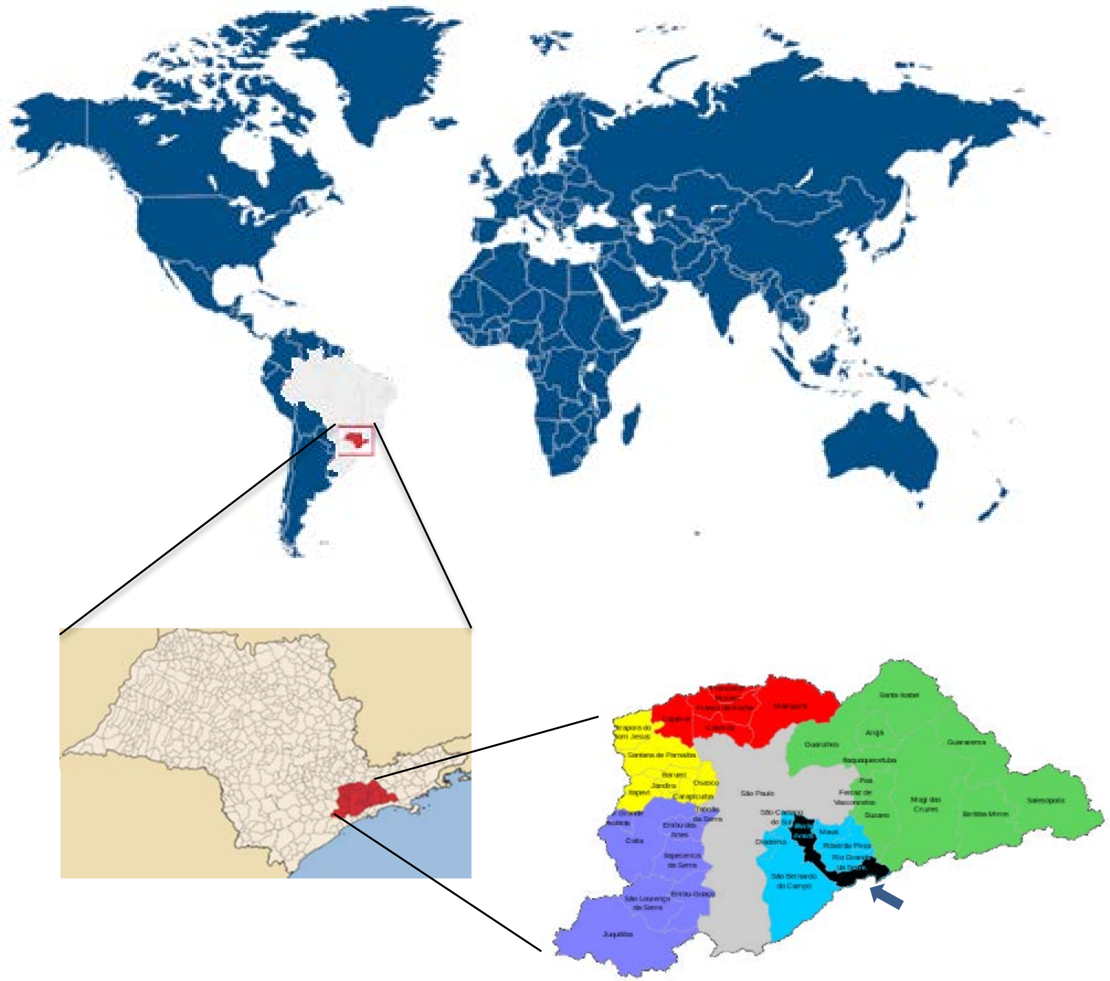
Universidade Federal do ABC – UFABC
Rigaku Latin America - RLA

Academic & Industrial Doctorate Program

PhD: Jenny Sayaka Komatsu
Professor: Wagner Alves Carvalho
Industrial Supervisor: Pol Willy Gerard de Pape

# Fabric Waste Valorisation: a neglected material for application as dye adsorbent and magnetic mesoporous carbon precursor

# BRAZIL – São Paulo State – Santo André



**Universidade Federal do ABC**

Science & Technology Bachelor

Humanities Science Bachelor

Research form Day One

(PDPD – Pesquisa Desde o Primeiro Dia)

Industrial & Academic Doctorate Program

(DAI – Doutorado Acadêmico Industrial)

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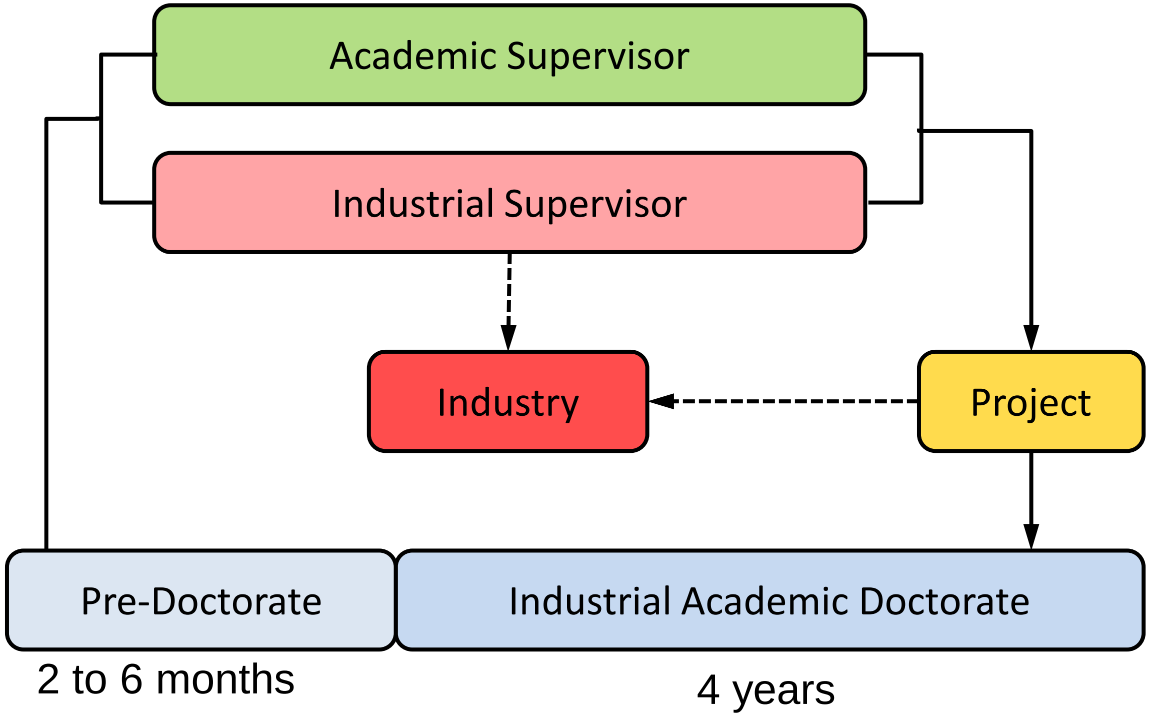
# DAI Program (Industrial Academic Doctorate program)

**DAI**
Doutorado Acadêmico Industrial




Start: 2013 UFABC + CNPq

2021
MAI:Mestrado Acadêmico para Inovação
First class in 2021 (now under Selection Process)

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DAIRIX

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# DAI – Partner Company

MAPA DOS PROJETOS DAI


http://dai.ufabc.edu.br/mapa.php

ALL WASHED Lavanderia Industrial
ARTECOLA QUÍMICA
bioenergia engenharia
deogi Biotecnologia
ECOLAB
UNIFLON
CHEVROLET
Henkel
Instituto Avançado de Robótica
in|metrics
MAHLE Driven by performance
Mercedes-Benz
SUZANO PAPEL E CELULOSE
ThyssenKrupp
WHEATON BRASIL
ZEPPELIN WE CREATE SOLUTIONS
ZF
MANTRIS
OXITENO
Rigaku
VALE
GO TRATCH
FLEXMEDIA
CLARIANT
ROMI
Eva SCIENTIFIC
ccee
AkzoNobel

# Research Context – Why Textile Fabrics ?

OR

YOUR Env

**Brazil MSW Generation[a]: 259,547 ton.day$^{-1}$**

**Textile**

**Latin America[b]: 2.6 % (IPCC, 2006)**

**Brazil: 2.5 million ton.year$^{-1}$**

**World[c]: 32 million ton.year$^{-1}$**

*Reference: a) Brazilian Institute of Geography and Statistics (IBGE)*
*b) IPCC Report 2006, for Latin America*
*c) Shepherd et al (2017)*

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# BRAZIL – Municipal Solid Waste


- Increase on Middle-class Population

- Fast Fashion Phenomena

**In last 15 years, clothing production has doubled**

170,000 ton(2) of
clean fabric scrap
from cloth making

*Reference (2) Associação Brasileira da Indústria Têxtil e de Confecção (Abit)*

# New CARBON Feedstock: FABRIC WASTE

## WHY NOT RECYCLE?

Traditional Recycling process require High chemical and procedures demand because of many different fibbers , colours, and other additives (heating, flame retardant, antistatic agent, softener, degreaser, etc)

**Table – Textile Fibber Classification, according to Brazilian Standard ABNT 12744-1992**

| NATURAL FIBER | | | CHEMICAL FIBER | |
|---|---|---|---|---|
| VEGETABLE | ANIMAL | MINERAL | ARTIFICIAL | SYNTHETIC |
| SEEDS | SECRETION | Asbesto | Acetate | Acrylic |
| Cotton | Silk | | Alginate | Aramid |
| Kapok | HAIR/FUR | | Rubber | Polyester |
| STALK | Alpaca | | Carbon | Polyvinyl Chloride |
| Hemp | Angora | | Casein | Polyvinylidene Chloride |
| Jute | Goat | | Cuprammomium | Elastane (Spandex®, Lycra® ) |
| Kenaf | Cashmere | | Slag | Modacrylics |
| Linen | Camel | | Lyocel | Multipolymer |
| Malva | Rabbit | | Metallic | Polyamide |
| Rami | Sheep (wool) | | Metallized | Polycarbamide |
| LEAF | Lhama | | Rock | PolyChloroFluoroethylene |
| Abaca | Mohair | | Triacetate | Polyurethane |
| Caroá | Vicunha | | Glass | Polyvinyl alcohol |
| Formio | | | Viscose | |
| Sisal | | | | |
| FRUIT | | | | |
| Coconut | | | | |

