

# Use of real-time *in situ* monitoring as a tool for comparison of electrochemical advanced oxidation processes for the decolourisation of azo and indigoid dyes

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## SUPPORTING INFORMATION

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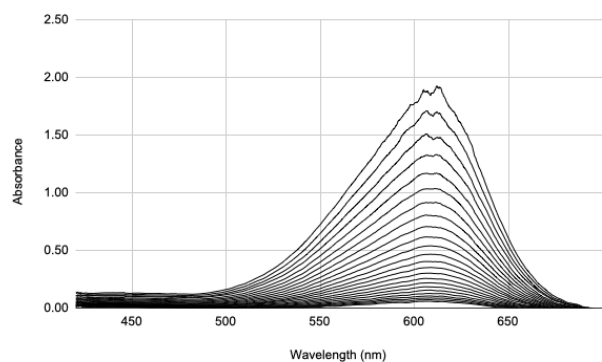
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## **STL Files for 3D Printed Apparatus**

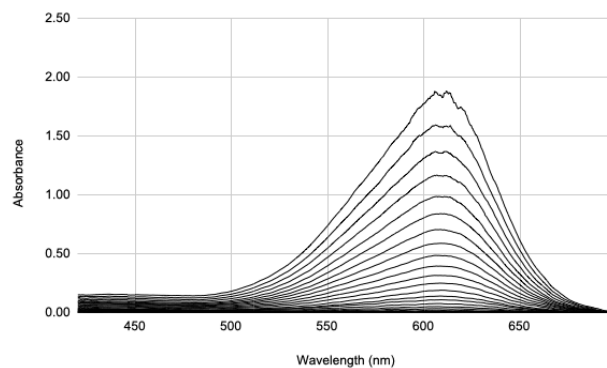
.stl Files for the 3D-Printed Continuous Monitoring System can be accessed at:

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

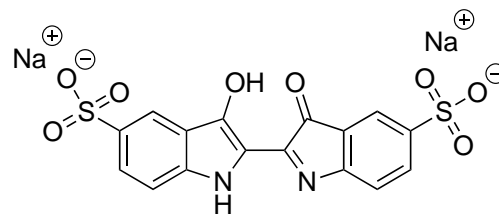
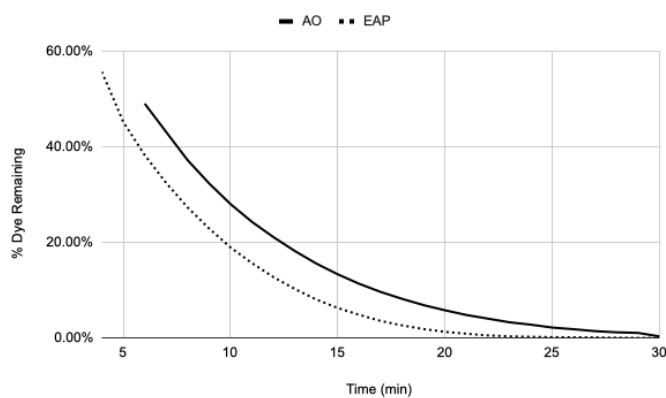
## Indigo Carmine (IC)



**Figure 1:** AO absorbance spectrum of IC. Conditions: graphite anode, graphite cathode, [IC] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 6 - 30 min. Trial 1 of 3.

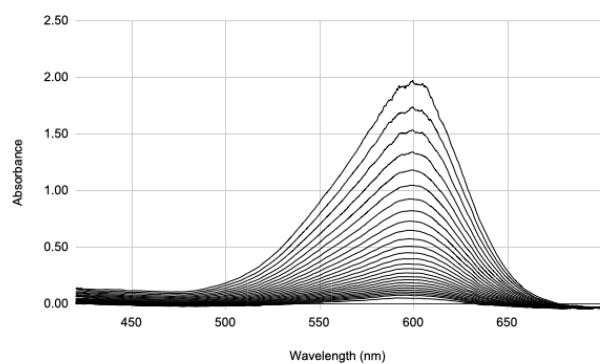


**Figure 2:** EAP absorbance spectrum of IC. Conditions: BDD anode, graphite cathode, [IC] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 5 - 30 min. Trial 1 of 3.

