The Effect of Solubility and Structure on Dye Wastewater Treatment with Electrochemical Process

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Problem

- Many dyes used in dye application processes
- A variety of dyes with distinct properties
- Challenge in selecting appropriate treatment processes for dye effluent

Dye Characteristics

- Classification
  - Reactive
  - Acid
  - Disperse dyes
- Organic compounds
- Soluble vs. suspended(disperse)

Dye effluent

- High concentration
- Many types
- Toxic
- Color

Physical chemical process

- Oxidation, coagulation, adsorption, separate and remove
- Problems:
  - Efficient for high soluble dyes, inefficient for barely soluble dye
  - Require sludge treatment

Biological process

- Aerobic, Anaerobic
- Problems:
  - Inefficient in treating Color and COD of high concentration dye effluent
  - Dye is usually toxic to microbial that degrade the biological efficiency

AOP: Advanced Oxidation Process

- Ozone:
  - de-color, de-odor, degrade toxic organics
  - Problem: high cost

- Fenton photo-catalytic:
  UV/H_2O_2 or O_3
  - high cost and energy intensive

Advanced Process for Dye Effluent treatment

- Fenton Process:

$$H_2O_2 + Fe^{2+} \rightarrow = \cdot OH + OH^- + Fe^{3+}$$

High efficiency, high cost and considerable sludge

- Electro-Chemical Process:
  - Electro-oxidation, Electro-coagulation
  - Simple facility and easily operation
  - Low cost and no secondary pollutants

Objectives

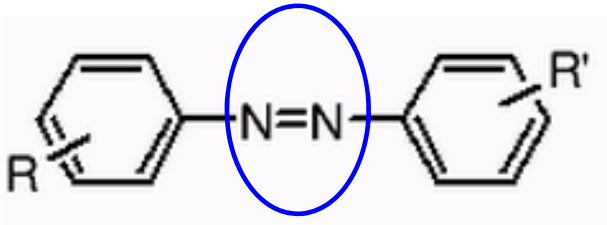
- The effects of dye solubility and structure on dye degradation with an electrochemical (EC) oxidation process
- Provide guidelines for selecting various dye effluent treatment

Selected Dyes in Study

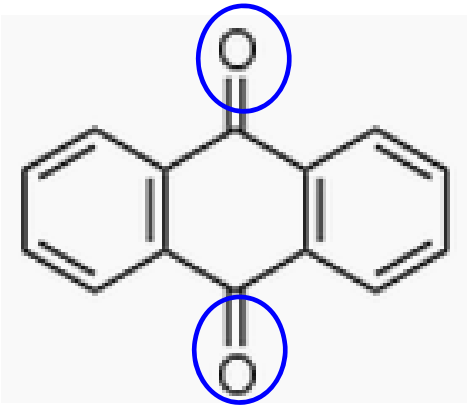
Solubility / Dye Structure	Easily soluble (10 g / 100 g)	Soluble (1 ~ 10 g / 100 g)	Barely soluble (0.01 g / 100 g)
Azo	Reactive Yellow 17	Acid Red 266 Acid Yellow 119	Disperse Blue 79
Disazo	Reactive Black 5	Acid Blue 113 Direct Red 81	
Anthraquinone	Reactive Blue 19	Acid Blue 40	Disperse Red 60

Dye Structure

- Azo (Dia-Azo) and Anthraquinone



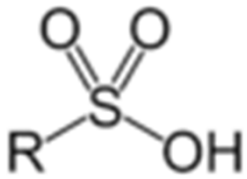
Azo dye



Anthraquinone Dye

Functional group used in dye

- To increase solubility
  - (-SO_3H) and (-COOH) are added



- To provide colorful
  - Anthraquinone(-NO2) and Azo (-N=N-) are added

Disperse Dye

- Without $-SO_3H$ or –COOH added, the disperse dye is barely soluable
- Add surfactant to increase dye solubility, usually exists in suspended status

Solubility on dye effluent treatment

- Reactive Blue 19 easily soluble dye :100% color removal in five min.
- Disperse Red 60 barely soluble dye: after 30~40 min. treatment, can’t achieve 100% color removal
- Solubility influence dye color treatment by EC process
- Is the solubility is the only factor affect the dye effluent treatment?

Dye structure on dye effluent treatment

Author	Study content	Results
A. R. Rahmani1(2010)	Apply Fenton to treat various conc. Acid Orange 7 and Reactive Black 5	Acid Orange 7 > Reactive Black 5 Reactive Black 5 has a complex double AZO bonds while Acid Orange 7 has only one AZO bonds的
Efthalia Chatzisymeon(2006)	Reactive Black 5 Reactive Red 198 Reactive orange 107	Reactive Black 5 > Reactive Red 198 and Reactive orange 107

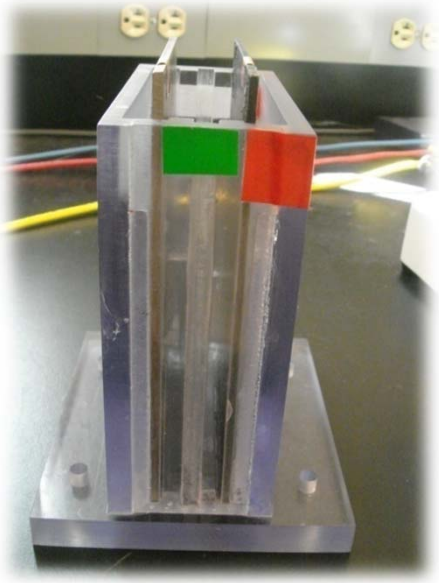
Experiment

Materials and Apparatus

- Electrode (140 mm × 100 mm × 2 mm)
  Anode:Titatium coated with (RuO_2)
  Cathode:Titanium

Anode

Cathode



- EC (Reactor)
  - PVC
  - Electrodes are placed on both sides
  - Distance between two electrodes is 2 cm

Experimental Materials and Apparatus

- ORP meter: Cole-Parmer® laboratory pH/mV/Exp meter digital
- pH meter: American Scientific Products, ASC®PORTA/pH 4
- Digital conductivity meter: Fisher Scientific Digital Conductivity and TDS/PPM Meter
- DC power supply: Tenma Laboratory
- Digital Multimeter: WAVETEK-DM15XL
- Photo spectroscopy(UV/Vis):HACH® DR-4000

Experimental Materials

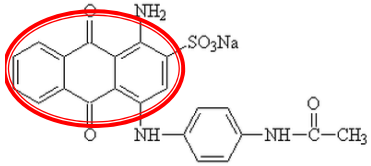
Dye	Dye Structure	Solubility	Molecular formula	Molecular Weight
Acid Blue 40	Anthraquinone	Soluble	$C_{22}H_{16}N_3NaO_6S$	473.43
Acid Blue 113	Disazo	Soluble	$C_{32}H_{21}N_5Na_2O_6S_2$	681.65
Acid Yellow 119	Azo	Soluble	$C_{19}H_{15}N_4NaO_6S$	450.4
Acid Red 266	Azo	Soluble	$C_{17}H_{10}ClF_3N_3NaO_4S$	467.78
Direct Red 81	Disazo	Soluble	$C_{29}H_{19}N_5Na_2O_8S_2$	675.6
Disperse Blue 79	Azo	Barely Soluble	$C_{24}H_{27}BrN_6O_{10}$	639.41
Disperse Red 60	Anthraquinone	Barely Soluble	$C_{20}H_{13}NO_4$	331.32
Reactive Black 5	Disazo	Easily Soluble	$C_{26}H_{21}N_5Na_4O_{19}S_6$	991.82
Reactive Yellow 17	Azo	Easily Soluble	$C_{20}H_{20}K_2N_4O_{12}S_3$	682.77
Reactive Blue 19	Anthraquinone	Easily Soluble	$C_{22}H_{16}N_2Na_2O_{11}S_3$	626.54

