

# Real-time in-situ monitoring using visible spectrophotometry as a tool for probing electrochemical advanced oxidation processes for dye decolorisation

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## SUPPORTING INFORMATION

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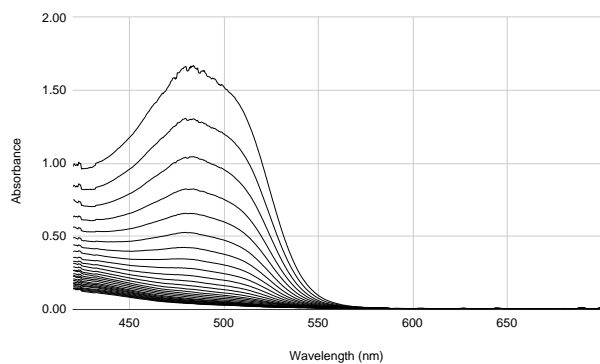
## **STL Files for 3D Printed Apparatus**

.stl Files for the 3D-Printed Continuous Monitoring System can be accessed at:

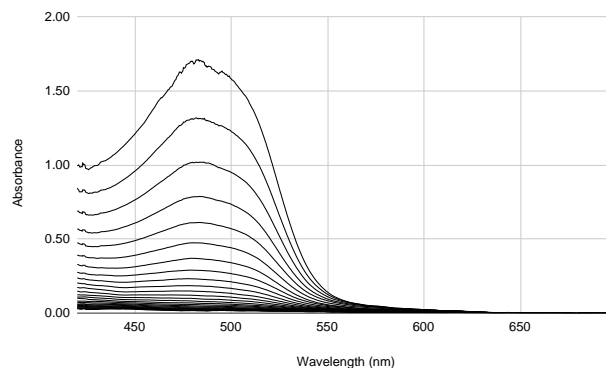
<https://drive.google.com/drive/folders/1mJG3-UcBzAMPNOvbM13GWpU37FFQ-Xp4?usp=sharing>

## Acid Orange 7 (AO7)

### Absorbance spectra

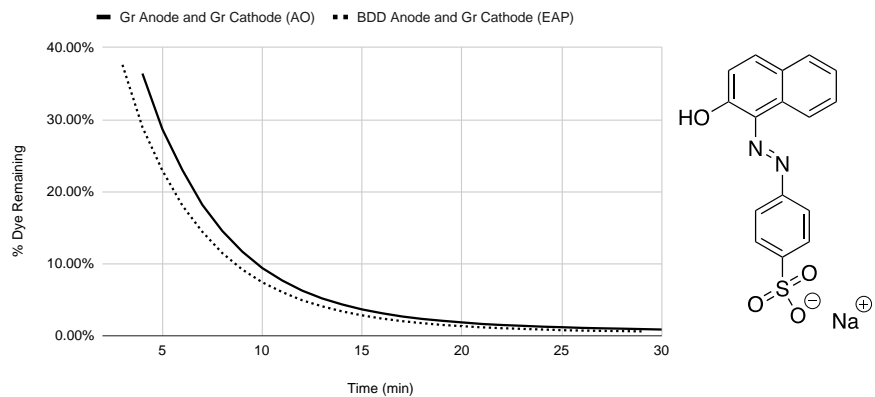


**Figure 1:** AO absorbance spectrum of AO7. Conditions: graphite anode, graphite cathode, [AO7] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 4 - 30 min. Trial 1 of 3.



**Figure 2:** EAP absorbance spectrum of AO7. Conditions: BDD anode, graphite cathode, [AO7] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 4 - 30 min. Trial 1 of 3.

