drug delivery [30], catalysis [31], as sensors [32], to name a few. Moreover, several studies employed template hollow structures for environmental remediation, like adsorption [33] or removal of various organic pollutants [34]. Based on their versatile applications, we wanted to test the properties of Eu_2O_3 as a photocatalytic material, but synthesized using carbon nanospheres as a template to achieve maximum surface area.

The main idea of this work is to prepare europium oxide with a unique structure, via controlled synthesis using a template-based procedure and to investigate the possible practical application of such materials in the removal of organic pollutants. The obtained material was characterized using morphological and electrochemical methods, and its application toward removal of RB52 was shown. Operating parameters of the applied method were investigated and, under optimized conditions, the material showed effective removal of the water pollutant, with a satisfactory decrease of the total organic carbon value.

Experimental

Chemicals

Reactive Blue 52 was purchased from Clariant, Switzerland, and used without further purification. Glucose (D-(+)-glucose, anhydrous, 99%, Alfa Aesar, Germany), ethanol (96% v/v, Sigma Aldrich), and ultra-pure water (Milli-Q water system, Millipore, MA, USA) we used for hollow spheres preparation. Europium (III) oxide (Eu_2O_3 , 99.99%, Merck, Germany), HNO_3 (65 wt.%, Suprapur[®], Merck KGaA, Darmstadt, Germany), distilled water, ammonia (28-30% v/v, Sigma Aldrich), and *N,N*-Dimethylformamide (DMF, 99.8%, v/v, Sigma Aldrich) were used to produce europium oxide material. All chemicals used in this study were of analytical grade and used as received. Ultrapure water (Milli-Q water system, Millipore, MA, USA; $18.2 \text{ M}\Omega\cdot\text{cm}$ at $25 \text{ }^\circ\text{C}$, and a TOC value below 5 ppb) was used for the solution preparation, while KCl and Na_2SO_4 (both $\geq 99\%$ and purchased from Sigma Aldrich) were tested as supporting electrolytes.

Synthesis of materials

Carbon spheres template. Colloidal carbon spheres were synthesized by the hydrothermal method, according to modified procedure by Jia et al [35]. Briefly, 8 g of glucose were dissolved in 35 mL of ultra-pure water, and then autoclaved at $160 \text{ }^\circ\text{C}$ ($\pm 2 \text{ }^\circ\text{C}$) for 9 h in a Teflon-lined stainless-steel

autoclave. The autoclave was naturally cooled to ambient temperature overnight. The resulting black-brown precipitate was washed with ultra-pure water and ethanol (96%, v/v) five times by centrifugation at 5000 rpm for 10 min. The precipitate was dried at 60 °C in an air-dried oven.

Sponge-like Eu_2O_3 . The $\text{Eu}(\text{NO}_3)_3$ aqueous solution was prepared by dissolving europium (III) oxide in diluted HNO_3 with heating and stirring. In order to obtain 1 mmol of $\text{Eu}(\text{NO}_3)_3$, 176.0 mg (0.5 mmol) of Eu_2O_3 was weighed and dissolved in 2 mL of HNO_3 solution (1:8, v/v) and distilled water was added up to 20 mL. To the resulting clear solution was added 90 mg of carbon spheres which were well dispersed in an ultrasonic bath for 20 min. Five mL of ammonia aqueous solution (1:9, v/v) was added dropwise to the mixture during 30 minutes, with vigorous stirring. The resulting mixture was then heated at 60 °C for 3 h gentle stirred. The precipitate was separated by centrifugation, washed with water and 70% ethanol, and dried at 60 °C. The final product, Eu_2O_3 with sponge-like morphology, was obtained through a calcination process at 800 °C for 2 h in air with a heating rate of 2 °C/min.

Electrode Preparation. The screen-printed carbon electrodes were produced from carbon ink (No. C50905DI, Gwent, Pontypool, UK) and laser pre-etched ceramic supports (No. CLS 641000396 R, Coors Ceramics GmbH, Chattanooga, TN, USA). Thick layers of carbon ink were formed by brushing the ink through an etched stencil (thickness 100 μm , electrode printing area 100 mm^2) with the aid of a screen-printing device (SP-200, MPM, Franklin, MA, USA) onto the ceramic supports. The resulting plates were dried overnight at room temperature. Each modified screen-printed electrode was prepared by dropping 60 μl of suspension of synthesized material in DMF onto the electrode surface and allowing it to dry for 3 h.

Characterization of materials

The morphology and surface properties of carbon spheres and the Eu_2O_3 used for SPCE modification were examined using a field emission scanning electron microscope FE-SEM MIRA3 (Tescan, Czech Republic) at an accelerating of 30 keV. The samples were fixated on a holder with conductive tape, vacuum dried, and spray-coated with gold using Sputter coater. The size of carbon spheres was determined by manual measurement of one hundred carbon spheres using the ImageJ public software. For the determination of mean size (d_{SEM}), standard deviation

(SD), and an index of polydispersity (*PdI*), the ImageJ data were fitted to a log-normal function

$$(y = y_0 + \frac{A}{\sqrt{2\pi}\omega x} e^{-\frac{[\ln \frac{x}{xc}]^2}{2\omega^2}}).$$

The material's crystal structure was determined using X-ray powder-diffraction (XRD) data performed on dried powders in a SmartLab (Rigaku, Japan) diffractometer that uses Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The patterns were collected within the 10-60° 2 θ range at a scan rate of 0.04 °/min under a voltage of 40 kV and the current 30 mA. The crystallite size was calculated using the Scherrer equation ($d_{hkl} = \frac{K\lambda}{\beta \cos \theta}$) for the most intensive diffraction peak.

Degradation experiments were performed in undivided cells containing 30 mL of the tested dye equipped with unmodified or modified screen-printed electrodes with an active surface area of 100 mm² (25×4 mm) as working electrodes. During all experiments, magnetic stirring ensured the homogeneity of the solution. Experiments were carried out under galvanostatic conditions, with adjustable DC power supply PS3010 (0–32 V DC, 0–10 A) E-HQ™. A UV-Visible spectrophotometer (Evolution 200 Series, Thermo Fisher Scientific, Bremen, Germany) was used for monitoring decolorization rates at the maximum absorption wavelength $\lambda_{max} = 615 \text{ nm}$.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were obtained using an electrochemical workstation (CHI 760B, CHInstrumentns, Austin, USA). The cell was equipped with a three-electrode system, comprising a working electrode (modified or unmodified screen-printed electrode), a reference electrode (Ag/AgCl 3 M KCl), and a counter (platinum wire). All measurements were made at ambient temperature.