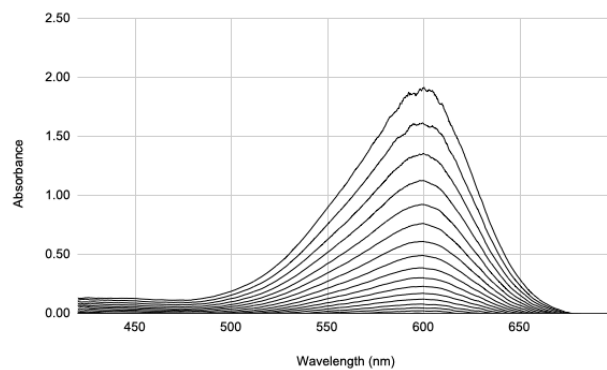


**Figure 3:** AO- and EAP-mediated decolourisation of IC as a function of time at a  $\lambda_{max}$  = 606.31 nm.

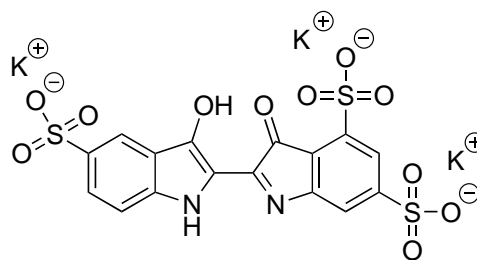
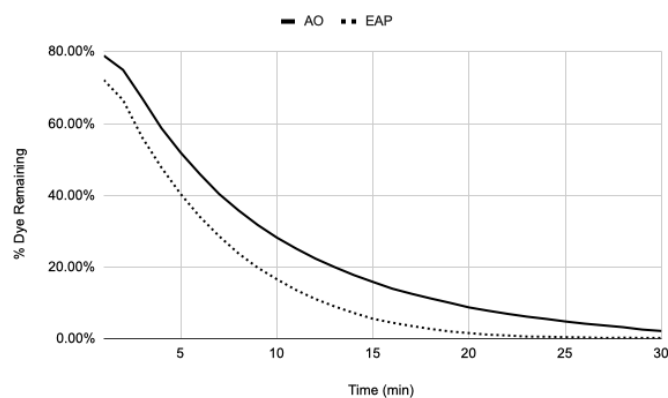
## Potassium Indigotrisulfonate (KIT)



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

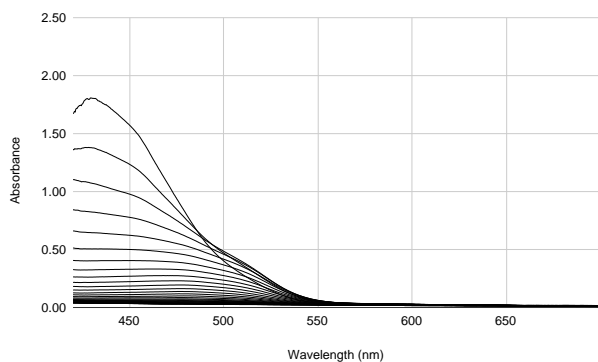


**Figure 5:** EAP absorbance spectrum of KIT. Conditions: BDD anode, graphite cathode, [KIT] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 2 - 30 min. Trial 1 of 3.