**! Only 1 % in the world**

~15,000 colorants type (Ref1)

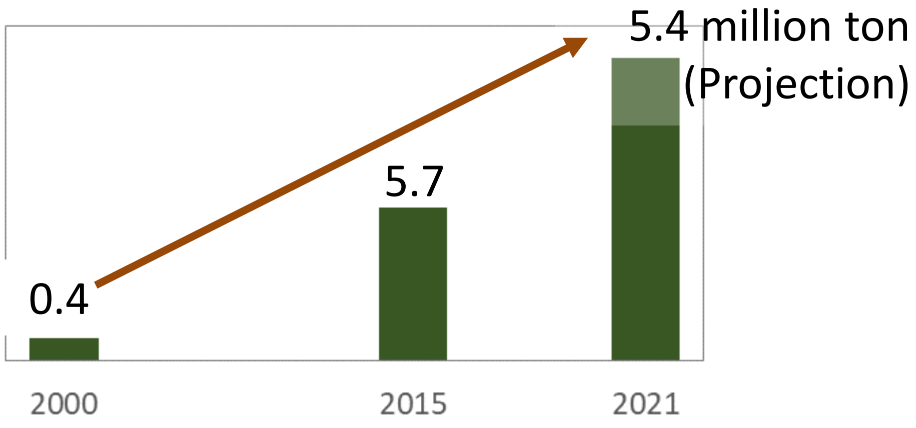
> 3150 additives listed in Industrial Guide (Ref2)

*Ref1 :ZOLLINGER, Heinrich. Color Chemistry - Synthesis, Properties, and Aplications of Organic Dyes and Pigments. Third ed. Zurich: Wiley-VCH and VHCA, 2003.*

*Ref2: FLICK, E.W. 1980. Textile Finishing Chemicals: An Industrial Guide. Noyes Publication. Nova Jersey, EUA*

# World Activated Carbon Market

## WORLD PRODUCTION [a]

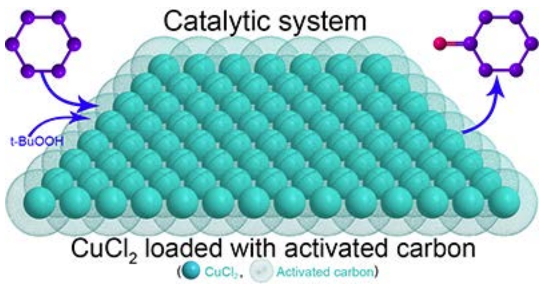



## BRAZIL FOREIGN TRADE[b]


## WIDE RANGE OF APPLLICATIONS PROMOTED MAINLY BY ENVIRONMENTAL APPLICATIONS

GAS

WATER




CATALYSIS

Ref.:X.Sun et. al. J. Braz. Chem. Soc. 2016;27(1)

Large Variety of applications

**Precursor scarcity**

*a) Market and Markets™ Private Reserch. https://www.marketsandmarkets.com/Market-Reports/activated-carbon-362.html, accessed on 8th October 2020*

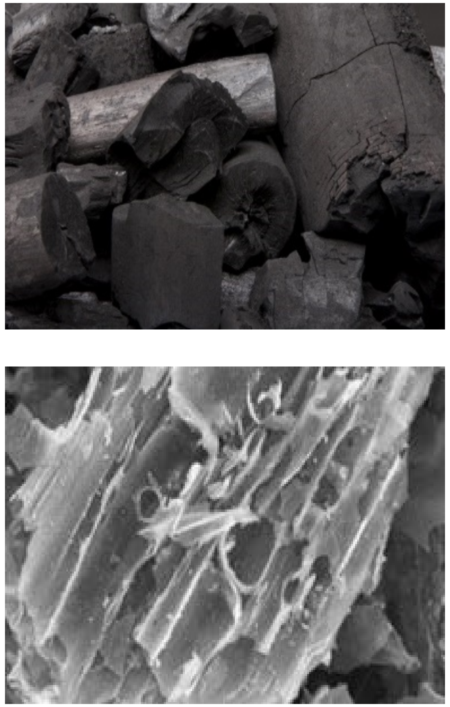
*b) The Observatory of Economic Complexity. https://oec.world/en/profile/hs92/63802/#trade, accessed on 08th October 2020*

# Polyester/Cotton for Adsorption and MAC characterization

# ACTIVATED CARBON Conventional Process

**Pyrolysis**

*Heat*
*Low Oxygen*



**Activation**

*Physical*
*($CO_2$/Steam)*
*Or*
*Chemical*
*Process*

***Biomass***

***Wood***
***Agro-Industrial***
***Residues***

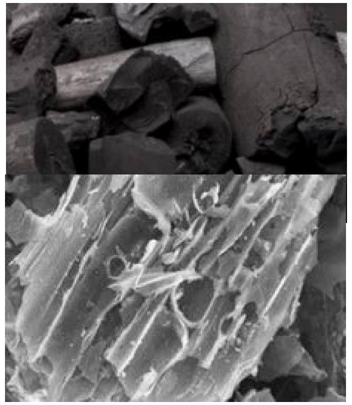
***Chrarcoal***

***Activated Carbon***
***Pore Development***

# ACTIVATED CARBON Chemical Activation

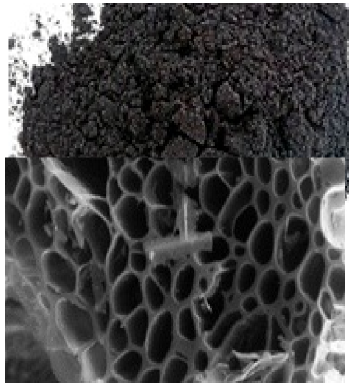
***Biomass***

**Pyrolysis**



***Charcoal***

**Activation**



***Activated Carbon***

**Pyrolysis and Simultaneous Activation**

Acid and/or Water Washing

EFFLUENTS
Heavy Metal
Acid, Salts

## Chemical Activation:

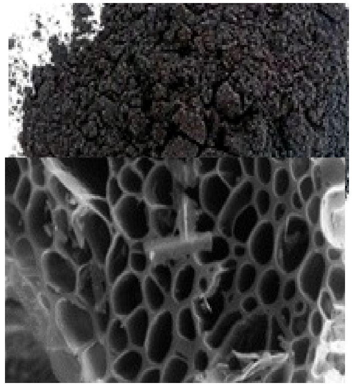
biomass OR charcoal Imprergnation with a Chemical compound ($H_3PO_4$, $ZnCl_2$, OH-,etc)

+ pyrolysis at 500-1000$^{o}$C, 2-4h ($N_2$, Ar)

+ washing → wastewater generation

# A NEW PROPOSAL Magnetic Activated Carbon from Textile

***Textile Residue***



***MAGNETIC Activated Carbon***

**NO Washing**

**Pyrolysis and Simultaneous Activation**

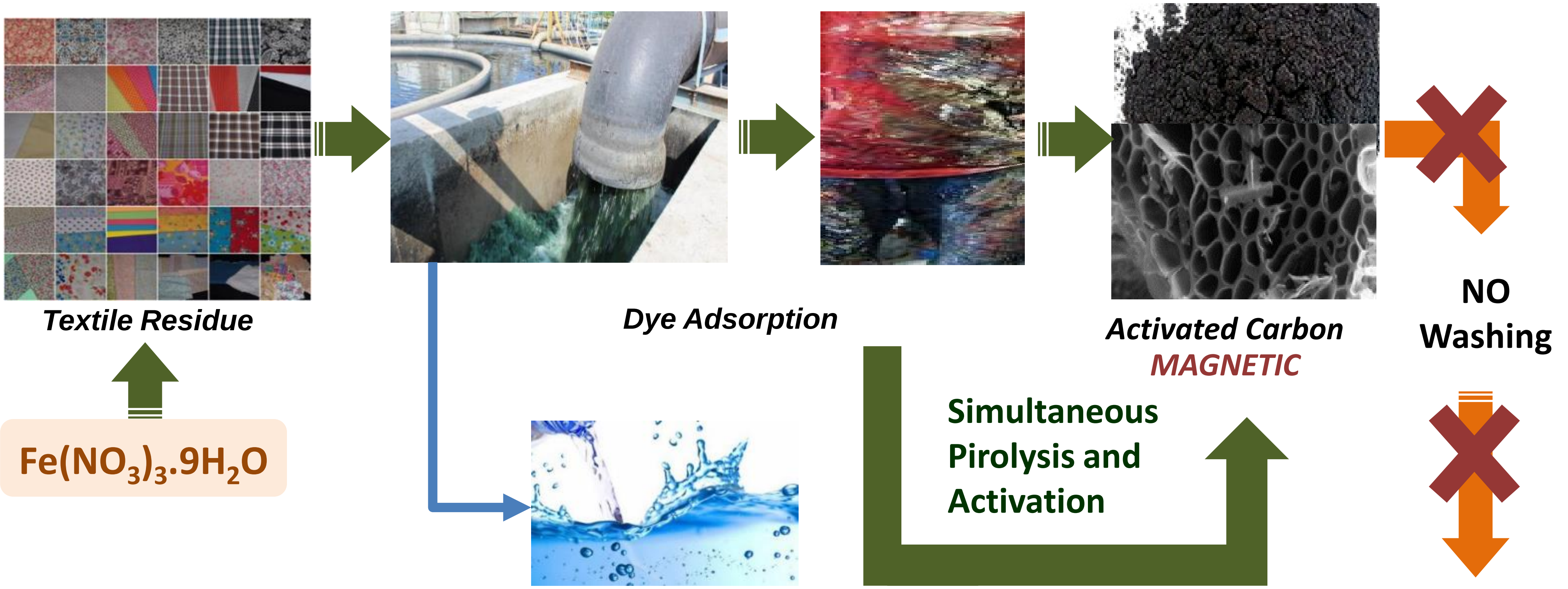
**NO Effluent**

**Chemical Activation**

impregnation with $Fe(NO_3)_3.9H_2O$

+ pyrolysis at 650-800$^oC$, 2h ($N_2$)