HPLC-DAD (ThermoFisher Scientific, Ultimate 3000 RS, Germany) was used for the additional evaluation of RB52 degradation. Samples (10 μ l, kept at 25 °C), previously filtered using Syringe filters (PTFE membrane, 0.45 μ m, 25 mm, Agilent Technologies), were eluted using ammonium-acetate (as component A; 10 mM, pH 5.2) and acetonitrile (as B component), at 0.5 mL/min. The column Hypersil Gold C8 (150mm ×3 mm, 3 μ m, ThermoFisher Scientific, Germany) was kept at 30 °C. The analytes were eluted in the following gradient mode: 0-1 min 5%, 3-5 min 10%, 6 min 20%, 10-12 min 70%, and 15-20 min 5% of the eluent B. The detector was set at 615 nm, 390 nm, 280 nm, and 254 nm.

Results and discussion

Morphological, structural and electrochemical analysis of materials

The sponge-like europium oxide (Eu_2O_3) were prepared using a template-directed route from hollow carbon spheres obtained from glucose, a readily available substance. Unlike some previously mentioned studies [9,10,36], which included HF treatment of Ti sheets, Al powder, or HAuCl_4 , the most expensive and environmentally unfriendly part of the proposed procedure for the Eu_2O_3 material preparation was Eu_2O_3 . Other chemicals and techniques needed for here investigated material are accessible and facile to perform. Scanning electron microscopy (SEM) was used (**Figure 1**) for morphological and size analysis. The synthesized carbon nanoparticles, shown in **Figure 1A**, were spherically shaped and uniform in size, with an average diameter of (162 ± 15) nm, which is less than Jia and coworkers reported (350-400 nm) [35]. The carbon nanoparticles undergo log-normal size distribution, as displayed in the inset of **Figure 1A**. After the statistical analysis, the calculated *SD* value of 0.73 and *PDI* of 10.3% were obtained. This suggests that carbon spheres are a suitable template for the synthesis of Eu_2O_3 , because aggregation and condensation lead to the porous structure of the resulting material, as stated elsewhere [35,37]. Moreover, a carbon sphere template permits a repeatable synthesis of the oxide material from metal salts, while the template is removed thermally as a gaseous CO_2 [35].

The sponge-like Eu_2O_3 hollow material, after the thermal removal of carbon spheres, is formed in a heavily branched structure, filled with spherical vacancies (**Figure 1B**). The size of the cavities at ~ 1.8 microns is roughly ten times higher than the C nanotemplate. This difference probably arose as a consequence of the expansion of the material during thermal treatment. Nevertheless, Eu_2O_3 possesses a high surface area that is preferable for environmental use.

>>>>HERE FIGURE 1<<<<

The crystal structure and microstructure of the prepared carbon template, as well as the sponge-like Eu_2O_3 , were determined using the XRD data (**Figure 2**). The diffraction of amorphous carbon spheres (*black line*) resulted in a characteristic broad peak at $\sim 22^\circ$ [38]. On the contrary, two remaining diffractograms (*red and green lines*) resulted in crystal reflections occurring at the same

position as those of europium oxide and can be indexed to $I2_13$ space group of the body-centered cubic unit cell (JCPDS #86-2476) [39]. The lack of any other phase is an indication of purity of the synthesized Eu_2O_3 and that this material can be used for further studies. The use of the Scherrer equation of the most intensive reflection (222) at $28.4^\circ 2\theta$ resulted in approximate crystallite size of 18.2 nm for $\text{Eu}_2\text{O}_3/\text{C}$ and 24.7 nm for Eu_2O_3 . It is worth mentioning that the average crystallite size seems to increase, which can be explained by the expansion originating from the thermal treatment.

>>>>HERE FIGURE 2<<<<

Electrochemical impedance spectroscopy is a powerful method for the evaluation of interfacial properties of modified electrodes and, in combination with cyclic voltammetry, can provide important information about modification processes, as well as to confirm successful immobilization of the modifiers at the electrode surface. With this in mind, we investigated the electrochemical behavior of the modified electrodes in a solution containing 5 mM $\text{Fe}^{2+/3+}$ in 0.1 M KCl supporting electrolyte, using these techniques. EIS measurements were done in the frequency region from 0.01 Hz to 1×10^5 Hz. The results are given in **Figure 3 A-C**. In all cases, EIS spectra (**Figure 3A**) consisted of a semi-circular part at higher frequencies corresponding to the electron-transfer resistance (R_{et}) and a linear part at lower frequencies belonging to the diffusion-limited processes, while the introduction of the nanoparticles at the bare SPCE surface ($\text{Eu}_2\text{O}_3/\text{SPCE}$) was followed with a decrease in the semi-circular part (R_{ct}) of the EIS spectra. This decrease in the R_{ct} can be explained by the increase in the interfacial properties of the modified electrode, and enhance the transportation of electrochemically-produced charges at the solution/electrode interface. Similar results were confirmed with the CV measurements (**Figure 3B**). Compared with the unmodified electrode, $\text{Eu}_2\text{O}_3/\text{SPCE}$ showed an increase in the redox currents of the $\text{Fe}^{2+/3+}$ couple. However, slight shifts in the peak potentials are noticeable. This can be attributed to modified electrodes that are made of a heterogeneous material, which very often exhibits slower electron transfer than homogeneous carbon electrodes, such as glassy carbon electrode. Moreover, such electrodes also have higher resistance depending on the composition of the printed layer and its thickness. The combination of these factors results in wider peak separation and higher background currents even for reversible processes, which is very well

documented in numerous papers. Also, with the increase of the scan rate during the CV measurements, gradual shifts in the peak potential with the increase of the peak current were reported (**Figure 3C**), indicating that adsorption processes also occur at the surface of the modified electrode. For the calculation of effective electrodes surface area, Randles-Sevcik equation ($I_p = 0.443 \left(\frac{F^3}{RT}\right) n^{3/2} A D_0^{1/2} \nu^{1/2} c_0^*$) was applied [40], in which I_p is the peak current, F represents the Faraday constant, R the universal gas constant, T is the absolute temperature, n the number of electrons involved in the reaction ($n = 1$), A refers to the surface area of electrodes, D is the diffusion coefficient of $K_3[Fe(CN)_6]$, ν is scan rate, and c_0^* is the concentration of testing solution of $K_3[Fe(CN)_6]$. The value of A was calculated as the best linear fit for the function $I_p = f(\nu^{1/2})$, and the obtained active electrode surface areas were 0.079 cm^{-2} and 0.105 cm^{-2} for bare SPCE and $Eu_2O_3/SPCE$, respectively.