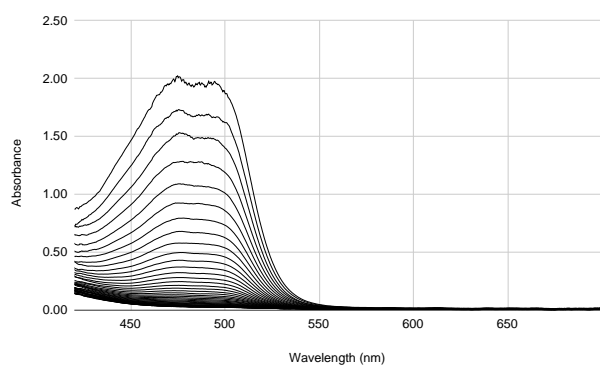
### Plot of percent dye remaining vs time



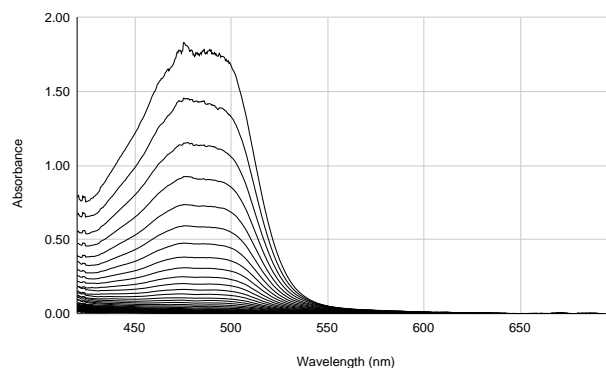
**Figure 3:** AO- and EAP-mediated decolorisation of Acid Orange 7 as a function of time at a  $\lambda_{max}$  = 484.16 nm.

## Acid Orange 10 (AO10)

### Absorbance spectra

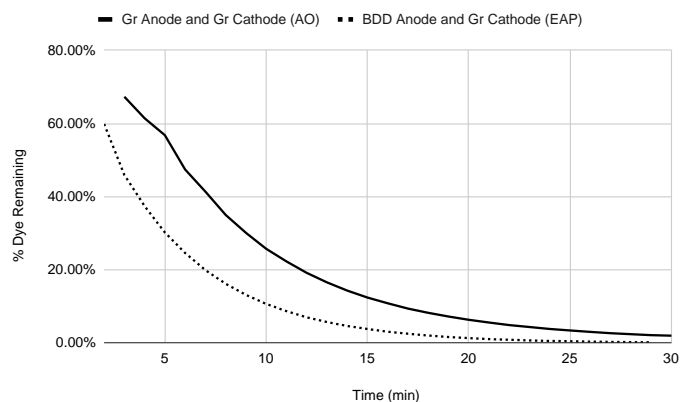


**Figure 4:** AO absorbance spectrum of AO10. Conditions: graphite anode, graphite cathode, [AO10] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 4 - 30 min. Trial 1 of 3.



**Figure 5:** EAP absorbance spectrum of AO10. Conditions: BDD anode, graphite cathode, [AO10] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 4 - 30 min. Trial 1 of 3.

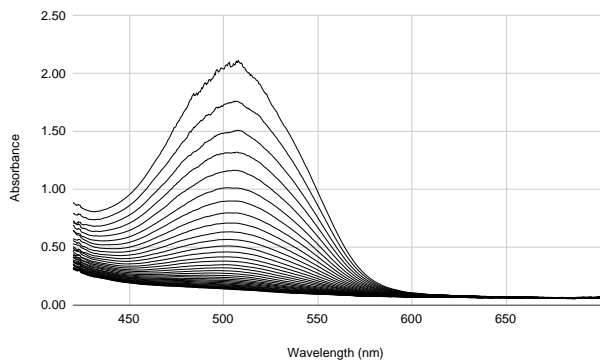
### Plot of percent dye remaining vs time



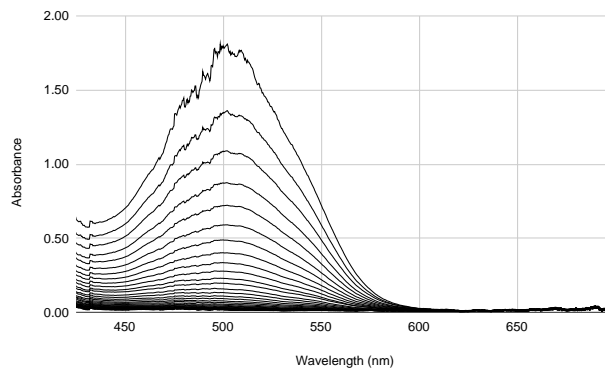
**Figure 6:** AO- and EAP-mediated decolorisation of AO10 as a function of time at a  $\lambda_{max}$  = 475.54 nm.