# A NEW PROPOSAL Magnetic Activated Carbon from Textile




NO
Effluent

**Alternative for Activated Carbon in Adsoprtion**

**Dye Destruction after adsorption**

**Increase C yield in the final AC**

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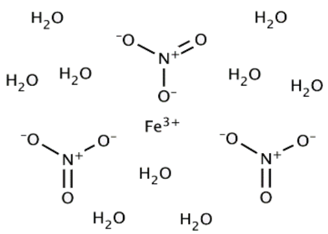
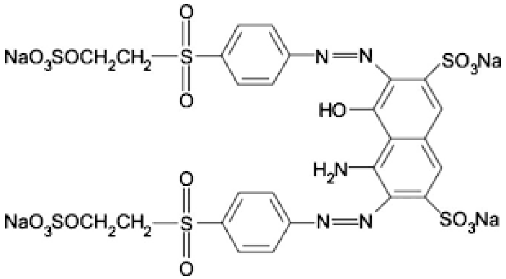
# METHOD Iron impregnation & Dye adsorption




**Reactive Black**
**50 mg $L^{-1}$**

**IMPREGNATION**
**(fabric:$Fe(NO_3)_3.H_2O$ )**
**1 g : 0.5 g**
**1 g : 1 g**
**(5 g fabric + 60-90 mL water)**

→

**DRYING**
**70 $^oC$, Overnight**

→

**DYE ADSORPTION**
**2 g Fabric : 1 L dye solution**
**2 h stirring @ 40 $^oC$**

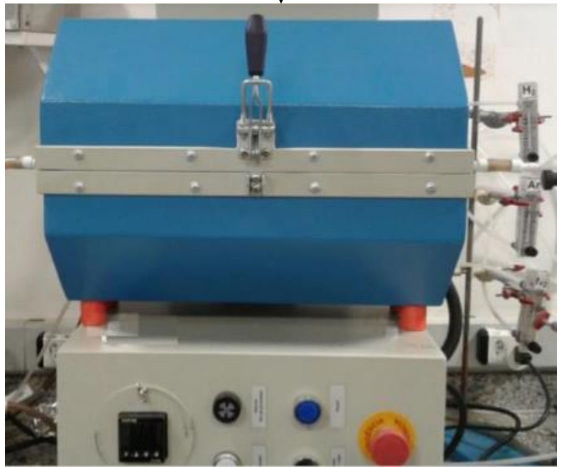
White AND Red
- Cotton
- Polyester
- Cotton/Polyester (50%)
- Polyester/Elastane (5%)

# METHOD Pyrolysis

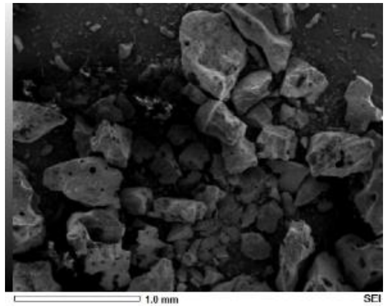
DYE ADSORPTION → FILTERING → DRYING 70 ºC, Overnight

FILTERING ↓

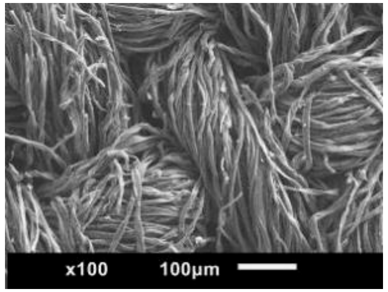
**UV-Vis**
**592nm**



Heating:
5 ºC.min$^{-1}$
700 ºC
2 h
$N_2$




Polyester based




Cotton based

Magnetic Mesoporous Activated Carbon

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# Cotton adsorption mechanism - kinetics

**Synthetic Dye Solution**

**Stock Solution:** 5g $L^{-1}$ Dye + 75 g $L^{-1}$ NaCl

**At Use:** Dilute to the required concentration

Add NaOH for pH=11

Oven 60 $^{o}$C, 1.5 h (hydrolysis)

Dilute 1:1 with water

## C) McKay-Poots intraparticle diffusion model

Multilinear plot $\Longrightarrow$ two steps occuring during colore removal process

Linear Coef ≠ 0 $\Longrightarrow$ intraparticle diffusion is NOT the only rate-controlling step

Linear Coef ∝ boundary layer thickness.

- indication of the ability of the adsorbents to remove the target pollutant from solution
- also seen as viscous drag which exists between the sorbent surface and solution

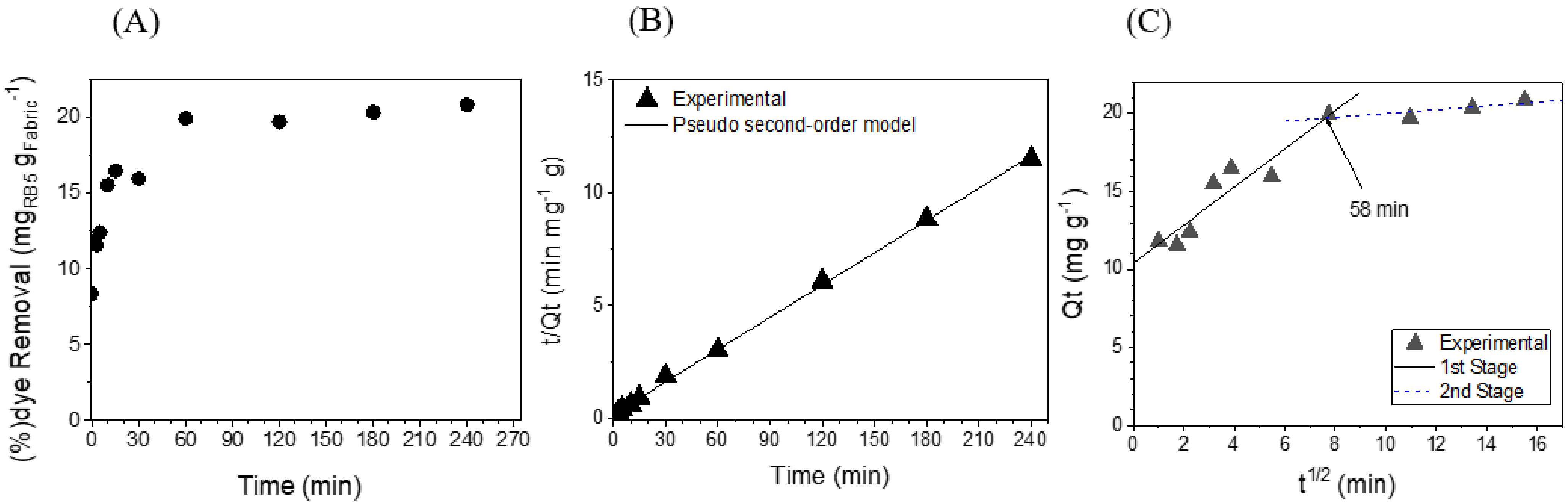
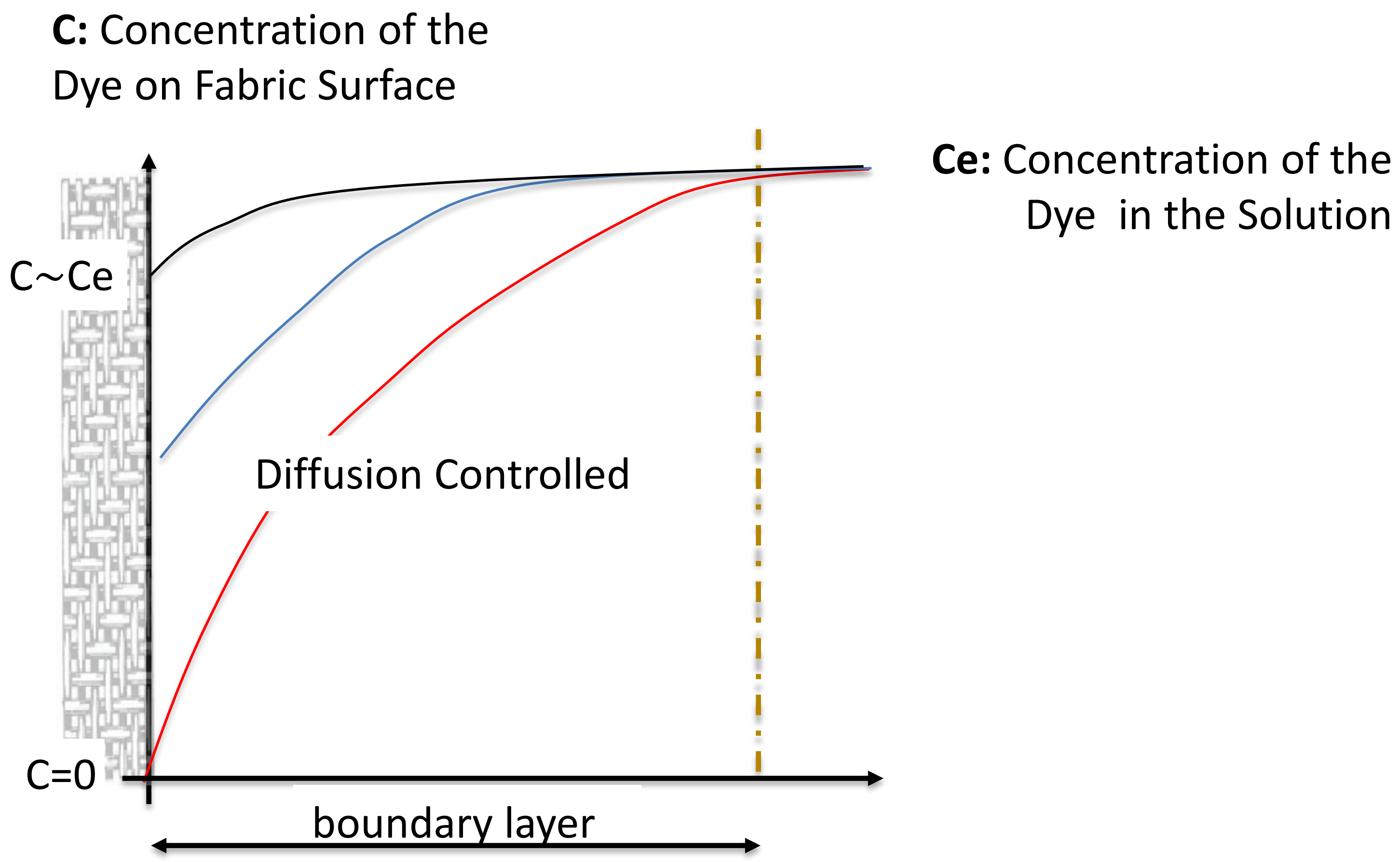