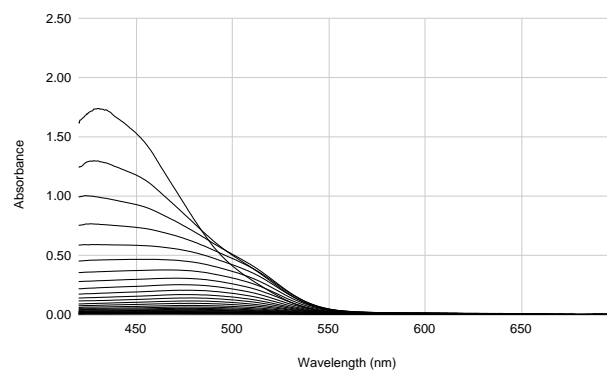


**Figure 6:** AO- and EAP-mediated decolourisation of KIT as a function of time at a  $\lambda_{max}$  = 599.44 nm.

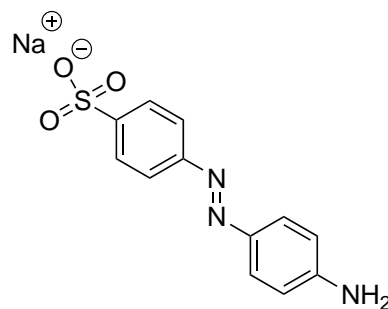
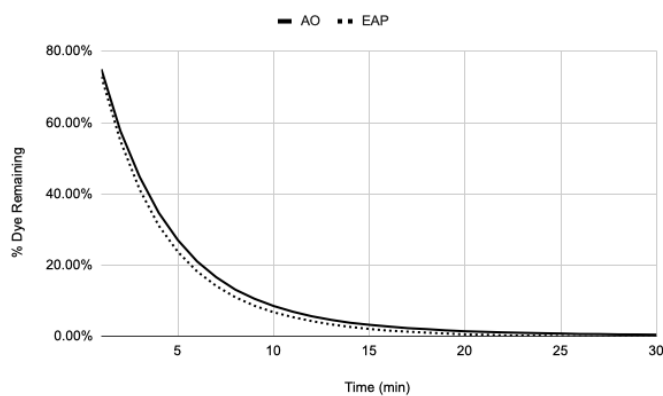
## Food Yellow 6 (FY6)



**Figure 7:** AO absorbance spectrum of FY6. Conditions: graphite anode, graphite cathode, [FY6] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 1 - 30 min. Trial 1 of 3.

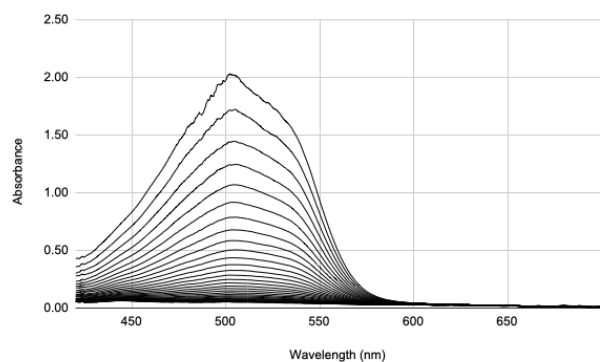


**Figure 8:** EAP absorbance spectrum of FY6. Conditions: BDD anode, graphite cathode, [FY6] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 1 - 30 min. Trial 1 of 3.