## Acid Red 18 (AR18)

Absorbance spectra

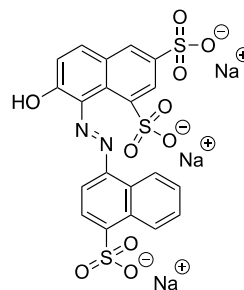
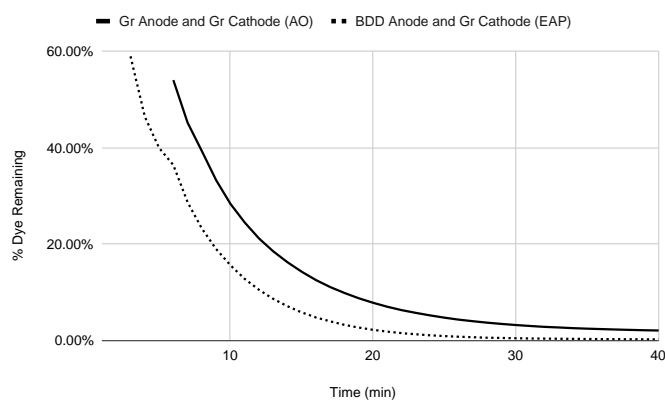


**Figure 7:** AO absorbance spectrum of AR18. Conditions: graphite anode, graphite cathode, [AR18] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 6 - 40 min. Trial 1 of 3.



**Figure 8:** EAP absorbance spectrum of AR18. Conditions: BDD anode, graphite cathode, [AR18] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 6 - 40 min. Trial 1 of 3.

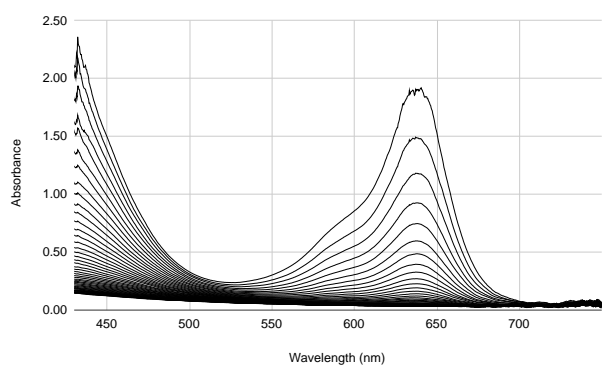
Plot of percent dye remaining vs time



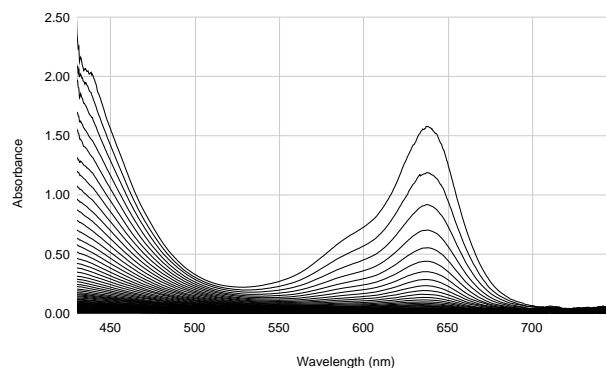
**Figure 9:** AO- and EAP-mediated decolorisation of AR18 as a function of time at a  $\lambda_{max}$  = 507.02 nm.