**Figure 1.** Reactive Black Dye Adsorption by White Cotton Fabric+Fe.
(A) Kinetics (starting dye/adsorbent = 50 mg/g), (B) pseudo-second order kinetics model, (C) McKay&Poots model.

# Cotton adsorption mechanism - kinetics



# Cotton adsorption mechanism – isotherm models

**Langmuir**:
$R^2$ = 0.967 (good Fit)  monolayer adsorption mechanism
$Q_{max}$ = 31 mg $g^{-1}$

(A)

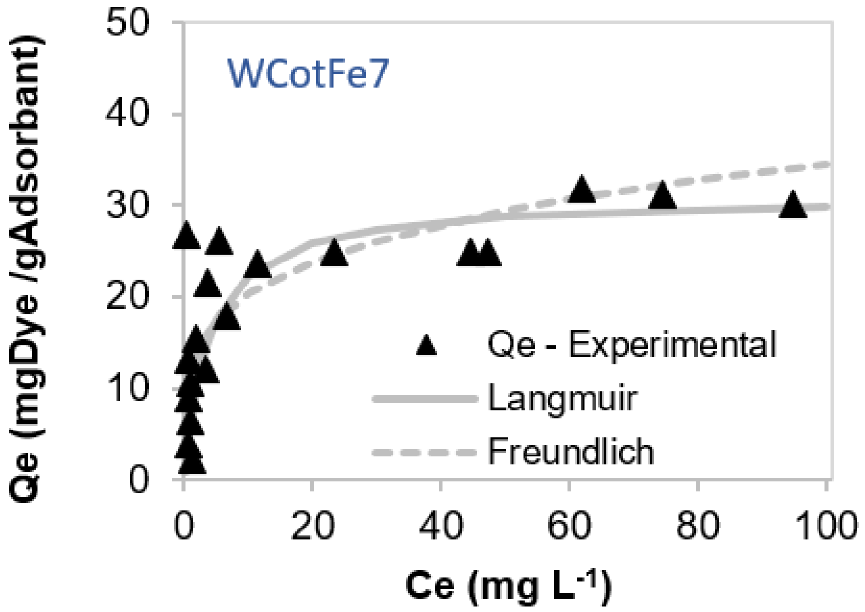



**Figure 2.** Reactive Black Dye Adsorption Isotherms at 40 $^oC$, 2 h contact.
(A) WCotFe7 in pH10

**Literature reference**

for reactive black dye adsorption:

Ferreira (2015), starting from 8.22 mg $L^{-1}$

Coal power plant Ash: 5.7 $mg_{RB5}$ $g^{-1}$, 60 h

Ip et al. (2009) , starting from 2000 mg $L^{-1}$

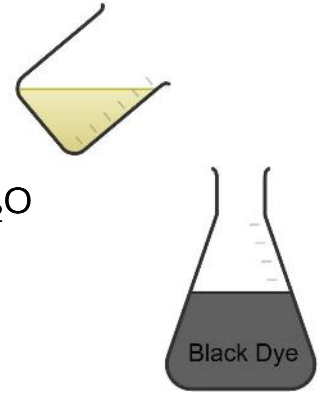
Peat 7 mg $g^{-1}$,

Bone char 157 mg $g^{-1}$

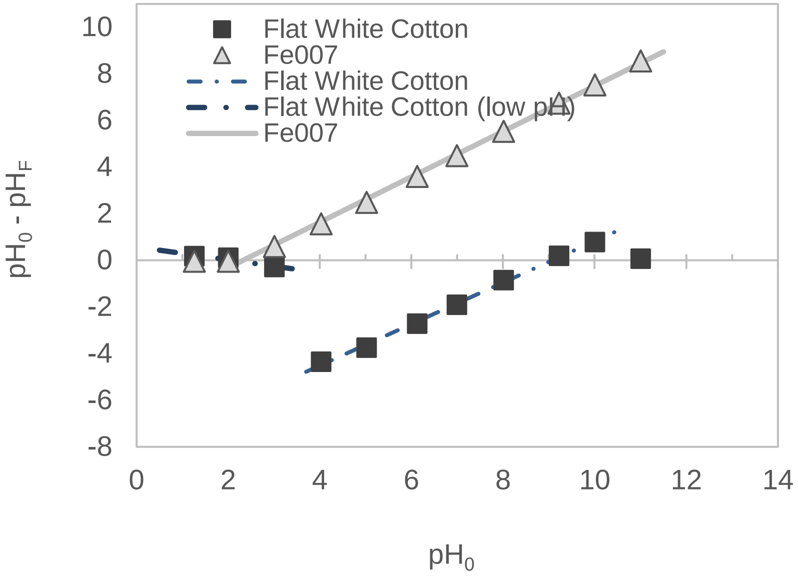
Commercial AC F400 and 176 mg $g^{-1}$

# Cotton adsorption mechanism – isotherm models (2)

$Fe(NO_3)_3.9H_2O$




**pH reduction**
**From ~10 to ~3**




| Adsorbent | PZC |
|---|---|
| Fabric (low pH) | 2.11 |
| Fabric (high pH) | 9.07 |
| WhiteC+Fe007 | 2.33 |

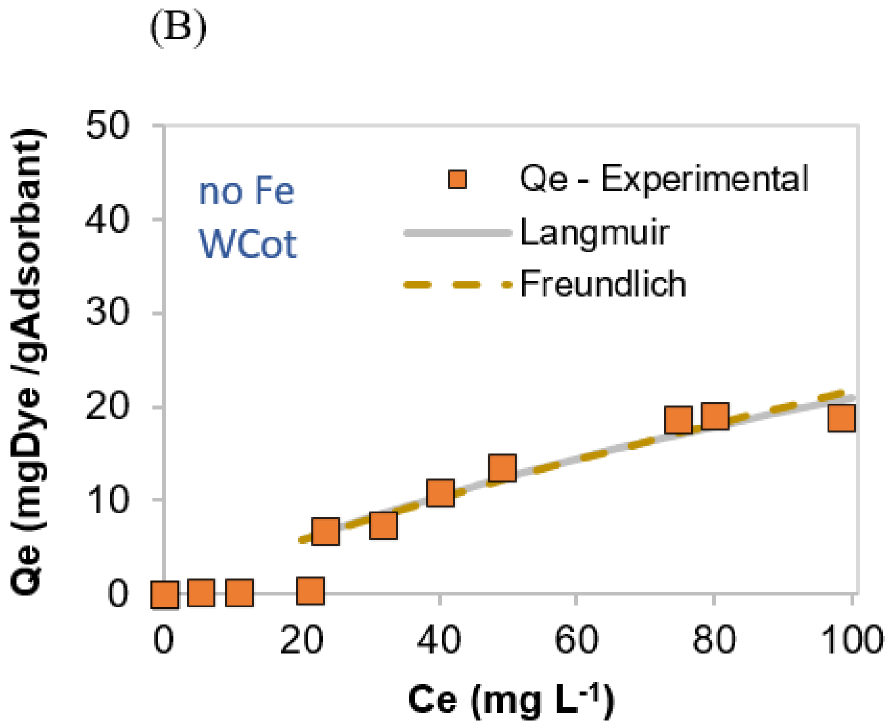


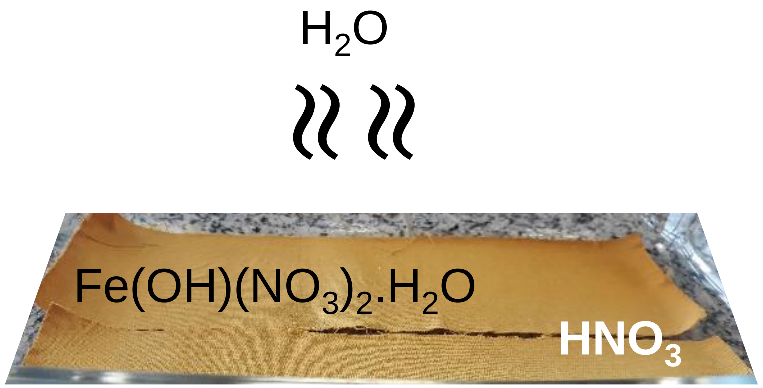

**Figure 2.** Reactive Black Dye Adsorption Isotherms at 40 ºC, 2 h contact.
(B) Pure Cotton in pH 2.5

# Color removal mechanism - theory

## 1) $HNO_3$ from $Fe(NO_3)_3.9H_2O$ reducing pH to PZC of Cotton

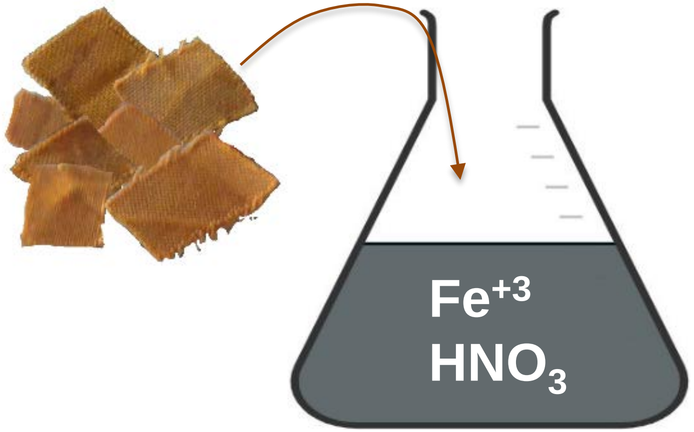
$$Fe(NO_3)_3.9H_2O \rightarrow Fe(OH)(NO_3)_2.H_2O + 7H_2O(g) + HNO_3$$