Definition of solubility

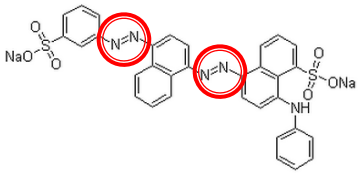
- Below 20˚C

Range of Solubility	Solubility
10 g / 100 g	Easily Soluble
1 ~ 10 g / 100 g	Soluble
0.01 ~ 1 g / 100 g	Barely Soluble
0.01 g / 100 g	Barely Soluble

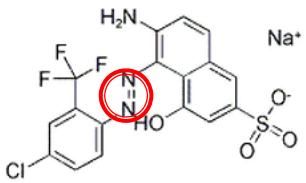
Dye Structure



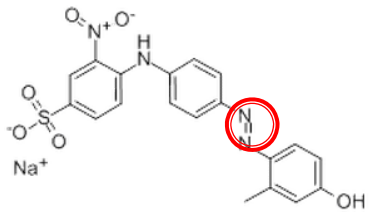
Acid Blue 40
(Anthraquinone)



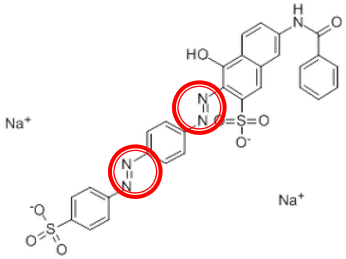
Acid Blue 113
(Disazo)



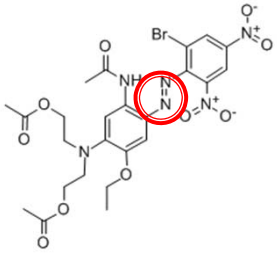
Acid Red 266
(Azo)



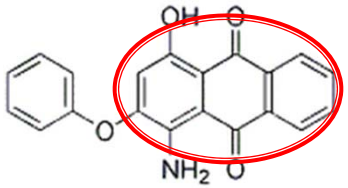
Acid Yellow 119
(Azo)



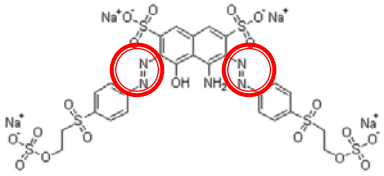
Direct Red 81
(Disazo)



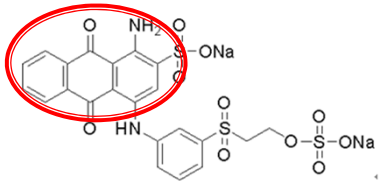
Disperse Blue 79
(Azo)



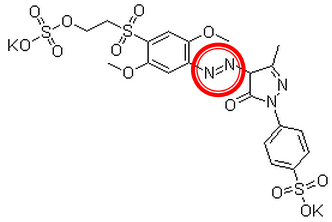
Disperse Red 60
(Anthraquinone)



Reactive Black 5
(Disazo)



Reactive Blue 19
(Anthraquinone)



Reactive Yellow 17
(Azo)

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實驗前置

- 將各種染料，配置已知濃度，稀釋不同倍數
- 使用分光光度計全波長掃描功能，測得不同稀釋倍數染料之最大吸收波峰
- 並以最大吸收波峰之值對不同稀釋倍數，製作檢量線以提供吸收值與染料濃度之換算

實驗方法

電化學主要區分為三個部分:

- 直接法:染料溶液加入之電解質(NaCl)混合直接電解
- 間接法:直接電解電解質(NaCl) ，再將產生之氧化劑與染料溶液混合反應
- 持續偵測:氧化劑與染料混合反應，持續監測染料於特定時間內之氧化裂解程度

Experimental Conditions

Low Solubility

Concentration：100 mg/L

1g/L NaCl：10V

2g/L NaCl : 10V、15V

Treatment Time： 0 ~ 30 mins

High Solubility

Concentration ：100 mg/L

1g/L NaCl：10V

2g/L NaCl : 10V、15V

Treatment Time ： 0 ~ 10 mins

直接法步驟

1.染料溶液混合NaCl電解質，置入250 ml於電解槽

2.置入陽、陰極二電極板並固定電壓與通電時間

3.量測實驗參數(ORP、pH、Cond)

4.偵測各別染料最大波長，吸收值換算去除率比較分析溶解度與化學結構

間接法實驗條件

- 低水溶性染料：

有機染料濃度：100 mg/L

1g/L NaCl：10V

2g/L NaCl： 10V、15V

操作時間： 0 ~ 30 mins

間接法步驟

1.注入NaCl電解液250 ml於電解槽

2.置入陽、陰極二電極板並固定電壓與通電時間

3.量測ORP、pH、Cond並偵測OCl^-最大波長292 nm

4.等體積混合當下偵測各別染料最大波長

5.靜置隔夜後重複偵測，吸收值換算去除率比較分析溶解度與化學結構

間接法持續偵測實驗條件

有機染料濃度：100 mg/L

1g/L NaCl：10V

2g/L NaCl : 10V、15V

操作時間： 5 mins

固定波長:個別染料最大吸收波峰

反應時間:5 min (每5s間隔取點)