## Acid Blue 1 (AB1)

### Absorbance spectra

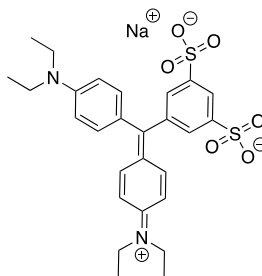
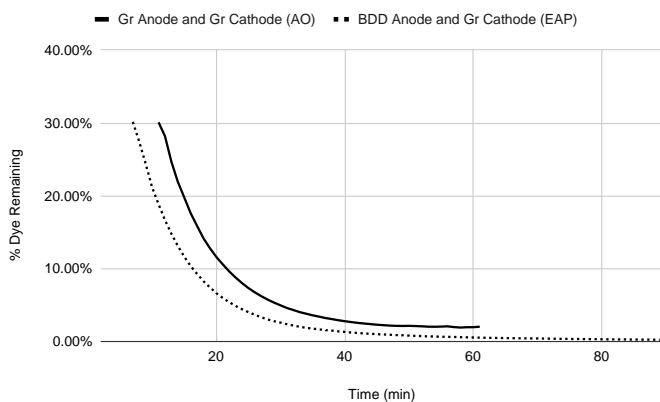


**Figure 10:** AO absorbance spectrum of AB1. Conditions: graphite anode, graphite cathode, [AB1] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 10 - 60 min. Trial 1 of 3.



**Figure 11:** EAP absorbance spectrum of AB1. Conditions: BDD anode, graphite cathode, [AB1] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 9 - 60 min. Trial 1 of 3.

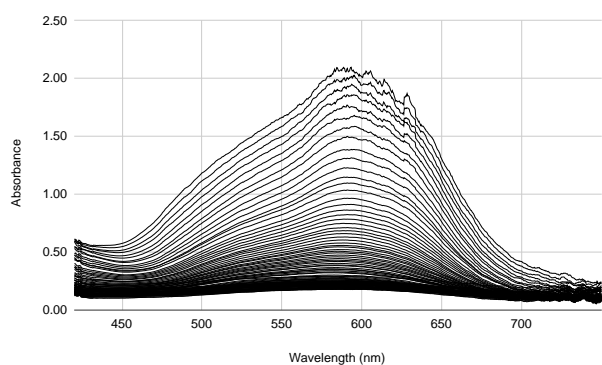
### Plot of percent dye remaining vs time



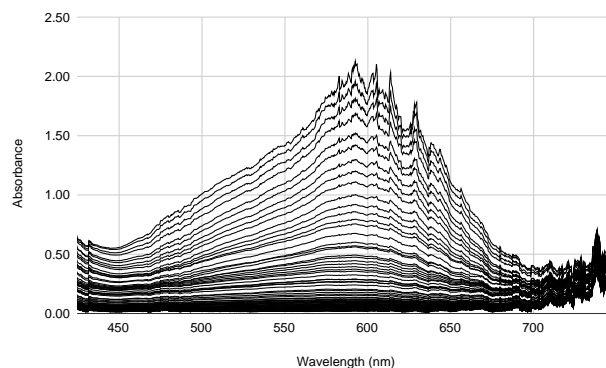
**Figure 12:** AO- and EAP-mediated decolorisation of AB1 as a function of time at a  $\lambda_{max}$  pH 0.62 = 436.82 nm,  $\lambda_{max}$  pH 7 = 638.04 nm.

## Basic Violet 3 (BV3)

### Absorbance spectra

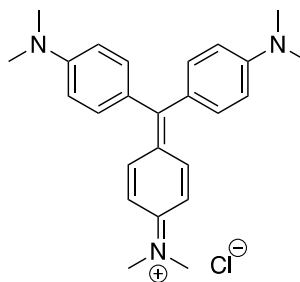
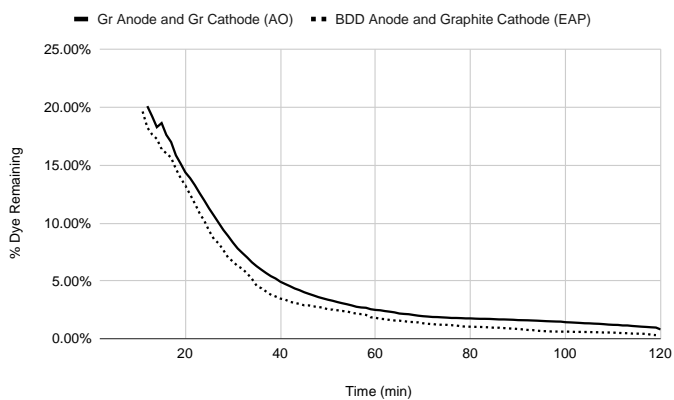


**Figure 13:** AO absorbance spectrum of BV3. Conditions: graphite anode, graphite cathode, [BV3] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 19 - 120 min. Trial 1 of 3.