During fabric/Fe drying at 60 ~ 70 $^oC$ ($HNO_3$ boiling point: 88 $^oC$)




$$Fe(OH)(NO_3)_2.H_2O + H_2O \rightarrow Fe(OH)_3 + 2HNO_3$$

During fabric/Fe pouring into the dye solution

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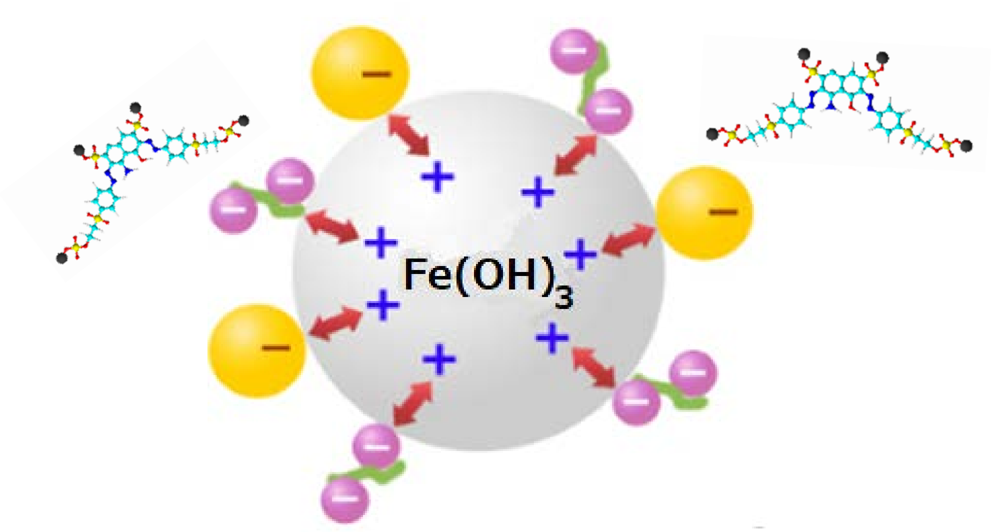
# Color removal mechanism – theory (2)

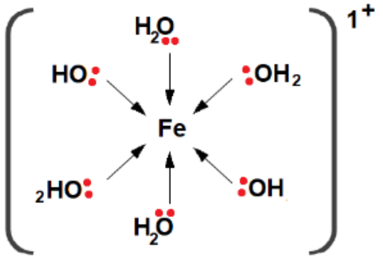
## 2) $Fe(OH)_3$ forming (+) aquocomplex agglomerating (-) dyes



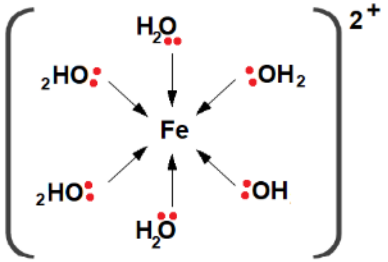

$$Fe^{3+} + 6H_2O \longrightarrow [Fe(H_2O)_6]^{3+}$$

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

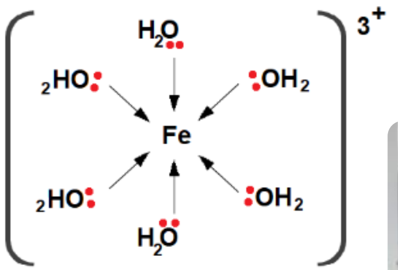
$$[Fe(H_2O)_5(OH)]^{2+} + 6H_2O \leftrightharpoons [Fe(H_2O)_4(OH)_2]^{1+} + H_3O^+$$



$[Fe(H_2O)_4(OH)_2]^+$

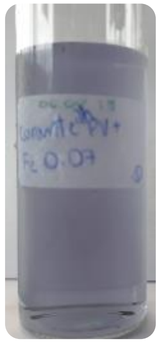


$[Fe(H_2O)_5(OH)]^{2+}$



$[Fe(H_2O)_6]^{3+}$

pale violet color

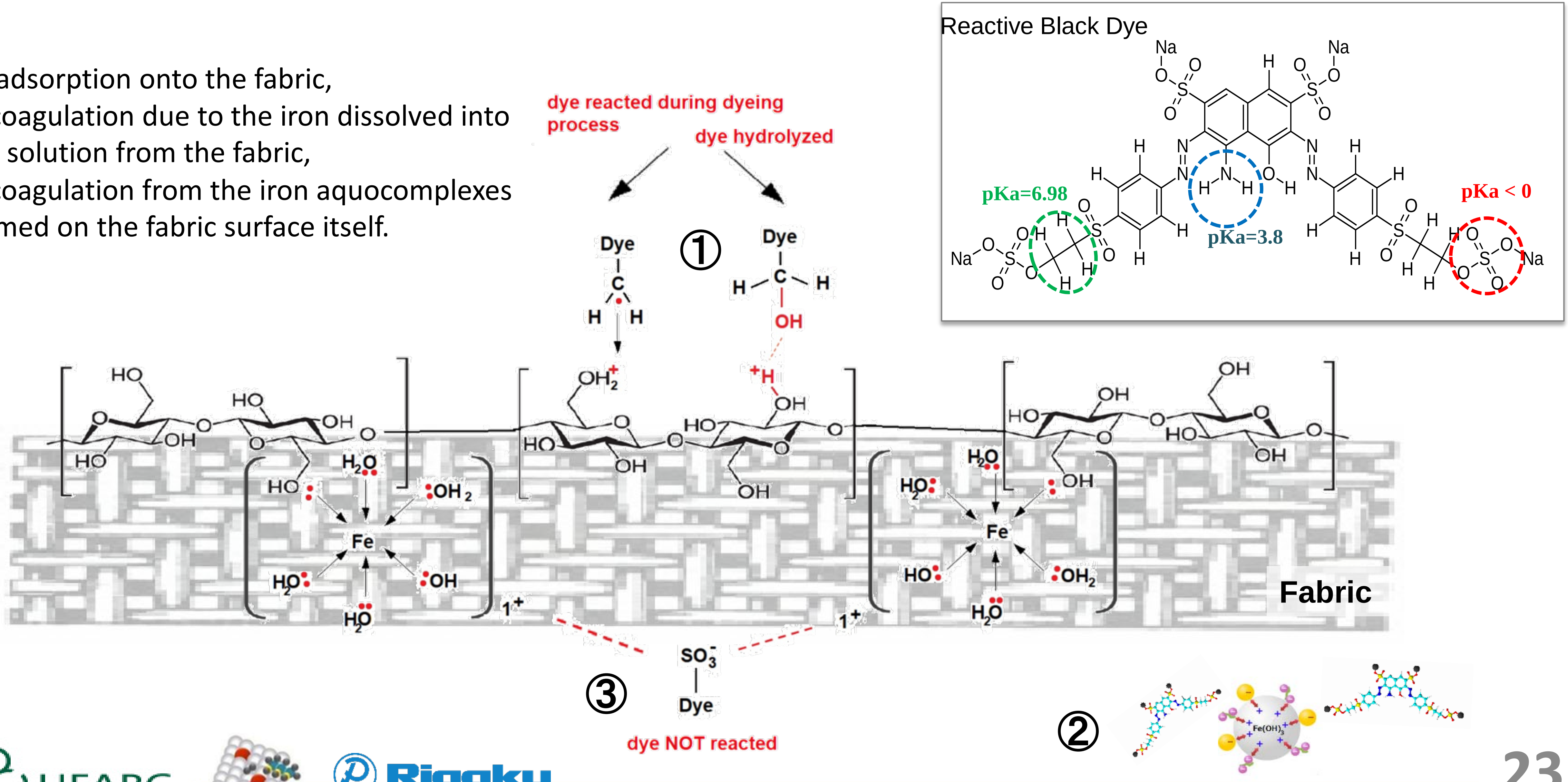


| | |
|---|---|
| $[Fe(OH)]^{2+}$ | <u>Bi-nuclear ions</u> |
| $[Fe(OH)]^{+}$ | $[Fe_2(H_2O)_8(OH)_2]^{4+}$ |
| $[Fe(OH)_3]^{0}$ | $[Fe_2(OH]_2)^{4+}$ |
| $[Fe(OH)_4]^{-}$ | |