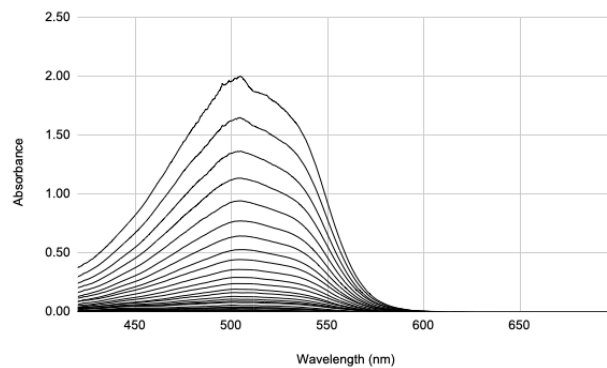


**Figure 9:** AO- and EAP-mediated decolourisation of FY6 as a function of time at a  $\lambda_{max}$  = 425.15 nm.

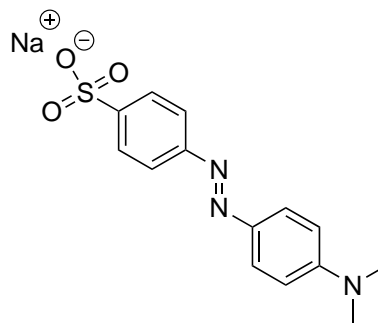
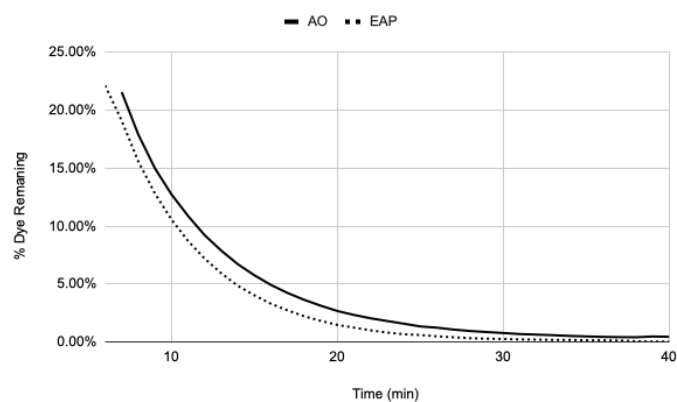
## Methyl Orange (MO)



**Figure 10:** AO absorbance spectrum of MO. Conditions: graphite anode, graphite cathode,  $[MO] = 100 \mu\text{M}$ ,  $[\text{Na}_2\text{S}_2\text{O}_8] = 14 \text{ mM}$ , stirring = 1000 rpm,  $I = 5 \text{ mA}$ , overlay spectrum recorded every minute from 7 - 40 min. Trial 1 of 3.

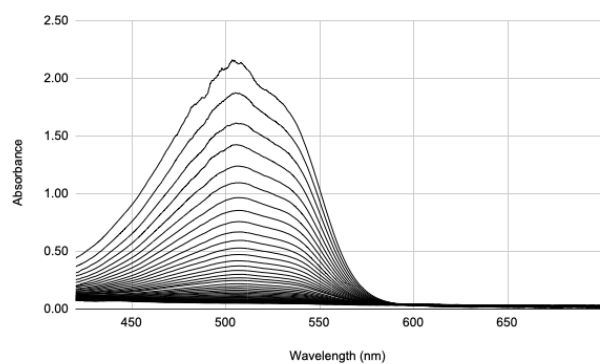


**Figure 11:** EAP absorbance spectrum of MO. Conditions: BDD anode, graphite cathode,  $[MO] = 100 \mu\text{M}$ ,  $[\text{Na}_2\text{S}_2\text{O}_8] = 14 \text{ mM}$ , stirring = 1000 rpm,  $I = 5 \text{ mA}$ , overlay spectrum recorded every minute from 6 - 40 min. Trial 1 of 3.

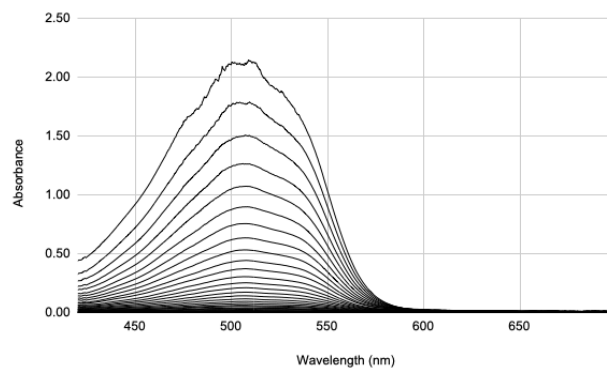


**Figure 12:** AO- and EAP-mediated decolourisation of MO as a function of time at a  $\lambda_{\text{max}}$  pH 0.62 = 436.82 nm,  $\lambda_{\text{max}}$  pH 7 = 507.66 nm.

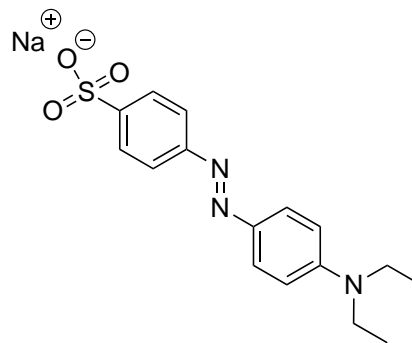
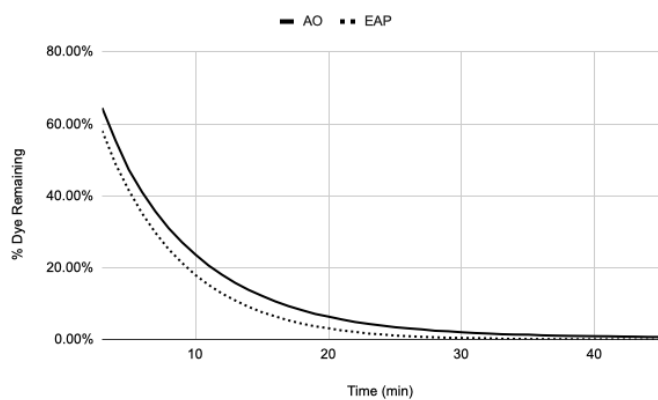
## Ethyl Orange (EO)