>>>>HERE FIGURE 3<<<<

Degradation of Reactive Blue 52

To investigate the activity of the proposed material, electrochemical degradation of RB52 was tested using bare SPCE and $Eu_2O_3/SPCE$. The concentration of RB52 was 15 mg/mL, the applied voltage 3 V, and the supporting electrolyte 0.05 M KCl. This study was conducted at the native pH of the RB52 solution (pH 5.6), without additional adjustment of the pH. Results are given in **Figure 4**. After a 50-minute electrolysis, the concentration of RB52 was reduced in both cases. However, the electrode modified with Eu_2O_3 showed faster degradation and dye removal. It can be concluded that the synthesized material accelerates the degradation of the pollutants, which can be related to the increase in OH^- yield with the modification of the bare electrode. The obtained results are consistent with previous electrochemical investigations. From these studies, we can infer that the incorporation of europium oxide as the working layer of the electrode can reduce the required working potential by promoting the electron transmission and enhancing the electron transfer reaction at the screen-printed electrode surface.

>>>>HERE FIGURE 4<<<<

Effect of operating parameters on the removal efficiency of $\text{Eu}_2\text{O}_3/\text{SPCE}$

Important factors that affect the removal efficiency of the electrochemical method, the choice of electrolyte (sodium sulfate or potassium chloride) and its concentration (0.01, 0.02, 0.05, 0.07, and 0.1 M), starting pH value (3.6, 5.6, 8.2, and 10.0), and dye concentration (15, 20, and 30 mg/L), were optimized before the investigation of the method's practical applicability through total organic carbon (TOC) analysis. The results are summarized in **Figure 5 A-C**. Firstly, we investigated the effect of the supporting electrolyte (**Figure 5A**). A significant improvement in the degradation rate was achieved with potassium chloride as a supporting electrolyte. Knowing that KCl is one of the best water-based electrolytes, this result can be additionally attributed to the low potential for chlorine evolution (1.36 V) and probably to the formation of reactive chlorinated species with the oxidation of the chloride anion. Selection of the appropriate concentration of the supporting electrolyte can lead to an effective degradation. Higher supporting electrolyte concentration could contribute to waste of chemicals with unnecessary high currents, which in turn leads to an increase in testing solution temperature after the treatment. We tested several concentrations of the KCl and it was found that the optimum supporting electrolyte, with a maximum in degradation efficiency of RB52 was 0.05 M KCl (**Figure 5B**). In this supporting electrolyte, the optimal power utilization, with no or negligible changes in the solution temperature after the treatment, was achieved. Furthermore, we optimized the starting pH value of the solution to achieve ideal efficiency with minimal chemical waste (**Figure 5C**). As can be seen, the decolorization was not favorable in basic media. A relevant reason could be that the reduction potential of the half-reaction under high pH conditions is much lower than under standard conditions (pH = 0), in which radical generation is favorable. Optimal degradation was obtained in the native dye solution – pH 5.6. This result can be indicative for the possible practical applicability of the method proposed here, as the amount of additional chemicals required for the degradation of RB52 is minimal. The concentration of the pollutant strongly affected the degradation rate and energy efficiency. We investigated the optimal RB52 concentration in a range from 15 to 30 mg/L at previously optimized parameters. The best results were achieved with the initial concentration of 15 mg/L and this concentration was used for further studies. A higher

concentration of RB52 can prevent contact between pollutant molecules and active sites at the electrode surface. Also, the obtained degradation products can compete with the parent pollutant and block the active surface. Thus, the selected starting concentrations, together with previously optimized parameters, contributed to an effective, high-rate degradation of the RB52 using the electrochemical advanced oxidation method.

>>>>HERE FIGURE 5<<<<

TOC removal efficiency using the proposed method and electrode recyclability

Under fully optimized parameters, the total organic carbon removal was monitored using $\text{Eu}_2\text{O}_3/\text{SPCE}$ during RB52 electrolysis. The TOC removal was monitored only after the full decolorization of RB52, which was achieved in less than one hour of the treatment, and then it was tracked for 3 hours of the electrolysis. It was found that the full decolorization of the starting dye, with the initial TOC = 9.2 mg/L, was followed with the TOC removal of only ~10% (TOC = 8.3 mg/L), while additional treatment of the solution, for two more hours, caused further decomposition of the initial electrolysis products and TOC reduction by 40% (TOC = 5.5 mg/L). These studies were monitored using HPLC and the corresponding chromatogram is shown in **Figure 6A**. **Figure 6B** shows the extended degradation kinetics, compared to **Figure 5**. Within the first 30 minutes, over 80% of RB52 was decomposed.

It is worth mentioning that electrode recyclability was monitored. Ten successive degradation processes were done using one $\text{Eu}_2\text{O}_3/\text{SPCE}$ as a working electrode, under optimized parameters. The decolorization efficiency did not decrease significantly (from 100% to 94% of tested solution absorbance) after ten cycles. It can be concluded that the proposed electrode system possesses satisfactory recyclability and stability.

>>>>HERE FIGURE 6<<<<

The comparison of the obtained degradation results for $\text{Eu}_2\text{O}_3/\text{SPCE}$ with similar found in the recent literature, in which electrochemical systems have proposed different RB dyes removal, is presented in Table 1. In comparison, our efficiencies were similar, based on degradation times and TOC values after the treatment, with the advantage of lower applied voltage, which leads to lower electricity consumption (Table 1).