持續偵測步驟

1.注入NaCl電解液250 ml於電解槽

2.置入陽、陰極二電極板並固定電壓與通電時間

3.偵測OCl^-最大波長292 nm

4.持續偵測功能，設定染料最大吸收波長、反應時間、取樣間隔點

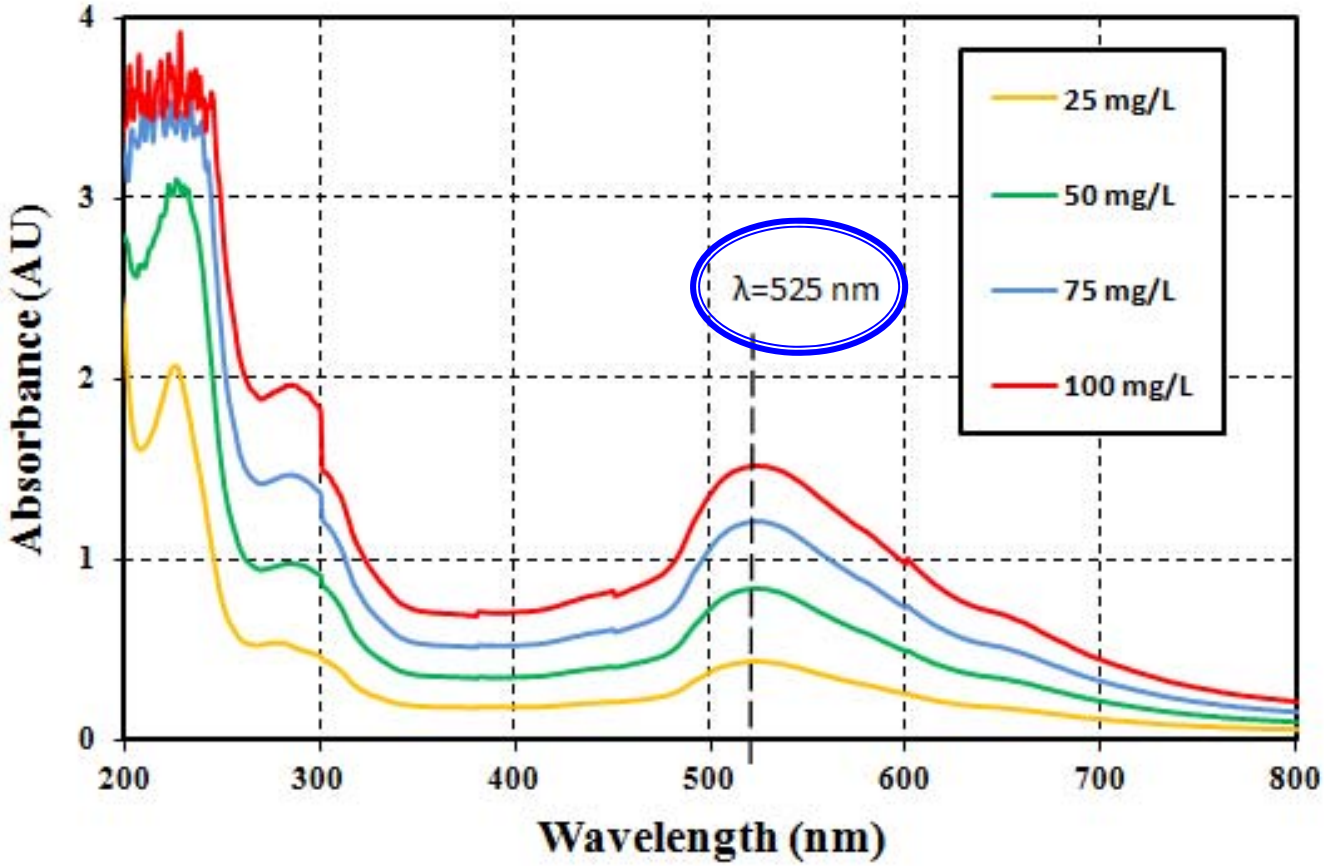
5.等體積混合當下持續偵測吸收值變化情形

6.吸收值換算去除率比較分析溶解度與化學結構

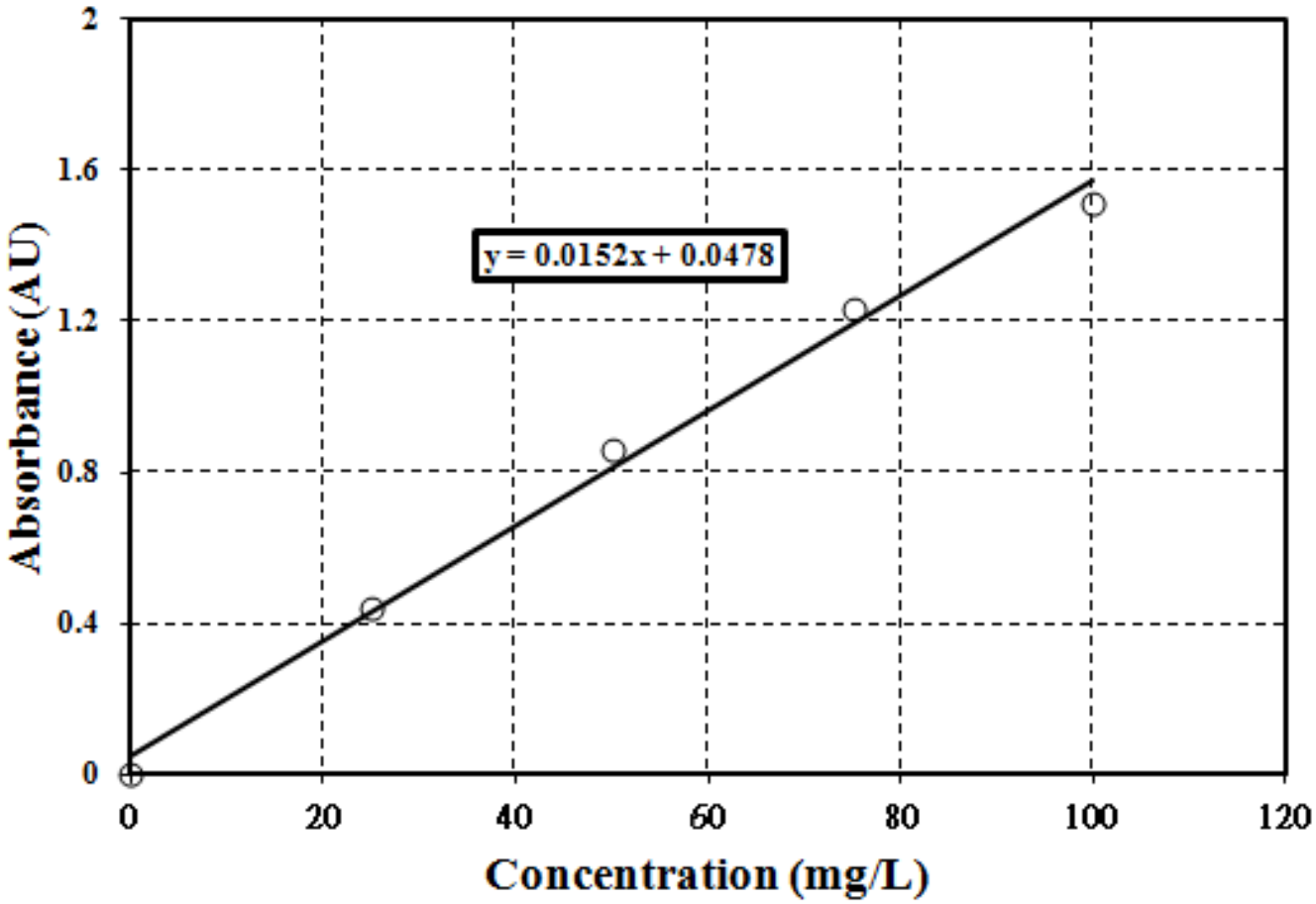
Results and Discussion

Photo-Spectroscopy scan of DB-79

- Absorption Peak=525 nm



Calibration curve (DB-79)