**Figure 14:** EAP absorbance spectrum of BV3. Conditions: BDD anode, graphite cathode, [BV3] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 19 - 120 min. Trial 1 of 3.

### Plot of percent dye remaining vs time

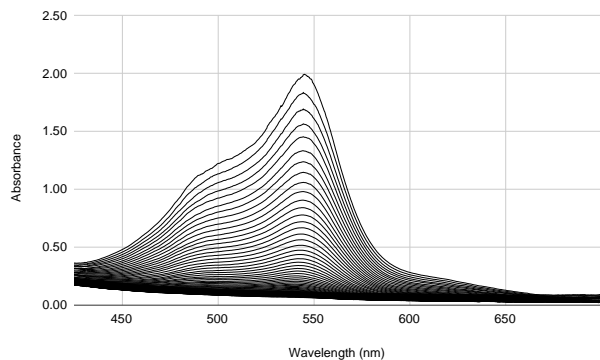


**Figure 15:** AO- and EAP-mediated decolorisation of BV3 as a function of time at a  $\lambda_{max}$  = 589.09 nm.

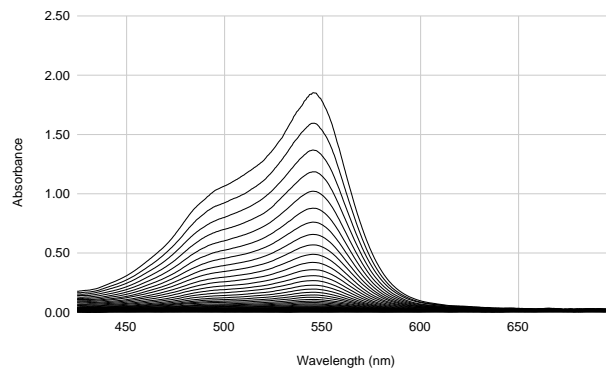


## Acid Violet 19 (AV19)

Absorbance spectra

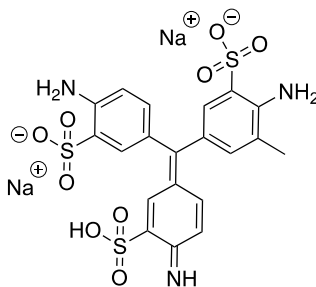
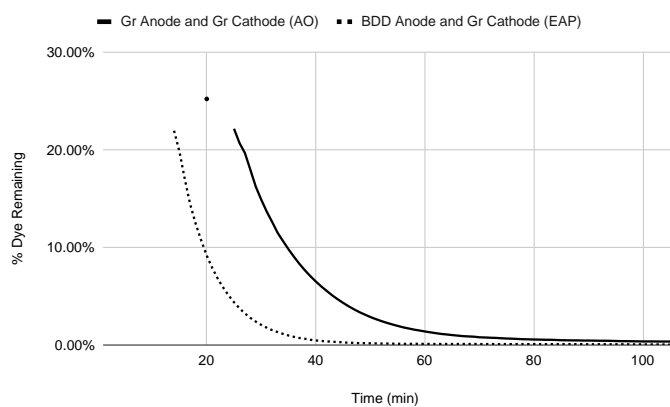


**Figure 16:** AO absorbance spectrum of AV19. Conditions: graphite anode, graphite cathode, [AV19] = 100  $\mu\text{M}$ , [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 25 - 105 min. Trial 1 of 3.



**Figure 17:** EAP absorbance spectrum of AR18. Conditions: BDD anode, graphite cathode, [AR18] = 100  $\mu\text{M}$ , [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 14 - 105 min. Trial 1 of 3.