Table 1. Comparison of the present results with electrochemical degradation of Reactive Blue found in the literature

Electrode	Pollutant	Electrolyte	Applied voltage (V)	Pollutant removal efficiency (%) / time (min)	TOC removal (%) / time (min)	Reference
IONF@RGO /SPCE	Reactive Blue 52	0.05 M KCl	3	99/30	40/60	[5]
Ti/SnO ₂ /SbO _x /RuO ₂	Reactive Blue 4	0.2 M Na ₂ SO ₄	2.4	100/60	60/60	[41]
Co _{47.5} /C _{47.5} -PVC5	Reactive Blue 21	0.5 M NaCl	20	94/90	/	[42]
Lead oxide/mesh steel	Reactive Blue 19	Water	10	90/120	56/120	[43]
rGO/Gr	Reactive Turquoise Blue 21	0.034 M NaCl	7.1	96/15	/	[44]
Eu ₂ O ₃ /SPCE	Reactive Blue 52	0.05 M KCl	3	100/60	40/180	<i>The present study</i>

/ - data not provided

Conclusions

In this work, we proposed an electrochemical degradation procedure for the removal of Reactive Blue 52. The electrode material was sponge-like europium oxide, synthesized over a hollow carbon sphere template. The electrode material was characterized using electrochemical, spectroscopic, and chromatographic methods. After an investigation of process parameters, a satisfactory removal of total organic carbon was reported, with long stability and recyclability of the electrode. The proposed method can be easily applied because it requires a minimal amount of chemicals, it has a relatively low cost, and a short treatment time. This study showed that the size of the cavities is very responsible for the efficiency of degradation. Small particles give the larger surface area to volume ratio and this can be accompanied by an increase in surface absorption and a general decrease in the active surface area of the electrode. In contrast, larger particles increase pore size, while the effective surface area is often smaller. In the following research, we will deal in detail with this phenomenon and try to improve the results so far by synthesizing composites of our material with some of the carbon materials.

CRedit author statement

Dalibor M. Stanković – Investigation, project administration, supervision, writing – original draft, conceptualization, **Andrej Kukuruzar**, **Ivona M. Janković-Častvan** – Investigation, conceptualization, **Sladana Savić** – Investigation, writing – original draft, data curation, writing – review & editing, **Miloš Ognjanović**, **Bratislav Antić** – Investigation, formal analysis, writing original draft, writing – review & editing, **Goran Roglić** – Methodology, **Dragan Manojlović** – Resources, writing – original draft, **Biljana Dojčinović** – Project administration, writing – original draft.

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Figure captions:

Figure 1. FE-SEM micrographs of A) Carbon hollow spheres and B) Sponge-like Eu_2O_3 .

Figure 2. XRD patterns of carbon spheres (black line), Carbon@ Eu_2O_3 (red line), and Eu_2O_3 after the thermal treatment. The standard pattern of Eu_2O_3 (JCPDS card #86-2476) is displayed in the figure for comparison.

Figure 3. A) EIS spectra of the bare SPCE and Eu_2O_3 /SPCE; B) CV voltammograms at 50 mV/s for bare SPCE and Eu_2O_3 /SPCE; C) CV voltammograms at various scan rates at Eu_2O_3 /SPCE. Testing solution 5 mM of $\text{Fe}^{2+/3+}$ in 0.1 M KCl.

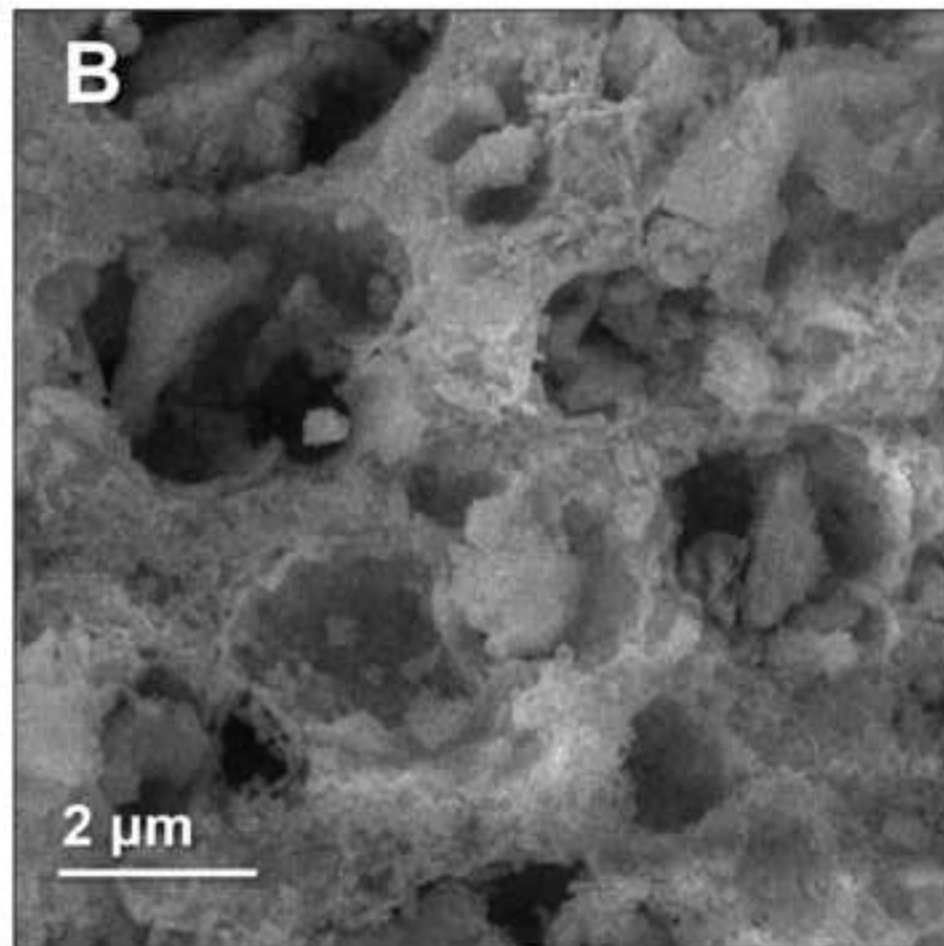
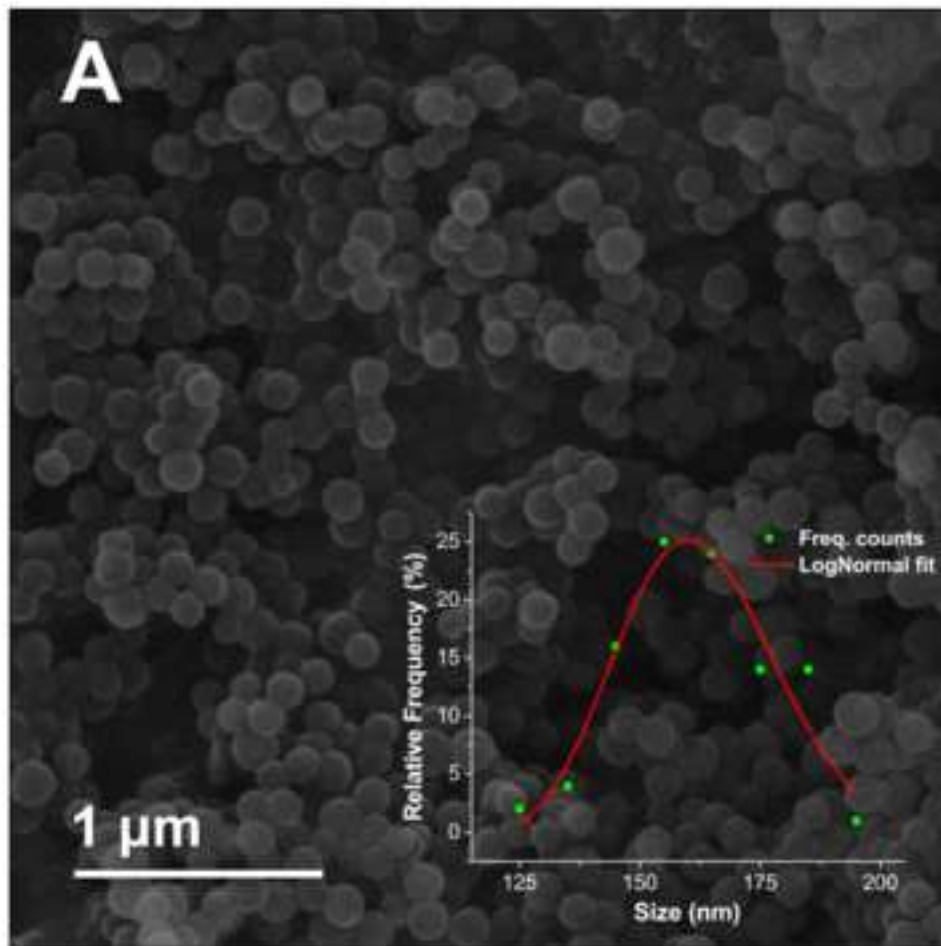
Figure 4. Comparison between bare and modified SPCE toward removal of RB52. Applied voltage 3 V, supporting electrolyte KCl at native pH (5.6) of the solution of the dye