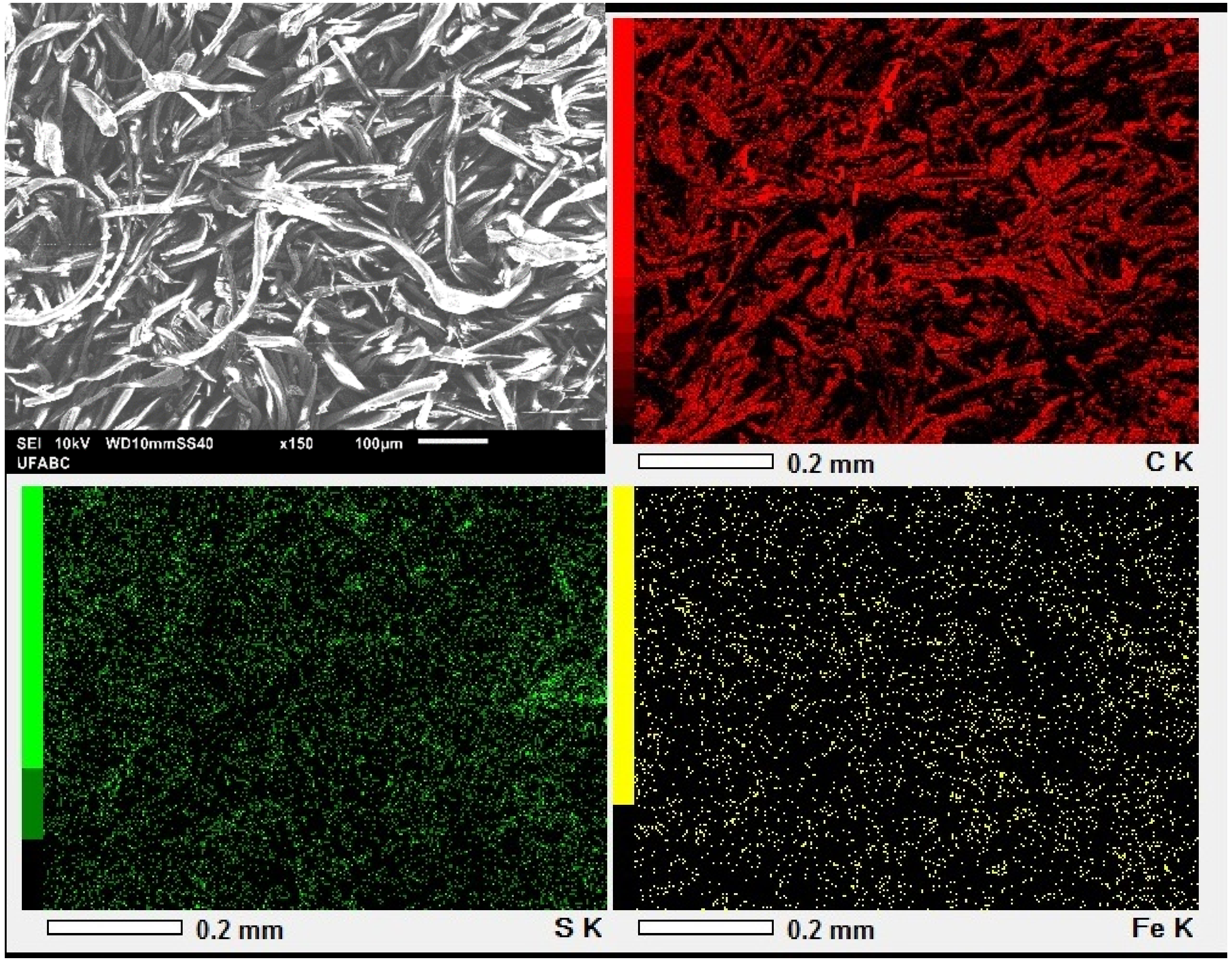
*(adapted from Lima, Abreu, 2018 and Bratby, 2006)*

# Color removal mechanism - theory

① adsorption onto the fabric,
②coagulation due to the iron dissolved into the solution from the fabric,
③coagulation from the iron aquocomplexes formed on the fabric surface itself.



# SEM images from Powder in Solution after adsorption

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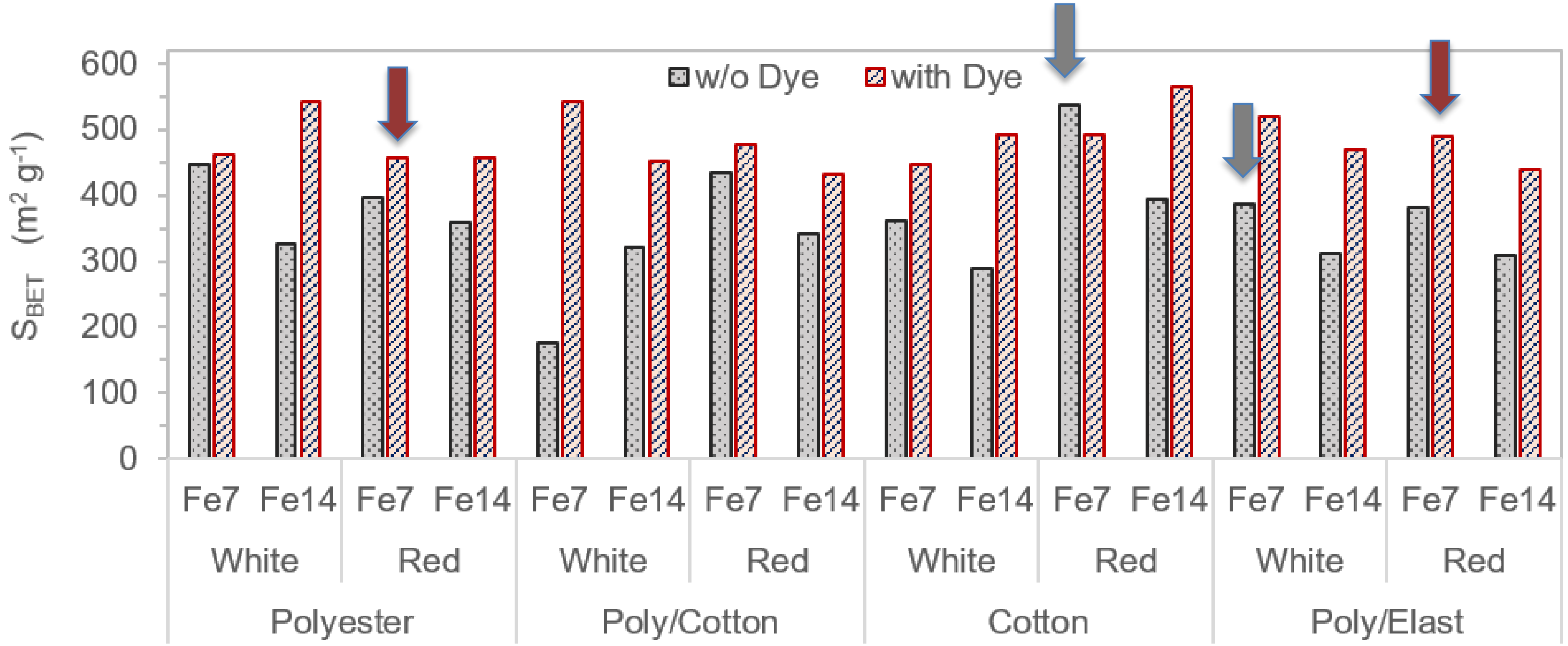
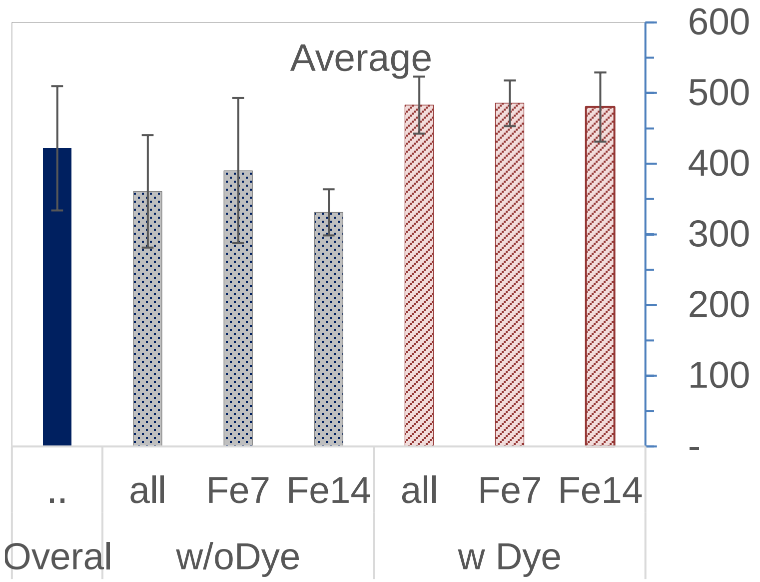
# MAC from Dye adsorbed fabrics – Surface Pore Area ($S_{BET}$)




Select only Fe7
2 w/o Dye and 2 wDye
For more detailed properties

Average $S_{BET}$($m^2\ g^{-1}$)

| | |
|---|---|
| All: | 422 ±88 |
| w/oDye: | 361 ±80 |
| wDye: | 483 ±40 |

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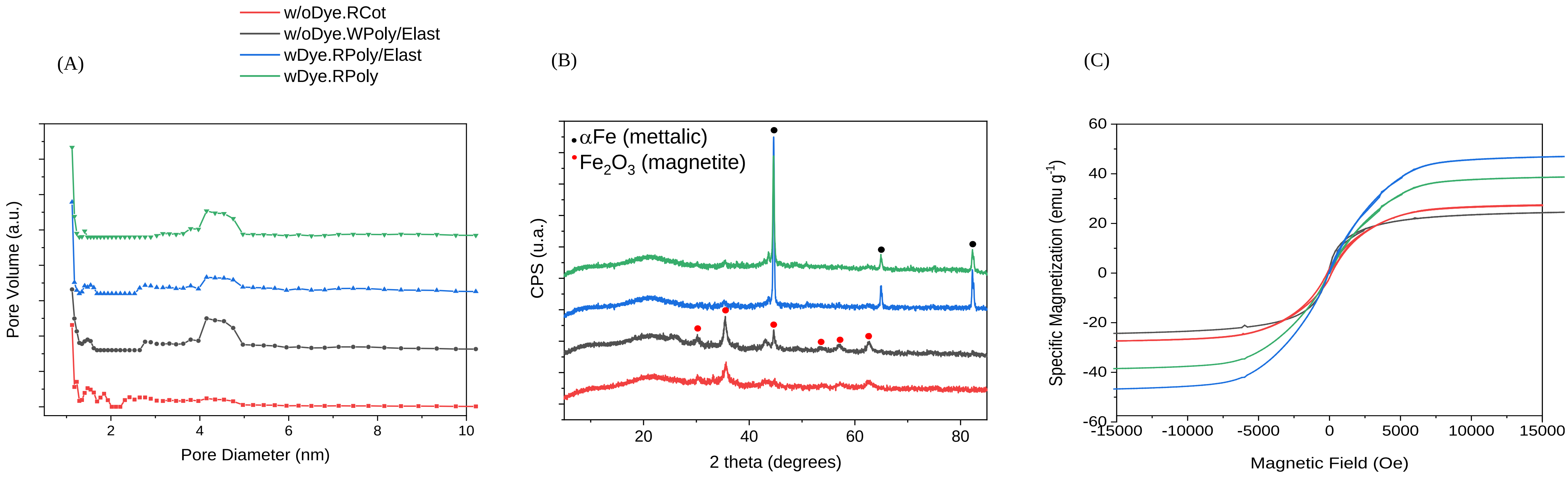
# MAC – 4 selected Properties