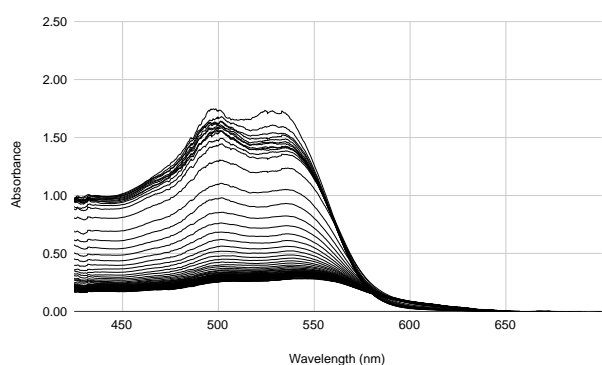
Plot of percent dye remaining vs time



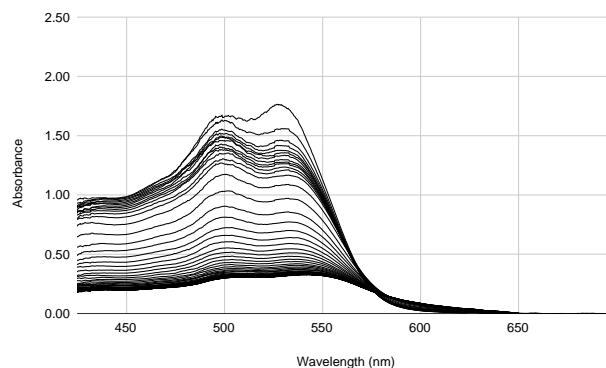
**Figure 18:** AO- and EAP-mediated decolorisation of AV19 as a function of time at a  $\lambda_{max}$  = 545.20 nm.

## Acid Red 51 (AR51)

### Absorbance spectra

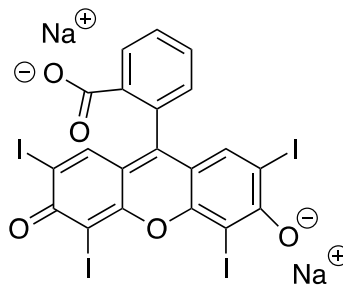
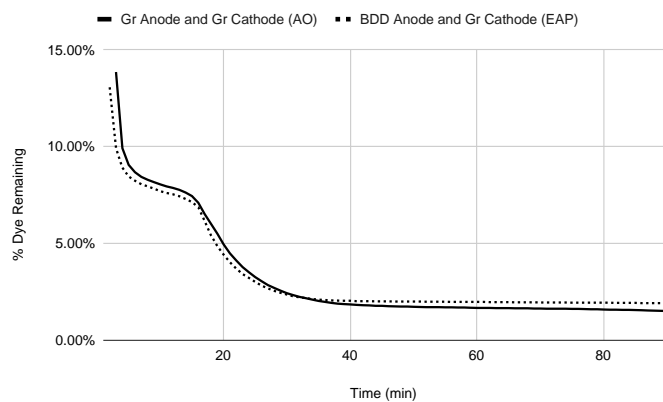


**Figure 19:** AO absorbance spectrum of AR51. Conditions: graphite anode, graphite cathode, [AR51] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 3 - 90 min. Trial 1 of 3.



**Figure 20:** EAP absorbance spectrum of AR51. Conditions: BDD anode, graphite cathode, [AR51] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 3 - 90 min. Trial 1 of 3.

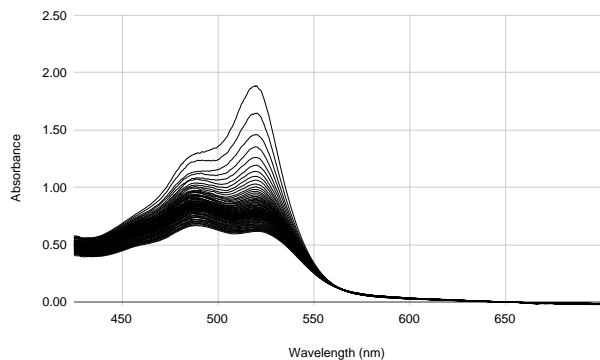
### Plot of percent dye remaining vs time