**Figure 13:** AO absorbance spectrum of EO. Conditions: graphite anode, graphite cathode, [EO] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 4 - 45 min. Trial 1 of 3.

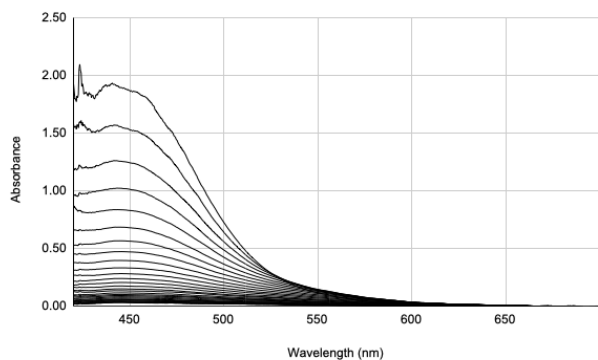


**Figure 14:** EAP absorbance spectrum of EO. Conditions: BDD anode, graphite cathode, [EO] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 3 - 45 min. Trial 1 of 3.

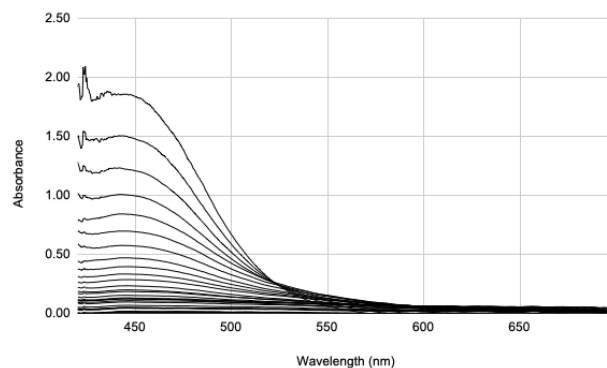


**Figure 15:** AO- and EAP-mediated decolourisation of EO as a function of time at a  $\lambda_{max}$  = 508.09 nm.

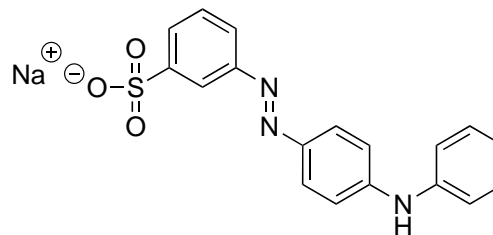
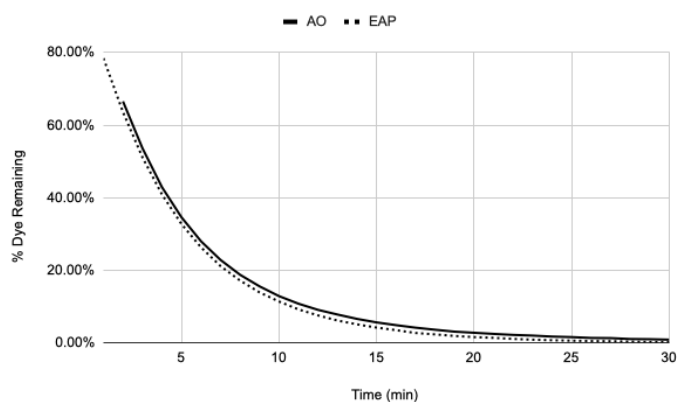
## Acid Yellow 36 (AY36)



**Figure 16:** AO absorbance spectrum of AY36. Conditions: graphite anode, graphite cathode, [AY36] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 2 - 35 min. Trial 1 of 3.