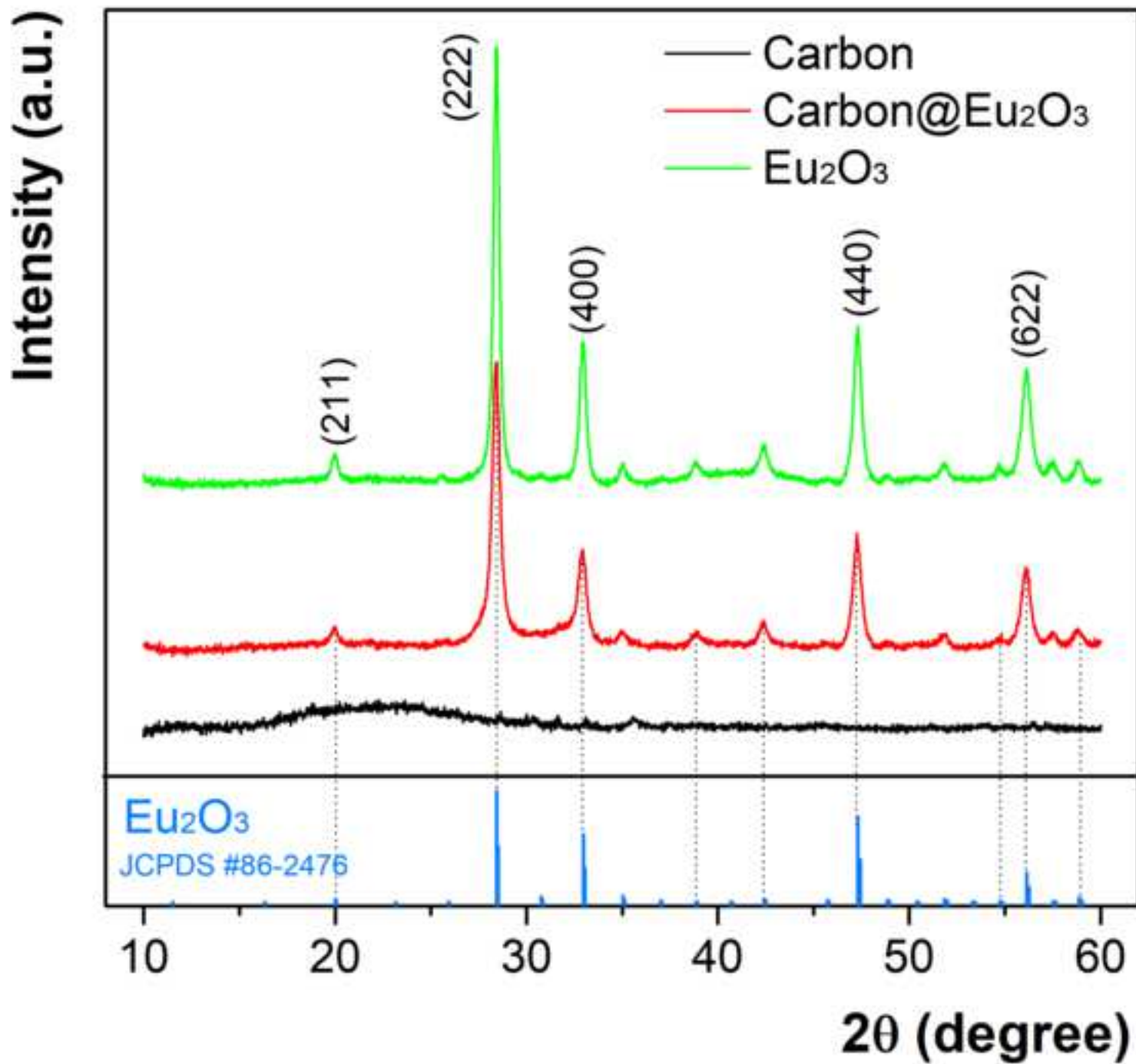
Figure 5. A) Effect of the supporting electrolyte for the removal of the RB52; B) Effect of the concentration of the supporting electrolyte for the removal of the RB52; C) Effect of the starting pH for the removal of the RB52