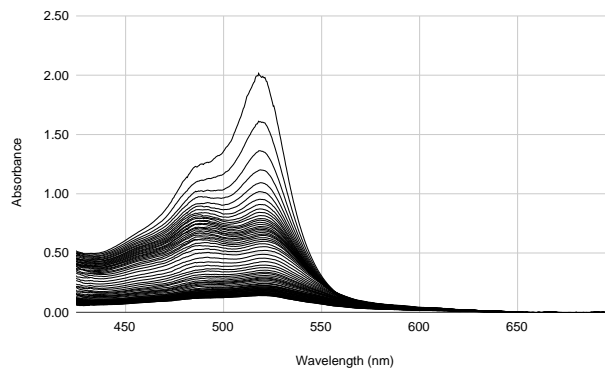
**Figure 21:** AO- and EAP-mediated decolorisation of AV19 as a function of time at a  $\lambda_{max}$  = 525.47 nm.

## Acid Red 87 (AR87)

Absorbance spectra

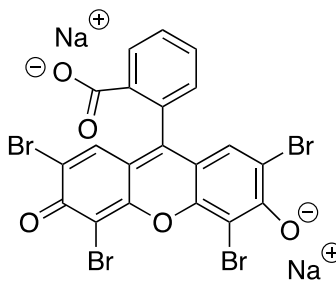
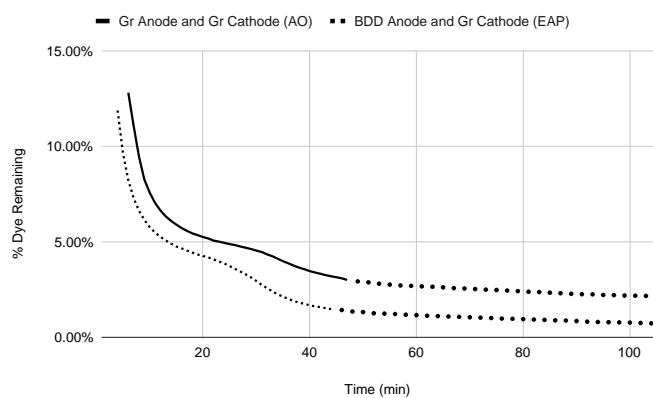


**Figure 22:** AO absorbance spectrum of AR87. Conditions: graphite anode, graphite cathode, [AR87] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 6 - 59 min, then every other minute until 105 min. Trial 1 of 3.



**Figure 23:** EAP absorbance spectrum of AR87. Conditions: BDD anode, graphite cathode, [AR87] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 5 - 59 min, then every other minute until 105 min. Trial 1 of 3.

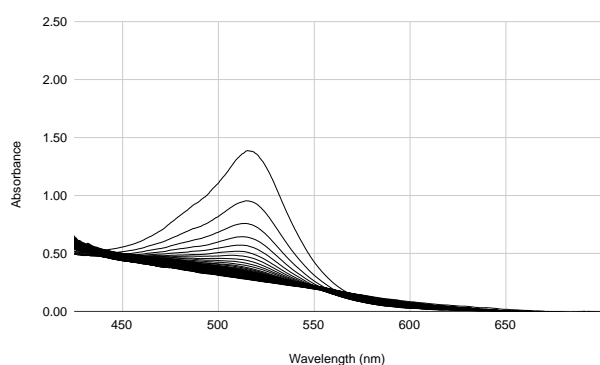
Plot of percent dye remaining vs time



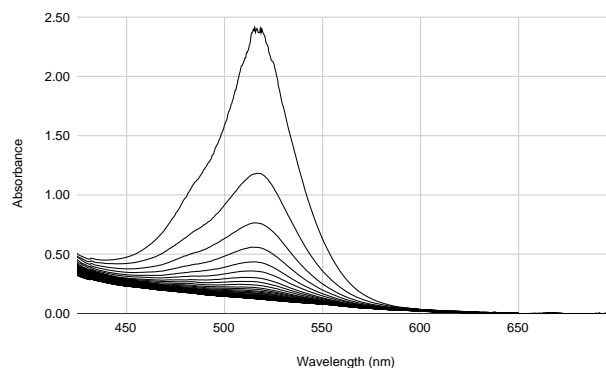
**Figure 24:** AO- and EAP-mediated decolorisation of AR87 as a function of time at a  $\lambda_{max}$  = 515.90 nm.