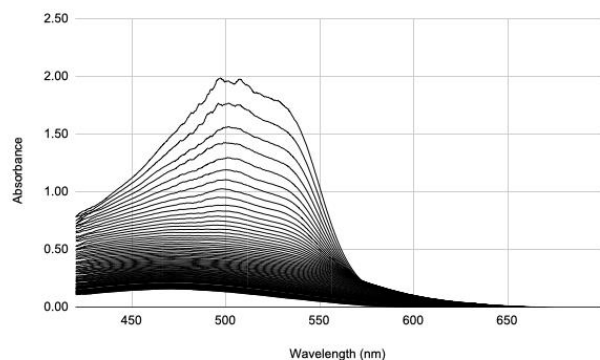
**Figure 17:** EAP absorbance spectrum of AY36. Conditions: BDD anode, graphite cathode, [AY36] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 2 - 30 min. Trial 1 of 3.



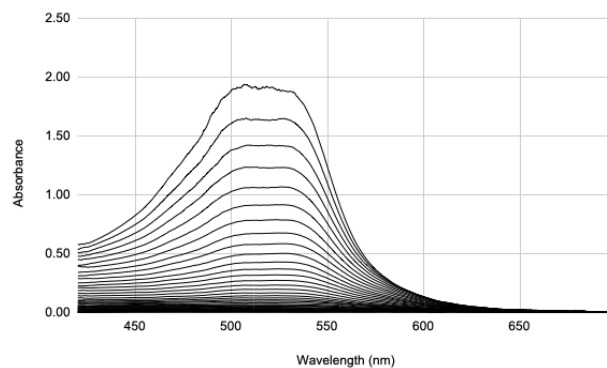
**Figure 18:** AO- and EAP-mediated decolourisation of AY36 as a function of time at a  $\lambda_{max}$  = 443.00 nm.



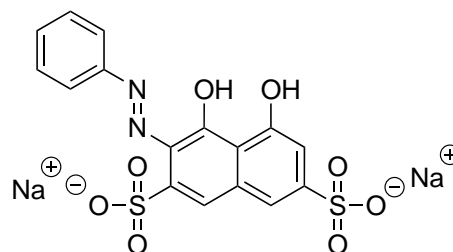
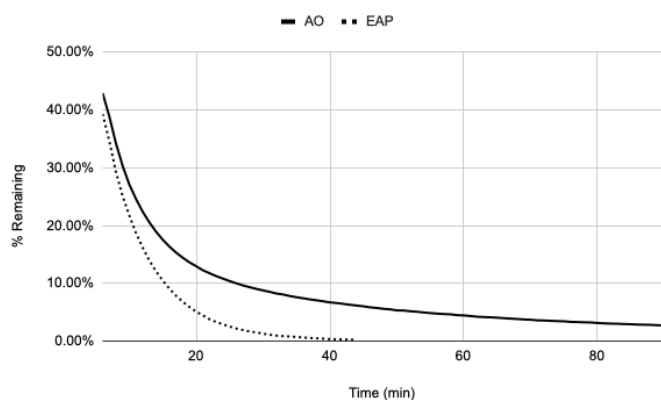
## Acid Red 29 (AR29)



**Figure 19:** AO absorbance spectrum of AR29. Conditions: graphite anode, graphite cathode, [AR29] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 8 - 90 min. Trial 1 of 3.

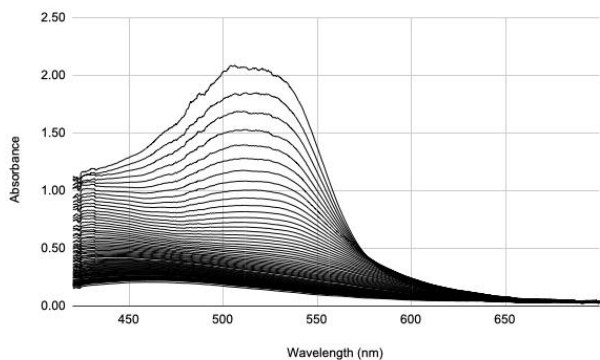


**Figure 20:** EAP absorbance spectrum of AR29. Conditions: BDD anode, graphite cathode, [AR29] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 7 - 45 min. Trial 1 of 3.