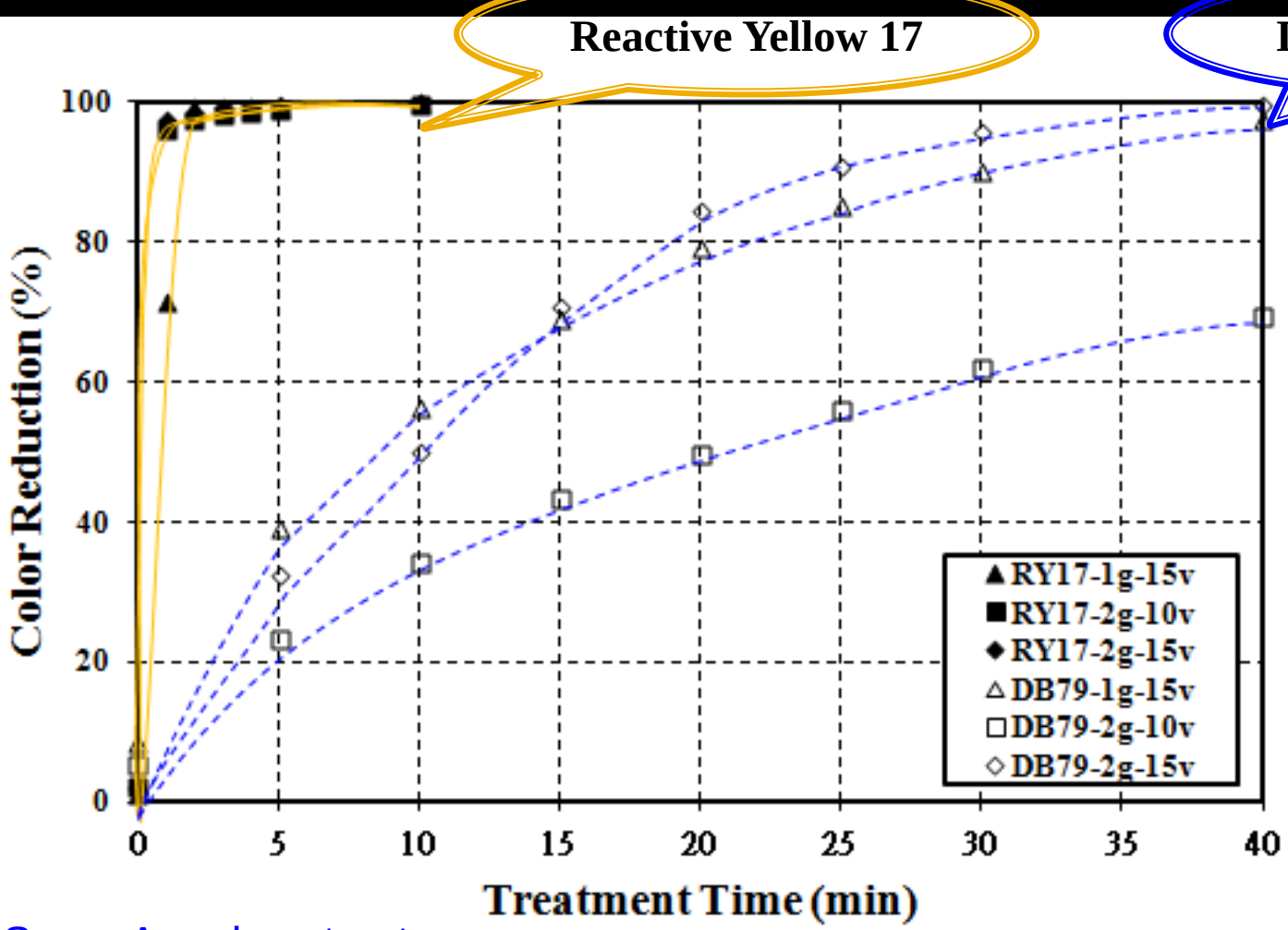


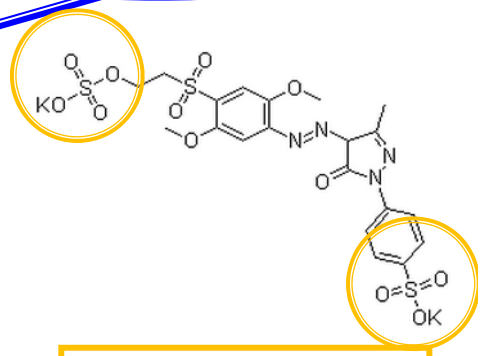
$$Abs. = 0.0152 \times Conc._{DB-79} + 0.0478 \ (mg/L)$$

Selected comparison of dye structure and solubility

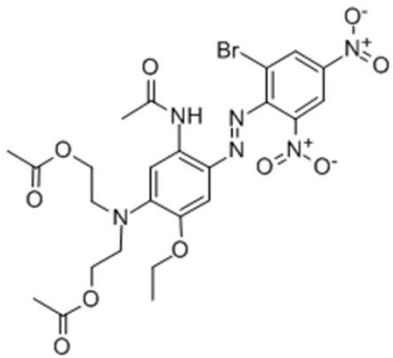
Dye	Dye Structure	Solubility
Disperse Blue 79	Azo	Barely soluble
Disperse Red 60	Anthraquinone	Barely soluble
Reactive Yellow 17	Azo	Easily soluble
Reactive Blue 19	Anthraquinone	Easily soluble

Same dye structure (Aoz) vs. Different solubility(barely and easily soluble)





Reactive Yellow 17



Disperse Blue 79

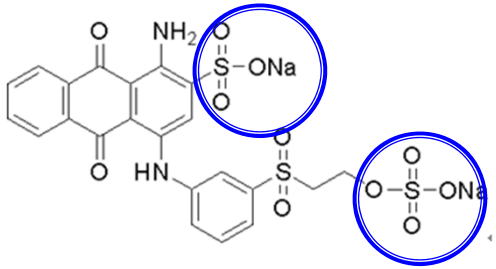
Same Azo dye structure

Treatment of Easily soluble is faster than barely soluble dye

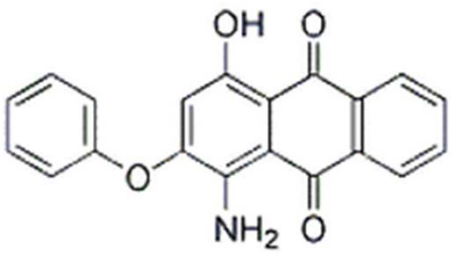
Same dye structure (Aq) vs. Different solubility(barely and easily soluble)