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# Conclusion

ADVANTEGES:

- Applicable in a wide pH range 3-12.
  Different from others that often requires acidic condition
- Easy separation of the adsorbent AFTER use
  As they are in fabric form, not in Powder
- Specific for negative charged pollutants
- Spent adsorbent and organic pollutants are destroyed during pyrolysis
- Fe component become metallic Fe instead of FexOy, with higher magnetization capacity as well as higher conductivity for eletrocatalysis applications
- New Income for the recycling agents in developing countries as Brazil.


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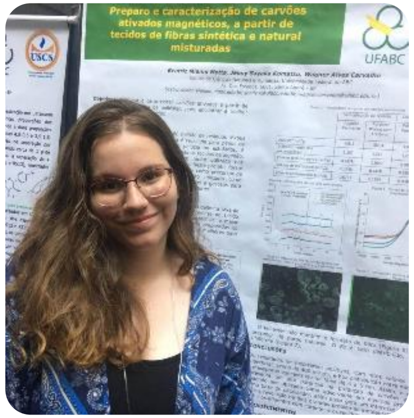
# TEAM

***ITIGO ITIE***

一期一会

**One Moment**

**One Meeting**




Beatriz Mianni
UnderGrad

Maria Vitória
UnderGrad

Academic Supervisor
Prof Dr Wagner Carvalho

(Former) Industrial Supervisor
Dr. Akihiko Iwata

Industrial Supervisor
Pol de Pape

NuTS

GCaso

Sustainable Technology Nucleus (NuTS)
Catalysis and Organic Sysnthesys Group (GCaso)

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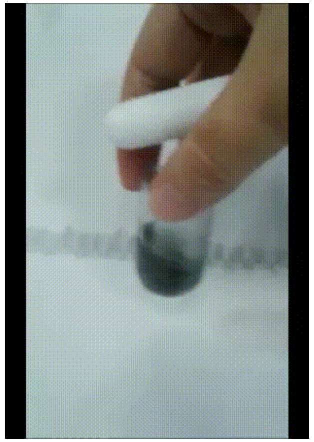
# THANK YOU FOR YOUR ATTENTION




*Jenny Sayaka Komatsu*

*UFABC – Campus Santo André*

*jenny.komatsu@gmail.com*


Sustainable Technologies Nucleus

# Related ODS

## Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all

Target 8.2: Achieve higher levels of economic productivity through diversification, technological upgrading and innovation, including through a **focus on high-value added and labour-intensive sectors**

## Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation

Target: 9.2 Promote inclusive and **sustainable industrialization**
9.5 Enhance scientific research, upgrade the technological capabilities of industrial sectors in all countries, in particular developing countries, including, by 2030, encouraging innovation and substantially **increasing the number of research and development workers** per 1 million people and public and private research and development spending

# Related ODS


## Make cities and human settlements inclusive, safe, resilient and sustainable

Target: 11.6 Reduce the adverse per capita environmental impact of cities, including by paying special attention to air quality and municipal and other waste management.

Indicator:

**11.6.1**

Proportion of urban solid waste regularly collected and with adequate final discharge out of total urban solid waste generated, by cities

**11.6.2**

Annual mean levels of fine particulate matter (e.g. PM2.5 and PM10) in cities (population weighted)

# Related ODS


## Ensure sustainable consumption and production patterns

12.5 By 2030, substantially **reduce waste generation** through prevention, reduction, **recycling and reuse**

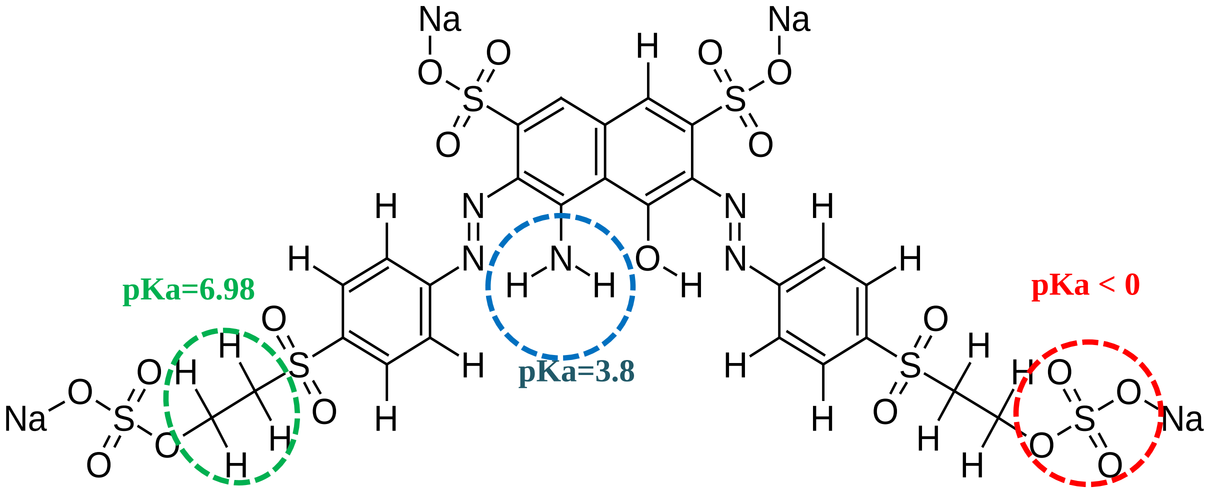

## Take urgent action to combat climate change and its impacts*

13.3 **Improve** education, awareness-raising and human and **institutional capacity on climate change mitigation**, adaptation, impact reduction and early warning

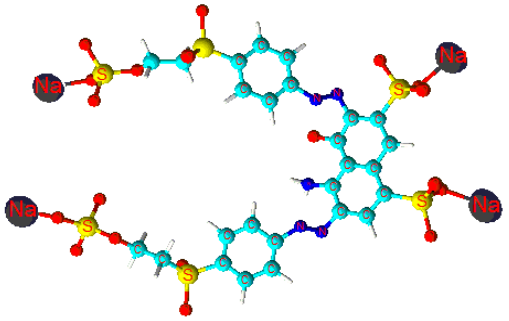

## Conserve and sustainably use the oceans, seas and marine resources for sustainable development

14.1 By 2025, prevent and significantly reduce marine pollution of all kinds, in particular **from land-based activities**, including marine debris and **nutrient pollution**

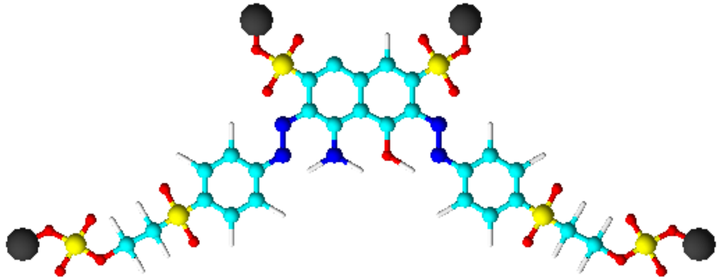
# Reactive Black Dye RB5, chemical structure




Reactive Black Dye 5: $C_{26}H_{21}N_5Na_4O_{19}S_6$ FW:991.816116



Bended structure: 2.9 nm x 1.25nm



Open structure: 3.3 nm x 1.2 nm

**Figure S2.** (a) Structural formula of RB5 and pKa values of each acidic group
(b) optimized three-dimensional structural formula of RB5, by ACD/ChemSketch software