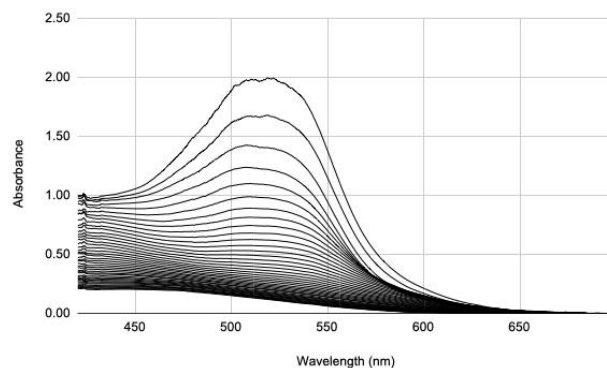


**Figure 21:** AO- and EAP-mediated decolourisation of AR29 as a function of time at a  $\lambda_{max}$  = 507.73 nm.

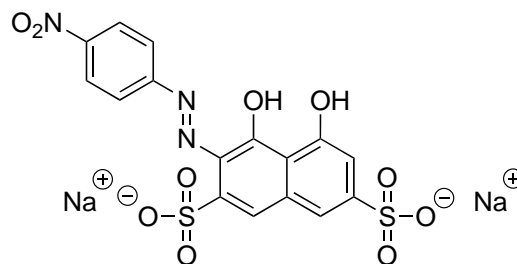
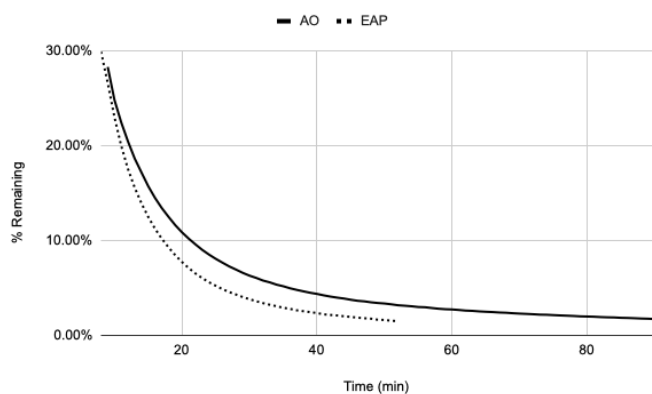
## Acid Red 176 (AR176)



**Figure 22:** AO absorbance spectrum of AR176. Conditions: graphite anode, graphite cathode, [AR176] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 9 - 90 min. Trial 1 of 3.

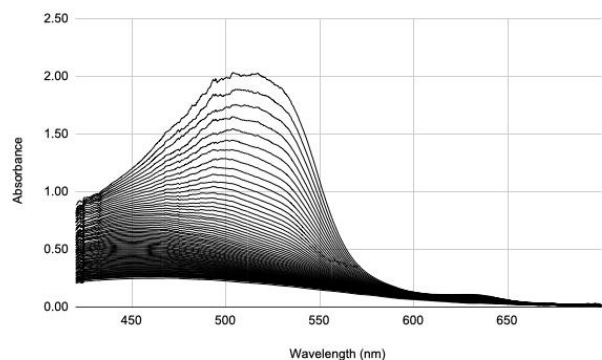


**Figure 23:** EAP absorbance spectrum of AR176. Conditions: BDD anode, graphite cathode, [AR176] = 100  $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 9 - 50 min. Trial 1 of 3.