Reactive Blue 19

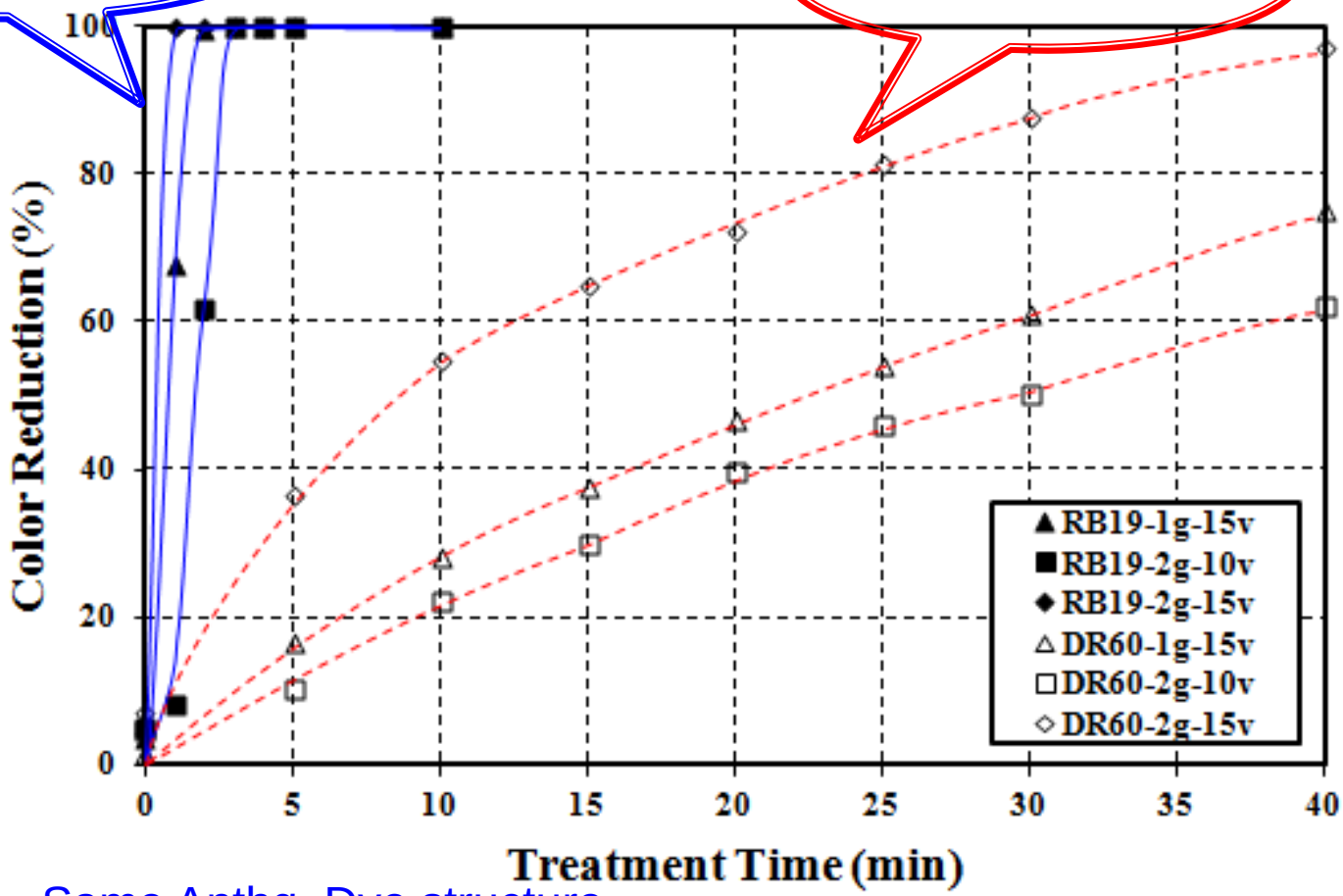
Disperse Red 60



Reactive Blue 19



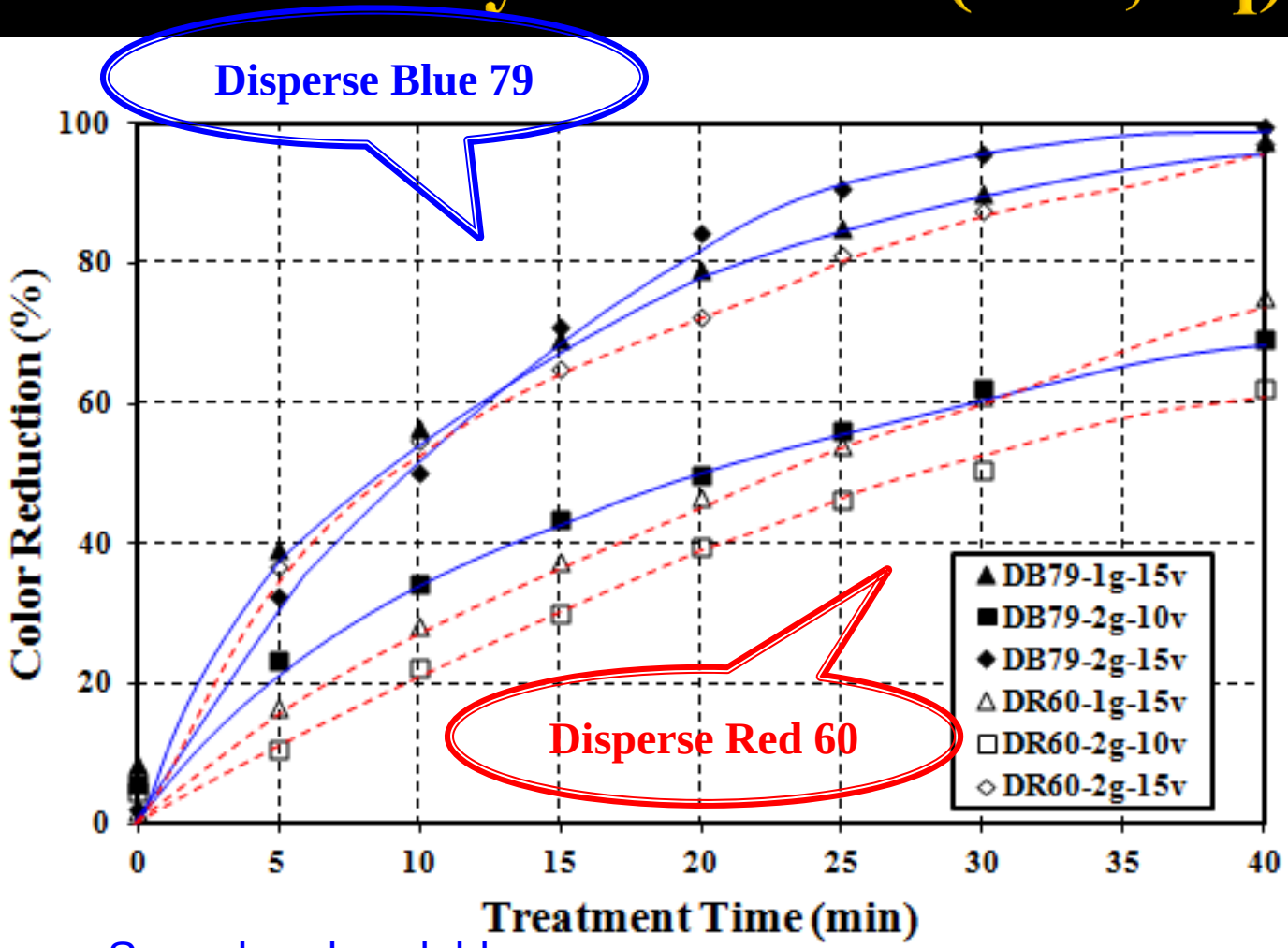
Disperse Red 60

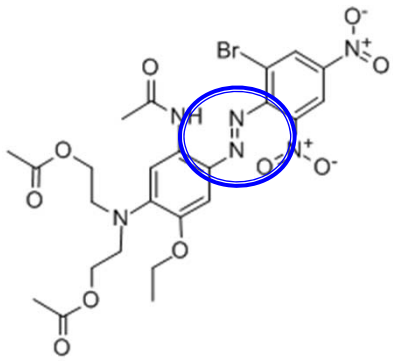


Same Anthq. Dye structure

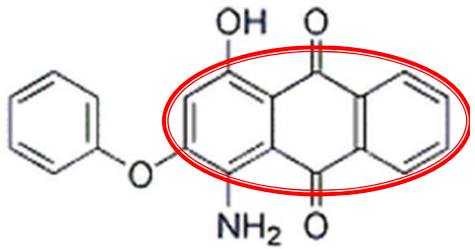
Treatment of Easily soluble dye is faster than barely soluble dye

Same solubility(barely soluble) vs. Different dye sturcture(Azo,Aq)