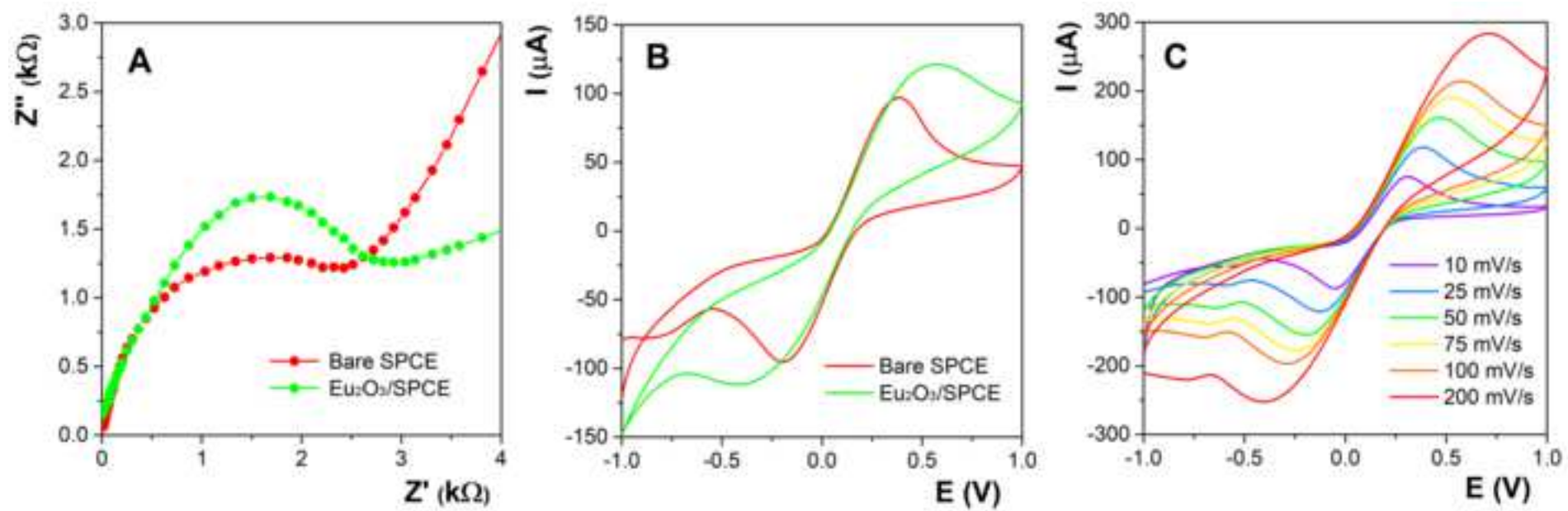
Figure 6. A) Chromatogram of RB52 samples in KCl (0.05 M), pH 5.6 using Eu_2O_3 /SPCE, monitored on HPLC-DAD, 615 nm; B) The decrease of RB52 concentration after 3 hours of treatment, quantified by HPLC-DAD, 280 nm.