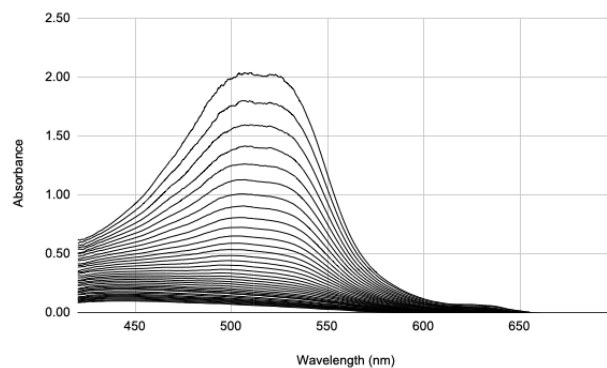


**Figure 24:** AO- and EAP-mediated decolourisation of AR176 as a function of time at a  $\lambda_{max}$  = 516.26 nm.

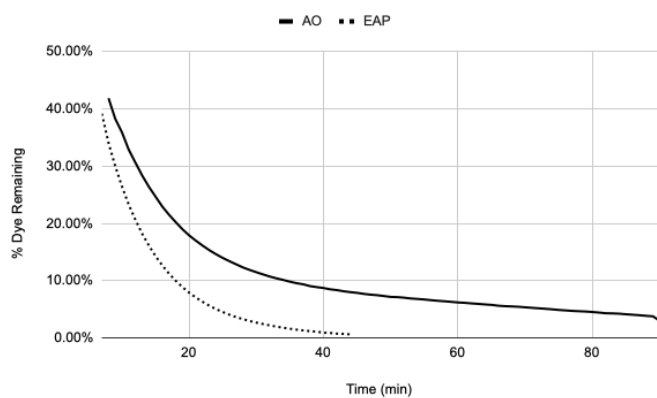
## Sulfanilic Acid Azochromotrop (SPADNS)



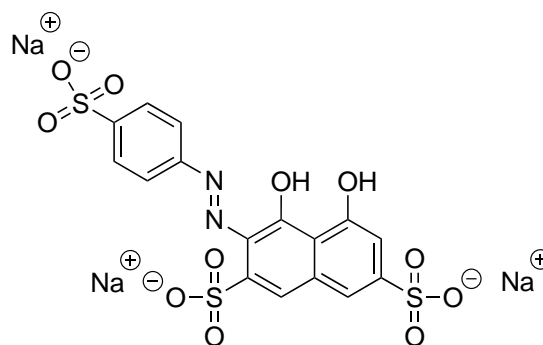
**Figure 25:** AO absorbance spectrum of SAPDNS. Conditions: graphite anode, graphite cathode, [SAPDNS] = 100 $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 9 - 90 min. Trial 1 of 3.



**Figure 26:** EAP absorbance spectrum of SAPDNS. Conditions: BDD anode, graphite cathode, [SAPDNS] = 100 $\mu$ M, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA, overlay spectrum recorded every minute from 7 - 45 min. Trial 1 of 3.



**Figure 27:** AO- and EAP-mediated decolourisation of SAPDNS as a function of time at a  $\lambda_{max}$  = 508.09 nm.



## First order rate constants

**Table 1:** First order rate constants at 20 min for nine dyes under two decolourisation protocols. AO conditions: Graphite anode and cathode, [Dye] = 100  $\mu\text{M}$ , [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA. EAP conditions: BDD anode, graphite cathode, [Dye] = 100  $\mu\text{M}$ , [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 14 mM, stirring = 1000 rpm, I = 5 mA.

	Indigo Carmine	Potassium indigotrisulfonate	Food Yellow 6	Methyl Orange	Ethyl Orange	Acid Yellow 36	Acid Red 29	Acid Red 176	SPADNS
AO (k s <sup>-1</sup> )	2.38 x10 <sup>-3</sup>	2.04 x10 <sup>-3</sup>	3.58 x10 <sup>-3</sup>	3.02 x10 <sup>-3</sup>	2.30 x10 <sup>-3</sup>	3.00 x10 <sup>-3</sup>	1.71 x10 <sup>-3</sup>	1.85 x10 <sup>-3</sup>	1.43 x10 <sup>-3</sup>
EAP (k s <sup>-1</sup> )	3.65 x10 <sup>-3</sup>	3.48 x10 <sup>-3</sup>	4.44 x10 <sup>-3</sup>	3.52 x10 <sup>-3</sup>	2.89 x10 <sup>-3</sup>	3.48 x10 <sup>-3</sup>	2.48 x10 <sup>-3</sup>	2.13 x10 <sup>-3</sup>	2.12 x10 <sup>-3</sup>