Disperse Blue 79

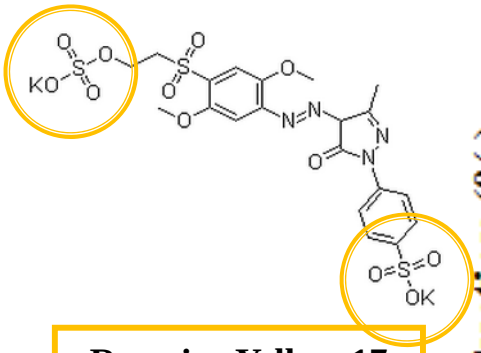


Disperse Red 60

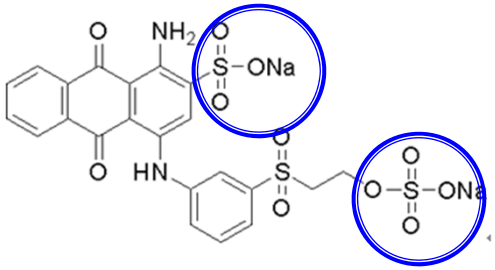
Same barely soluble

The treatment of Azo is faster than Anthq. dye

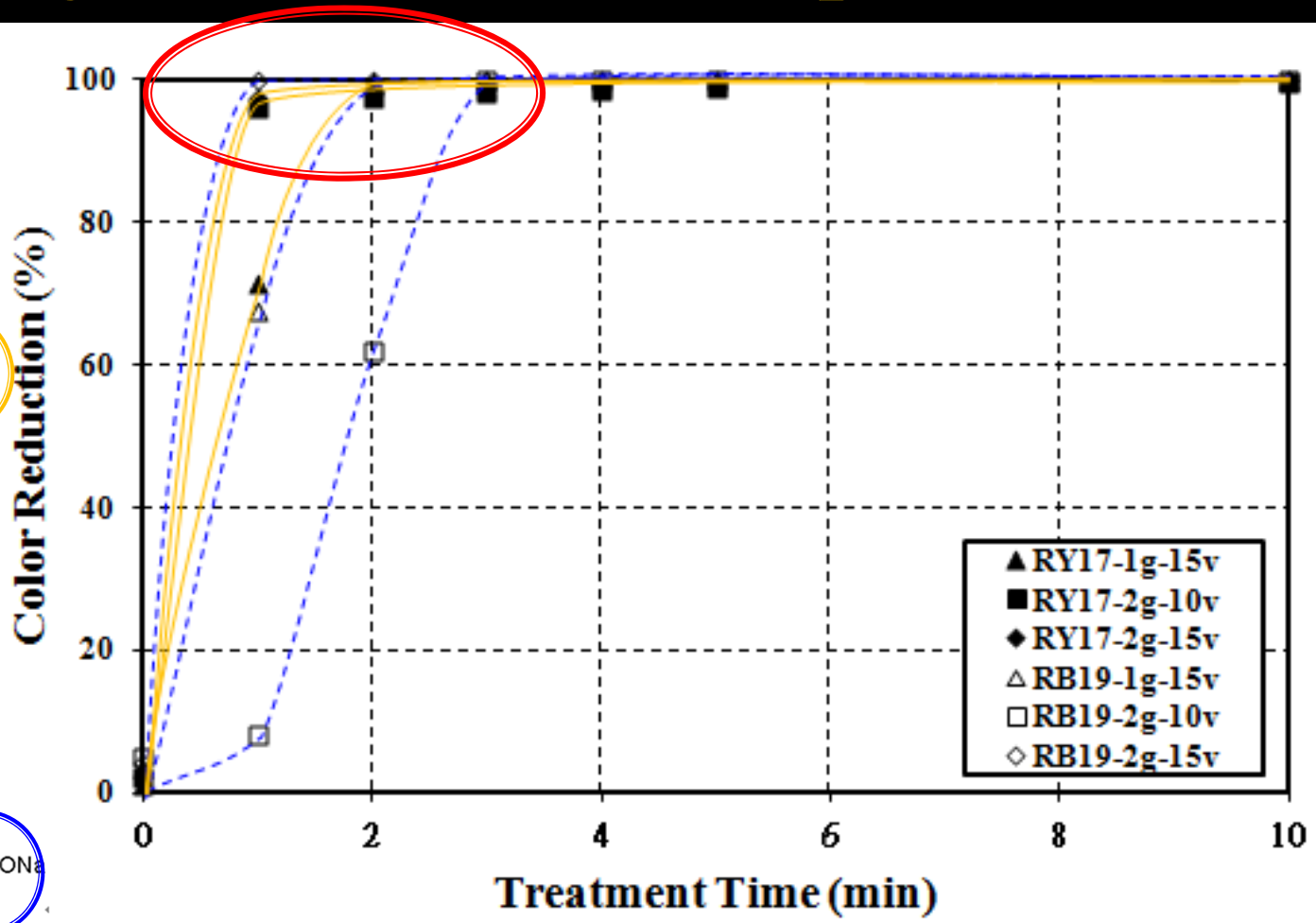
Same solubility(Easily soluble) vs. Different dye structure(Azo,Aq)



Reactive Yellow 17



Reactive Blue 19

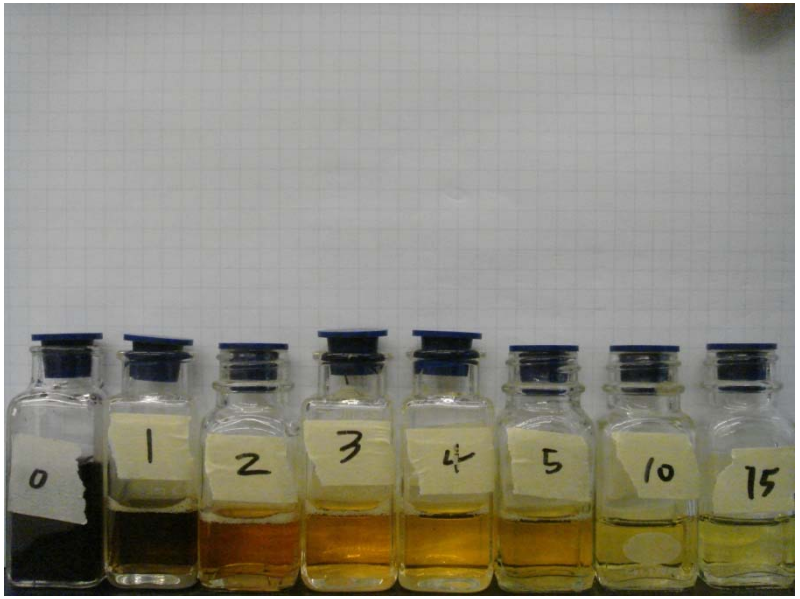


No significant treatment difference between dyes with same easily soluble but different dye structure

Color change in the treatment process

Dye	Dye structure	Color change	Measured wave length(nm)
Acid Blue 40	Anthraquinone	Black→Red	467
Acid Blue 113	Disazo	Red →Yellow	385
Direct Red 81	Disazo	Blue →Yellow	340
Reactive Black 5	Disazo	Blue →Purple	357