## Acid Red 91 (AR91)

### Absorbance spectra

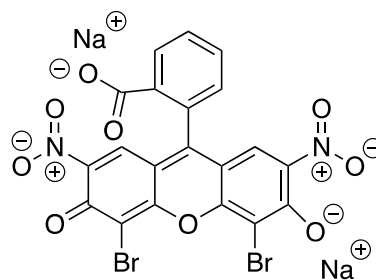
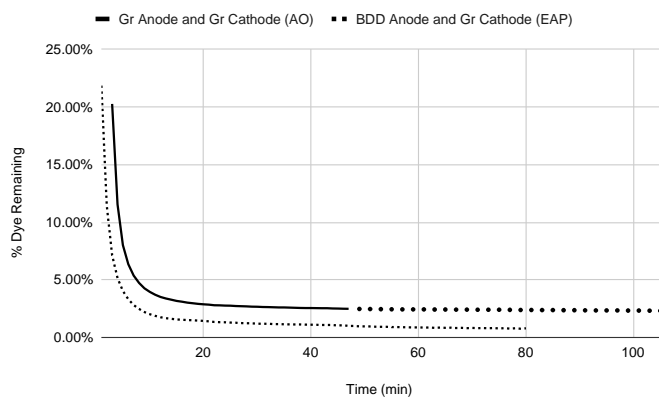


**Figure 25:** AO absorbance spectrum of AR91. Conditions: graphite anode, graphite cathode,  $[AR91] = 100\mu\text{M}$ ,  $[Na_2S_2O_8] = 14\text{ mM}$ , stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 2 - 45 min, then every other minute until 105 min. Trial 1 of 3.



**Figure 26:** EAP absorbance spectrum of AR18. Conditions: BDD anode, graphite cathode,  $[AR18] = 100\mu\text{M}$ ,  $[Na_2S_2O_8] = 14\text{ mM}$ , stirring = 1000 rpm, current = 5 mA, overlay spectrum recorded every minute from 1 - 80 min. Trial 1 of 3.

### Plot of percent dye remaining vs time



**Figure 27:** AO- and EAP-mediated decolorisation of AR91 as a function of time at a  $\lambda_{max} = 519.45\text{ nm}$ .

## First order rate constants

**Table 1:** First order rate constants at 20 min for nine dyes under two decolorisation protocols. AO conditions: Graphite anode and cathode, [Dye] = 100  $\mu\text{M}$ , [ $\text{Na}_2\text{S}_2\text{O}_8$ ] = 14 mM, stirring = 1000 rpm,  $I$  = 5 mA. EAP conditions: BDD anode, graphite cathode, [Dye] = 100  $\mu\text{M}$ , [ $\text{Na}_2\text{S}_2\text{O}_8$ ] = 14 mM, stirring = 1000 rpm,  $I$  = 5 mA.

	Acid Orange 7	Acid Orange 10	Acid Red 18	Acid Blue 1	Basic Violet 3	Acid Violet 19	Acid Red 51	Acid Red 87	Acid Red 91
AO ( $\text{k s}^{-1}$ )	$3.51 \times 10^{-3}$	$2.42 \times 10^{-3}$	$2.12 \times 10^{-3}$	$1.87 \times 10^{-3}$	$1.64 \times 10^{-3}$	$1.15 \times 10^{-3}$	$2.59 \times 10^{-3}$	$2.47 \times 10^{-3}$	$2.97 \times 10^{-3}$
EAP ( $\text{k s}^{-1}$ )	$3.71 \times 10^{-3}$	$3.48 \times 10^{-3}$	$3.17 \times 10^{-3}$	$2.17 \times 10^{-3}$	$1.64 \times 10^{-3}$	$1.99 \times 10^{-3}$	$2.60 \times 10^{-3}$	$2.61 \times 10^{-3}$	$3.54 \times 10^{-3}$