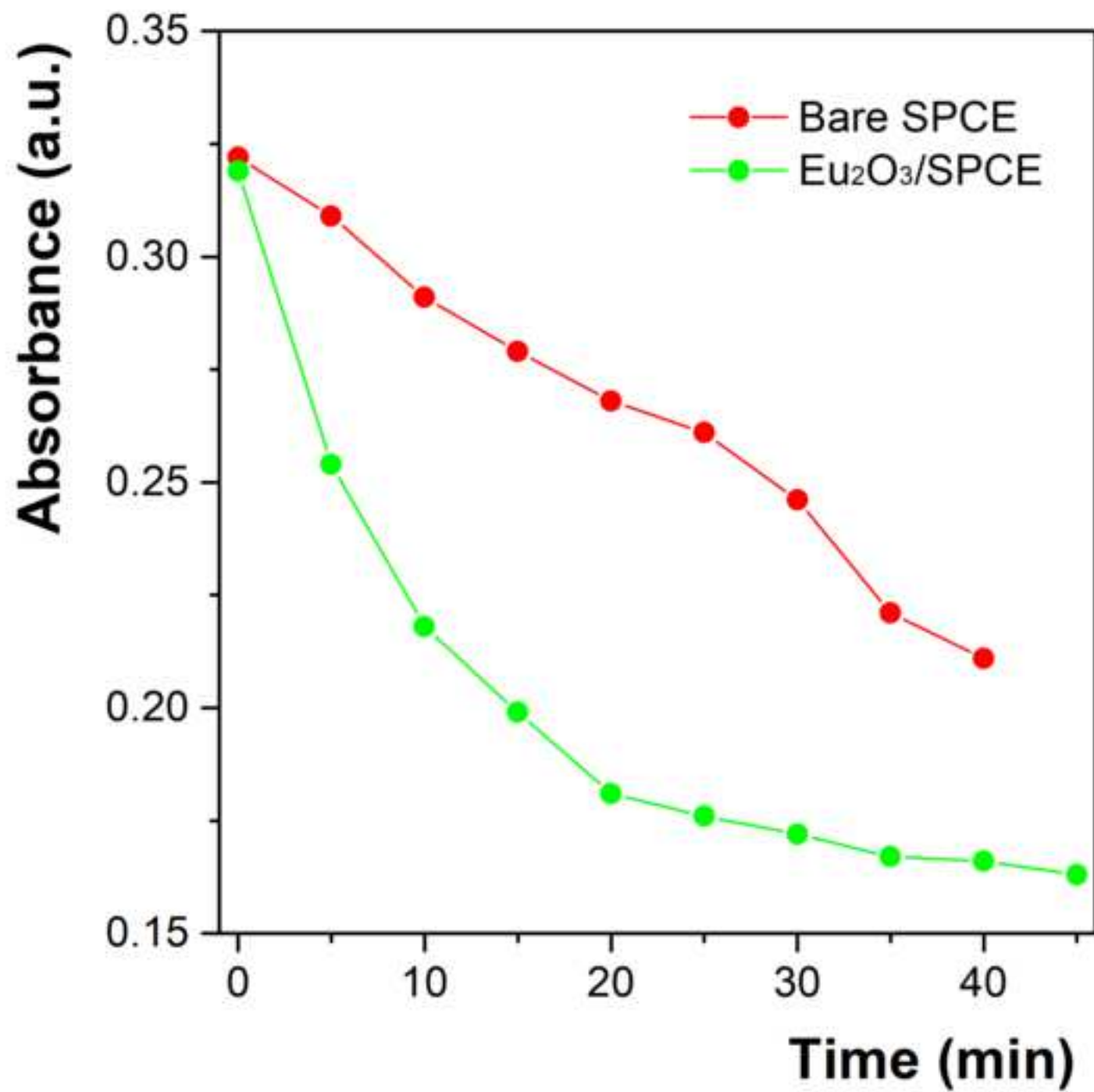
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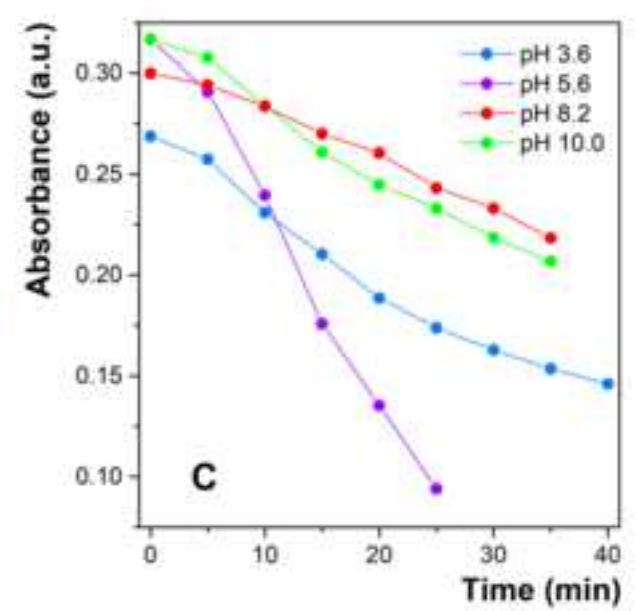
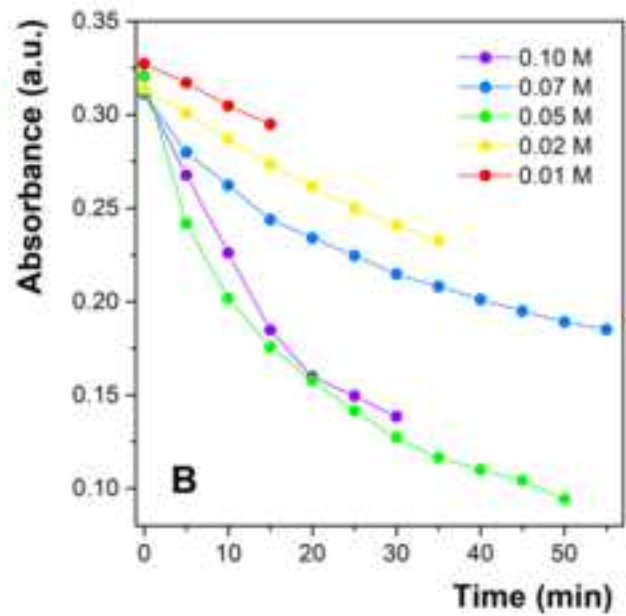
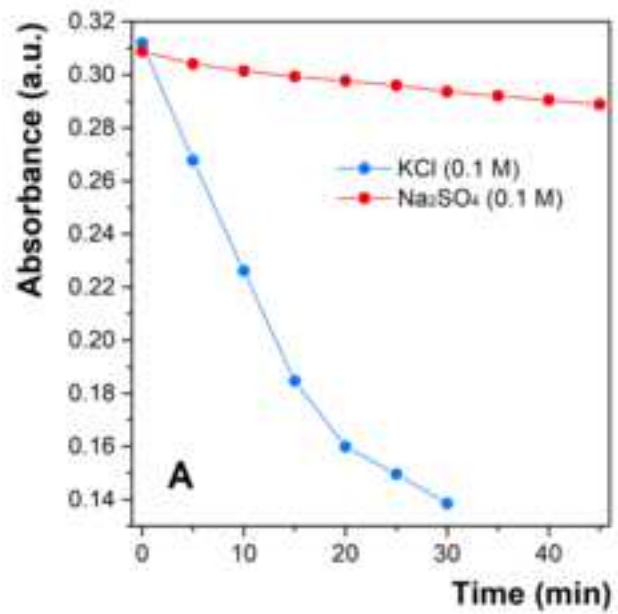
Dalibor M. Stanković – Investigation, project administration, supervision, writing – original draft, conceptualization, **Andrej Kukuruzar**, **Ivona M. Janković-Častvan** – Investigation, conceptualization, **Sladana Savić** – Investigation, writing – original draft, data curation, writing – review & editing, **Miloš Ognjanović**, **Bratislav Antić** – Investigation, formal analysis, writing original draft, writing – review & editing, **Goran Roglić** – Methodology, **Dragan Manojlović** – Resources, writing – original draft, **Biljana Dojčinović** – Project administration, writing – original draft.