Color Change



Acid Blue 40

Color change： **Black**

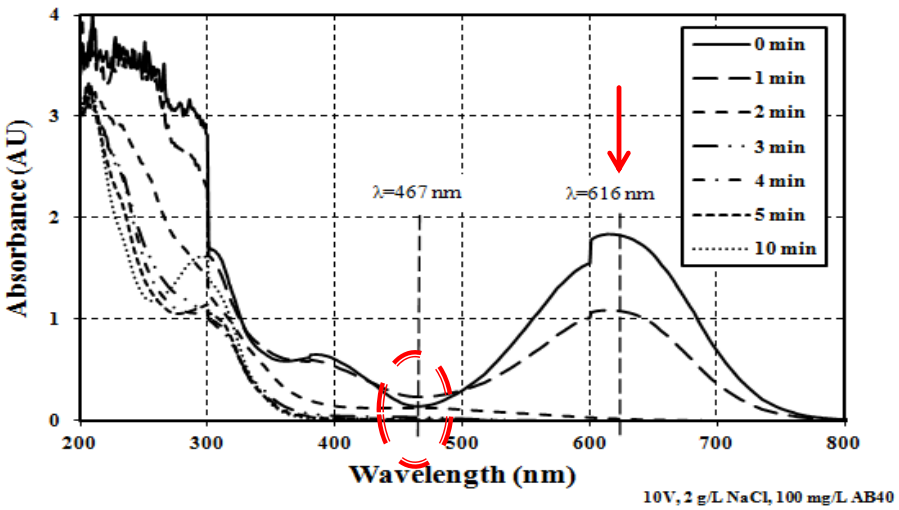
→Red→tellow→Non

Progressive change of dye color in the treatment process

Acid Blue 113

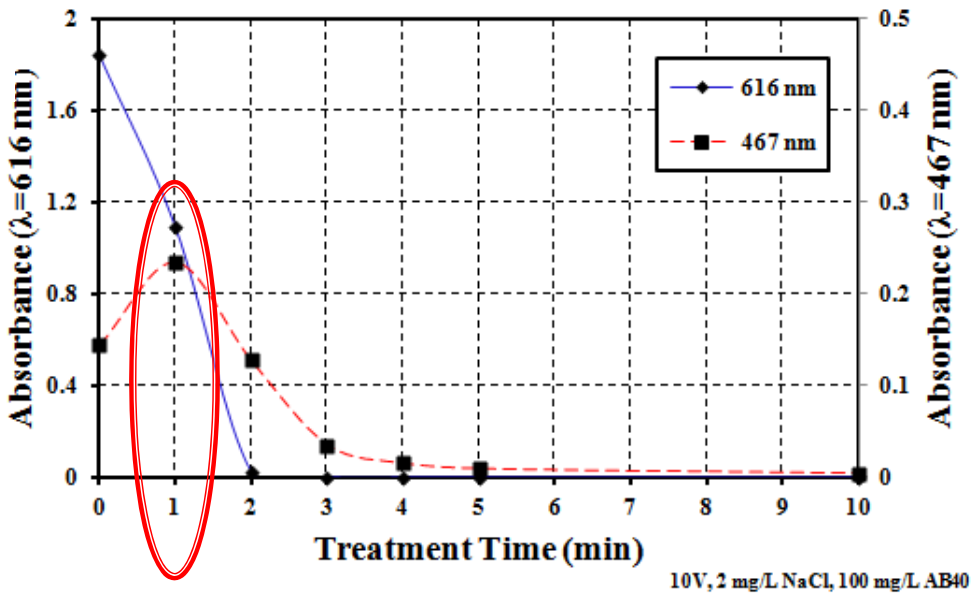
Color change:**Red→Yellow→Non**

Example: AB-40 dye



Scan spectrum

Peak at 616 nm is continuously declined
Peak at 467 nm is raised then declined

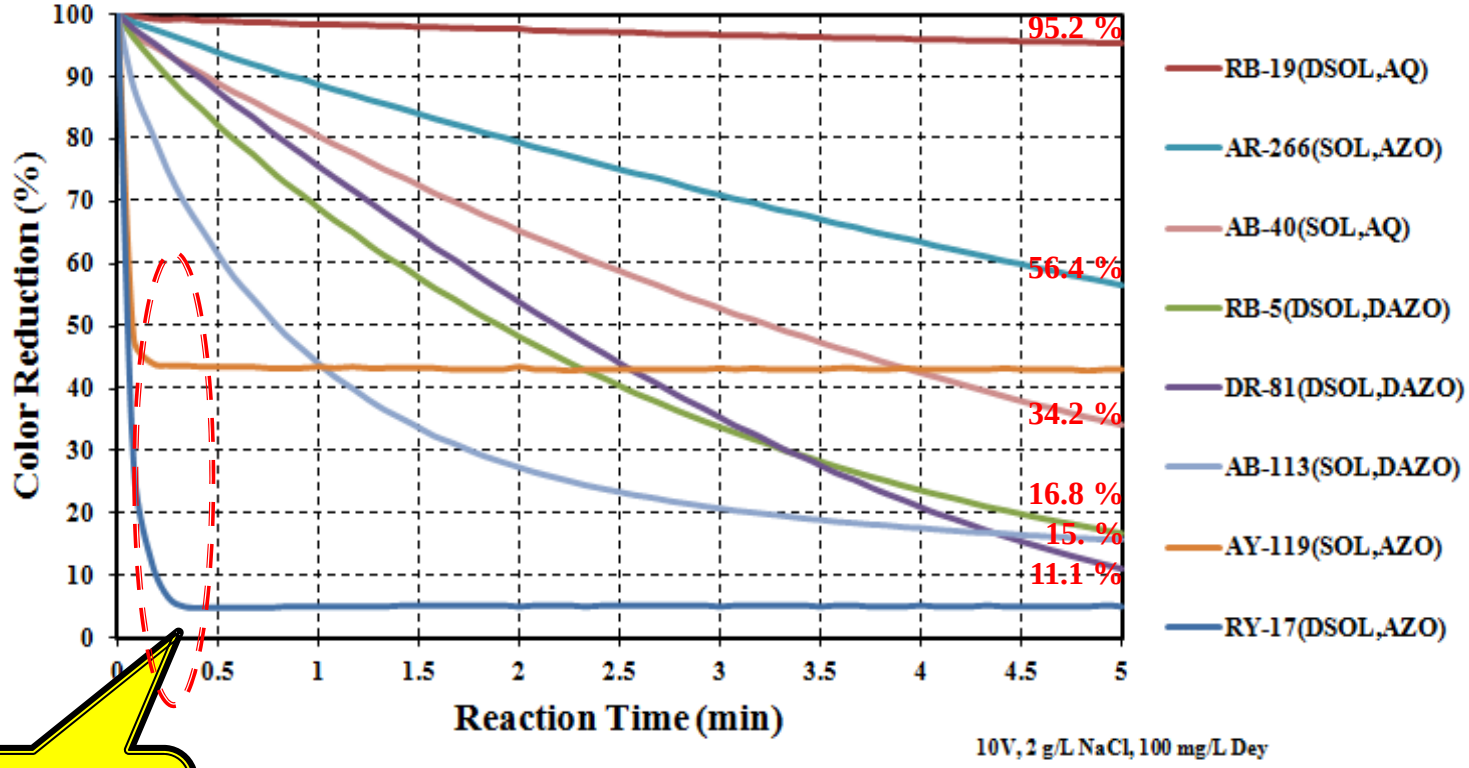


Comparison of peak wave length

Comparison of chemical kinetic constants for easily soluble dyes

Dye	Dye Structure	Solubility
Acid Blue 40	Anthraquinone	Soluble
Acid Blue 113	Disazo	Soluble
Acid Yellow 119	Azo	Soluble
Acid Red 266	Azo	Soluble
Direct Red 81	Disazo	Soluble
Reactive Black 5	Disazo	Easily soluble
Reactive Yellow 17	Azo	Easily soluble
Reactive Blue 19	Anthraquinone	Easily soluble

Dye structure and solubility vs. Color treatment(%)



RY-17 (426 nm)
AY-119 (417 nm)
OCl^- Oxidant(292 nm)

- No obvious difference bt. easily soluble and soluble dye
- For dye structure comparioson:**Azo>Disazo>Anthraquinone**

Chemical reaction kinetics

Dyes (mg/L)
100

$$-r_A = -\frac{dC_{Dye}}{dt} = k \times C_{Dye}^{\ 1} \times C_{OCl^-}^{\ 1}$$

$$\frac{(ABS_A - ABS_0)}{(t_A - t_0)}$$

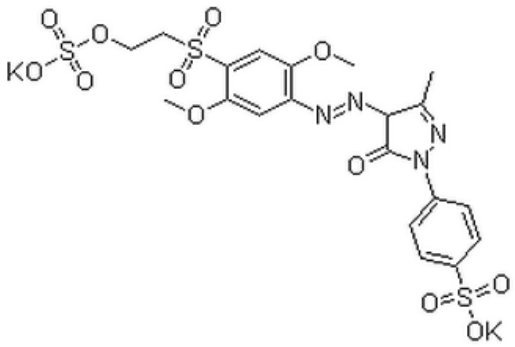
OCl^-		
NaCl(g)	Voltage(V)	Reaction Time(min)
2	15	5
2	10	
1	15	

Reaction constants vs. Dye structure

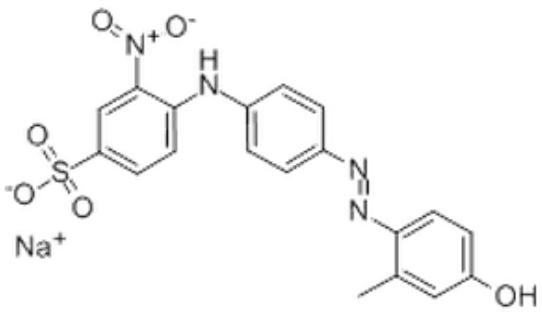
k(sec^{-1})	Dye	Dye Structure	Solubility
0.105371	Reactive Yellow 17	Azo	Easily soluble
0.089203	Acid Yellow 119	Azo	Soluble
0.040002	Acid Blue 113	Disazo	Soluble
0.026389	Direct Red 81	Disazo	Soluble
0.021743	Reactive Black 5	Disazo	Easily soluble
0.011336	Acid Blue 40	Anthraquinone	Soluble
0.00669	Acid Red 266	Azo	Soluble
0.000465	Reactive Blue 19	Anthraquinone	Easily soluble

15V, 2 g/L NaCl, 100 mg/L Dye

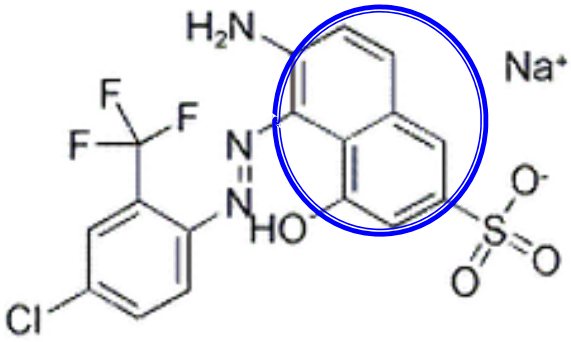
Exception:Acid Red 266(Azo) is less effectively treatment than other Azo dyes



Reactive Yellow 17



Acid Yellow 119



Acid Red 266

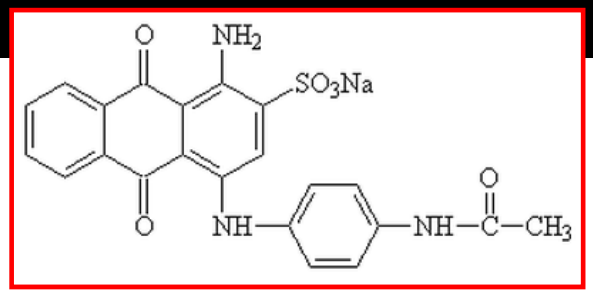
- 破壞偶氮基的同時，產生不同物質在芳香中間體形成 Mohammed Faouzi Elahmadi (2009)
- 其中間產物為類似具有雙苯環相連之萘的結構。不斷產生於反應槽中 A.I. del Río(2011)

AB-40 vs. RB-19 COD and Color

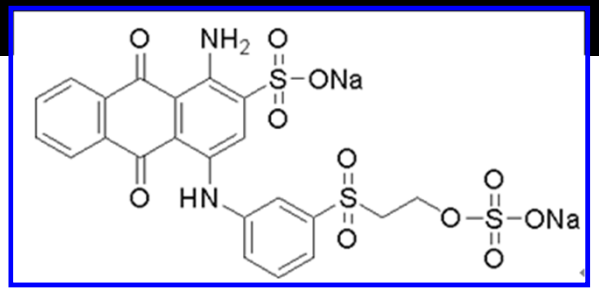
Solubility: RB-19>AB-40

Color Reduction:AB-40 >RB-19

COD Reduction:RB-19>AB-40

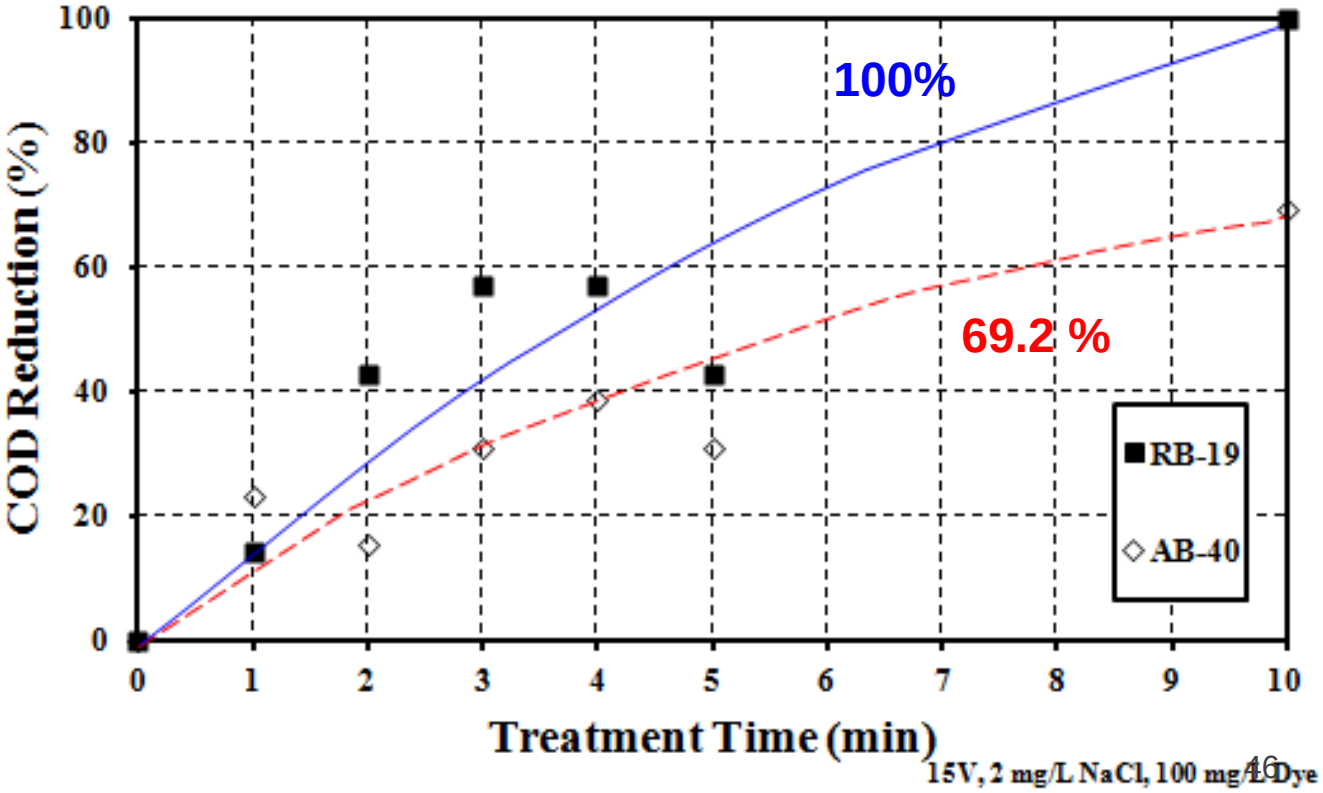


Acid Blue 40



Reactive Blue 19

RB-19染料溶解度較高但支鏈卻較AB-40染料來長，所以RB-19的染料固色性能越強，氧化劑切斷的發色基團時間上較長，推估Color與COD去除率差異的主因



Other studies

Dye	Structure	Solubility
Acid Orange 7	Azo	(30 ºC) 116 g/L易溶
Reactive Black 5	Disazo	(20℃) 200 g/L易溶

Author	Study content	Results	Comparison with this study
A. R. Rahmani1(2010)	Apply Fenton process to degrade various conc. Acid Orange 7 and Reactive Black 5	Acid Orange 7> Reactive Black 5 作者解釋RB5有一個複雜的結構和兩個偶氮鍵結，AO7的化學結構很簡單，它有一個偶氮鍵， 因此有所差異	AO7與RB5溶解度皆為100 g/L 以上，且兩種染料溶解程度非常接近，與化學結構相比之下較不明顯 而比較兩種染料化學結構AO7 (Azo)和RB5(Disazo)後，與本研究Azo結構較Disazo結構易於去除之論點相符合

Other studies

Dye	Structure	Solubility
Reactive Black 5	Disazo	(20℃) 200 g/L
Reactive Red 198	Azo	(50℃) 100 g/L
Reactive orange 107	Azo	-

Author	Study Content	Results	Comparison with this study
Efthalia Chatzisymeon(2006)	Treat with EC process Reactive Black 5 Reactive Red 198 Reactive orange 107	Reactive Black 5 >Reactive Red 198 >Reactive orange 107 作者解釋RB5去色率大於 RR198和RO107是由於RB5具有2個N=N鍵之結構，造成發色基團較易於被氧化劑去除	RB5染料結構為雙偶氮，但溶解度卻高於RR198染料的偶氮結構 降解程度的影響，溶解度比化學結構之影響來的明顯與本研究中所提出的論點相符合

Conclusions(1/2)

- De-colorization of ten dyes with three solubility classifications(easily soluble, soluble and barely soluble) and three dye structures(azo, disazo and anthraquinone) were tested by an EC oxidation process
- the solubility of dye rather than dye structure is the major influence on dye degradation.

Conclusions(2/2)

- dye degradation efficiency going from the highest to the lowest efficiency, follows the order: azo >disazo > anthraquinone
- In some specific cases, azo dye has a lower de-colorization efficiency than anthraquinone dye because some intermediates resist the de-colorization process.
- A COD degradation test re-confirms that dye solubility is the dominant factor influencing dye degradation by an EC oxidation process

People may look at the same thing but see it differently (Q/A)