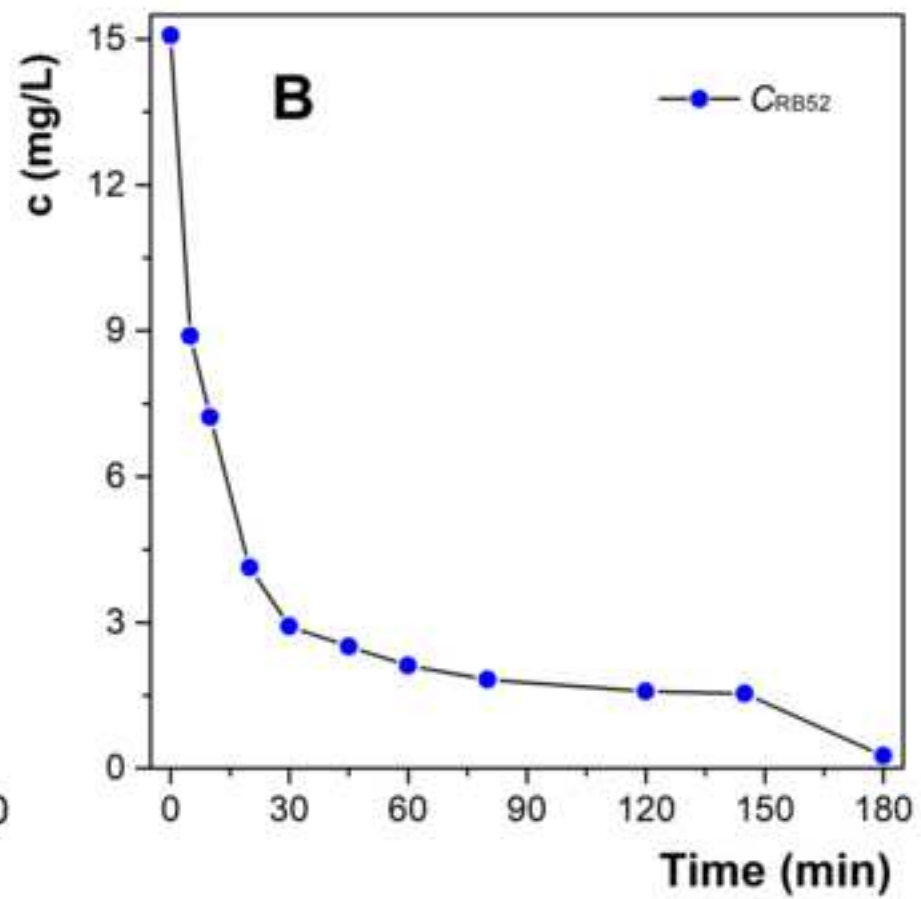
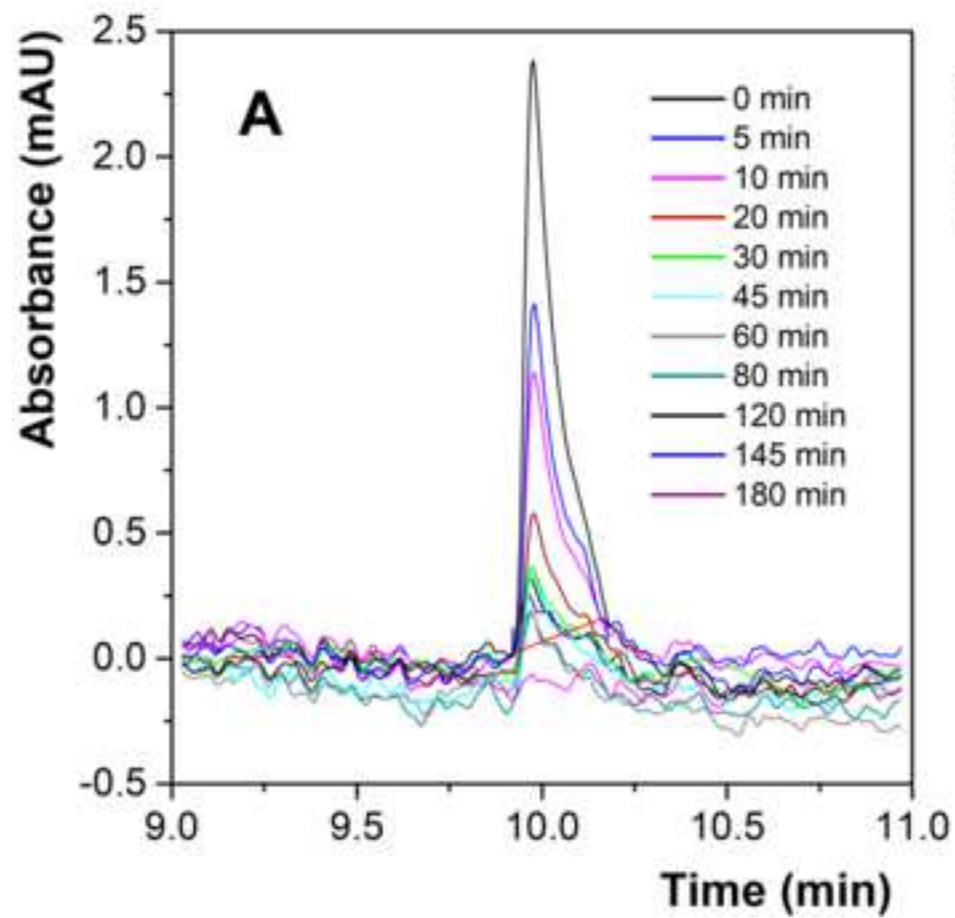




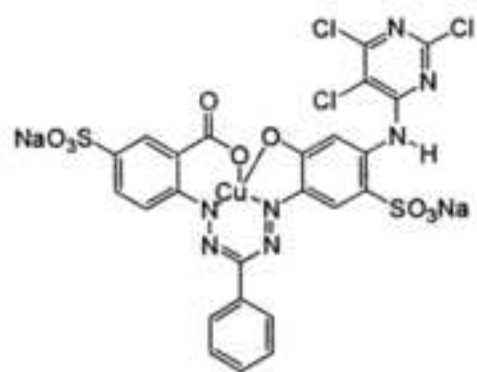




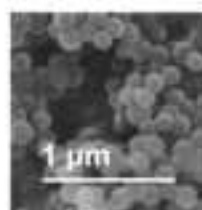




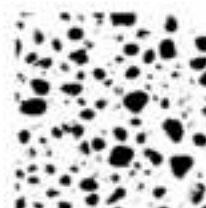
Electrochemical AOP



Reactive Blue 52



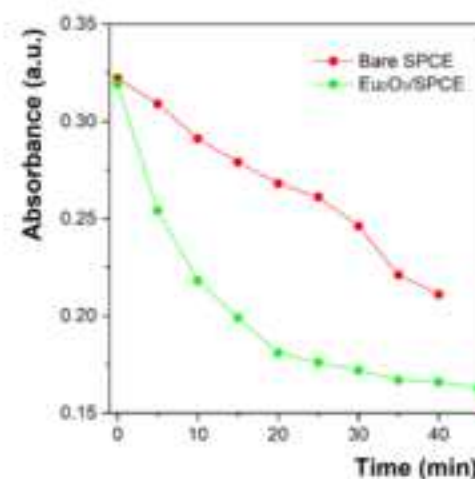
carbon hollow spheres



Eu_2O_3



$\text{Eu}_2\text{O}_3/\text{SPCE}$



Decolorization