# Iron hydroxide complex

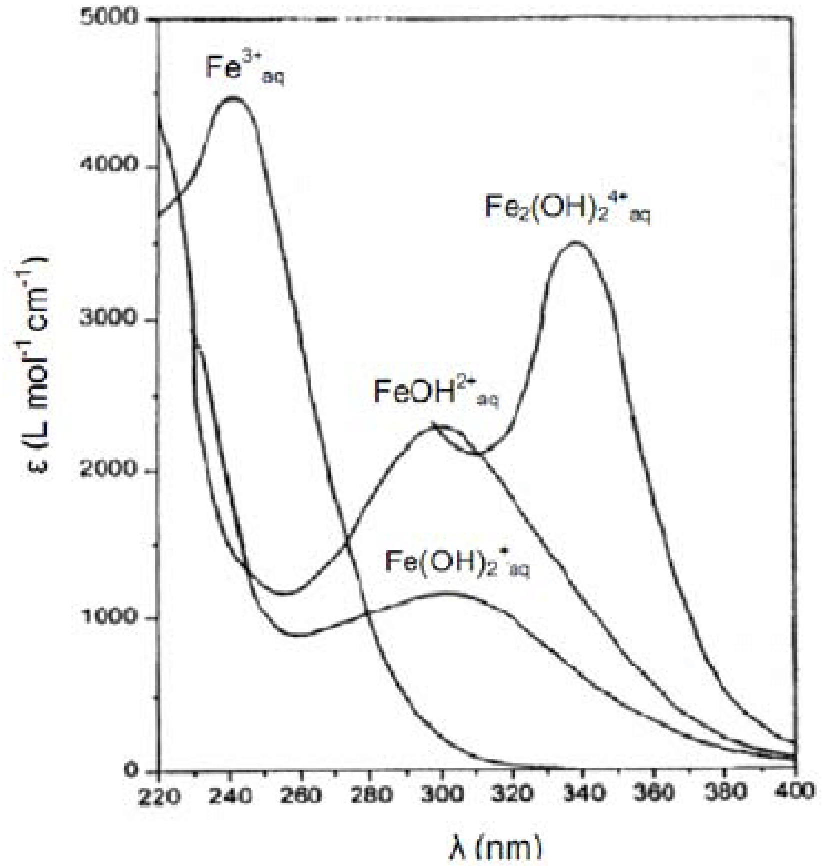
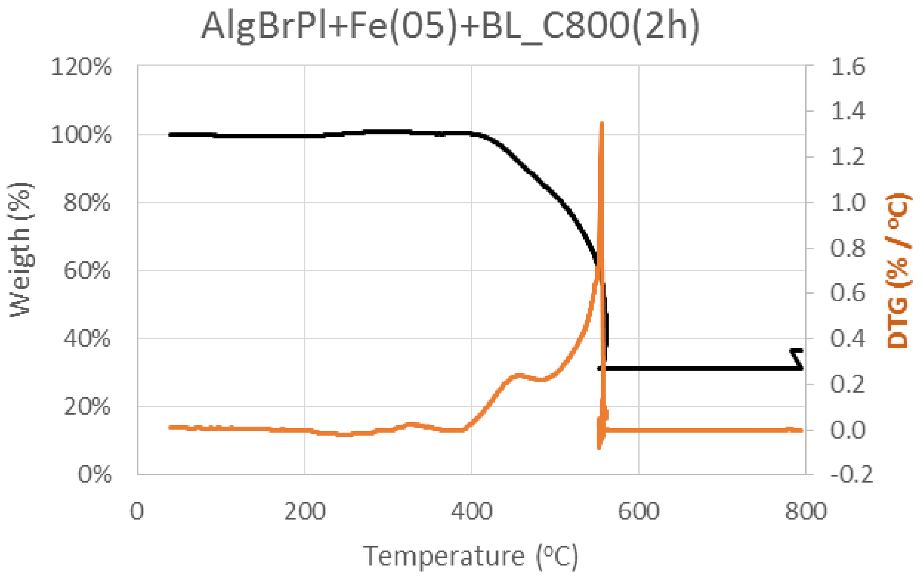



*Figure. UV-visible absorption spectra of Fe(III) complexes in aqueous solutions. Fe 3+ corresponds to the hexa-aquo complex (ferric ion),*

*Ref.: Loures, Carla C.A. et al. International Review of Chemical Engineering (I.RE.CH.E.), Vol. 5, N. 2*

Estabilidade térmica do carvão, sob $O_2$

(apresentação DAI 2018)




Umidade: 0,48%   volatéis: 62,84%   Cinzas: 36,68%
Comparando com carvão sem Fe, diferença de cinzas: +32,9%.
Se tudo Fe2O3, então carvão possui 23% Fe (pelo XRF: 12,8%)
Máxima temperatura para uso: 400ºC (antes da degradação)
Temperatura de auto-ignição: 556ºC (sem Fe: 468ºC)

# AC activated by $ZnCl_2$ x $Fe(NO_3)_3$

| Activating Agent | $Fe(NO_3)_3 9H_2O$ | | $ZnCl_2$ | |
|---|---|---|---|---|
| Nomenclature | C_FWC +Fe(0.07) | C_FWC +Fe(0.07)+BL2h | C_FWC +Zn(0.5) | C_FWC +Zn(1) |
| BET area ($m^2.g^{-1}$) | 183 | 417 | 1,543 | 1,404 |
| Total Pore Volume ($cm^3.g^{-1}$) | 0.162 | 0.287 | 0.674 | 0.814 |
| Micropore Volume ($cm^3.g^{-1}$) | 0.040 | 0.158 | 0.559 | 0.504 |
| Mesopore Volume ($cm^3.g^{-1}$) | 0.122 | 0.129 | 0.115 | 0.310 |
| % Micropore | 43 % | 55% | 83 % | 62 % |
| Hardness / Visual Aspect | Soft and malleable fabric AC.<br><br>Easy to handle, as a fabric. Possible to cut with scissors, although being very fragile, turning to powder very easily. | | Very Hard.<br><br>-Not possible to handle as fabric. -Keeps little fiber aspect<br>-Require maceration to make handling possible. | Do not keep fiber aspect, which is completely destroyed |
| Other observation | Magnetic specie: $Fe_3C$<br><br>Ms: 7.2 $emu.g^{-1}$ | Magnetic specie: Fe0<br><br>Dye solution prepared only by dissolving in distilled water. | Mass loss during handling, due to its hardness, and low density<br><br>High mass loss due to repeated cycles of acid and water washing/filtering | |

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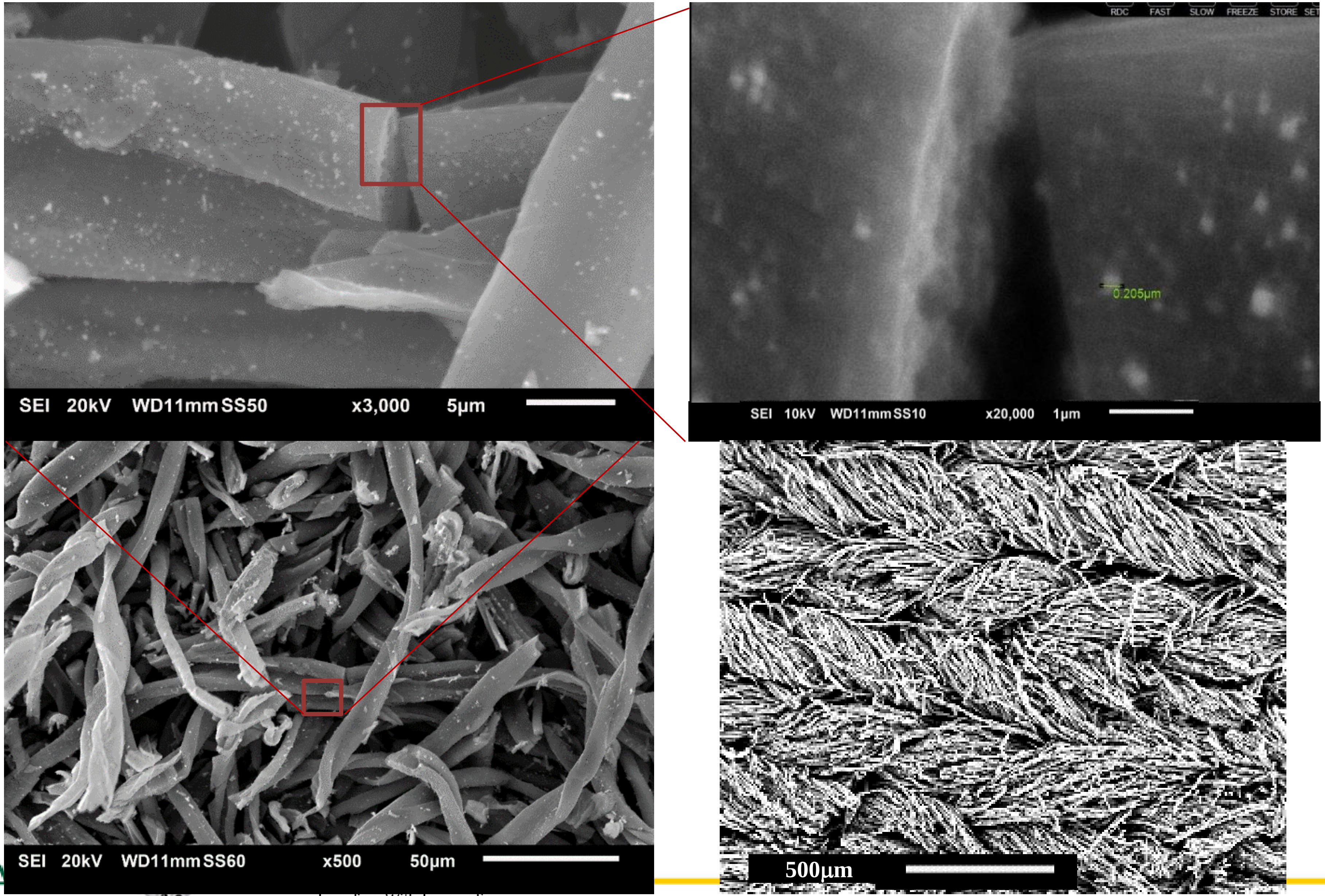
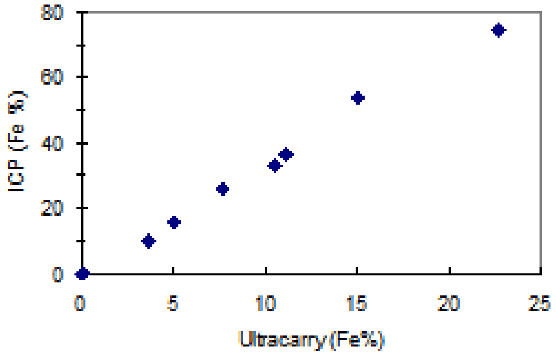
# SEM – C_F+Fe(11)+BL



# Fe quantification - ICP x WDXRF

*Figure 33*
*WDXRF UltraCarry® x ICP*

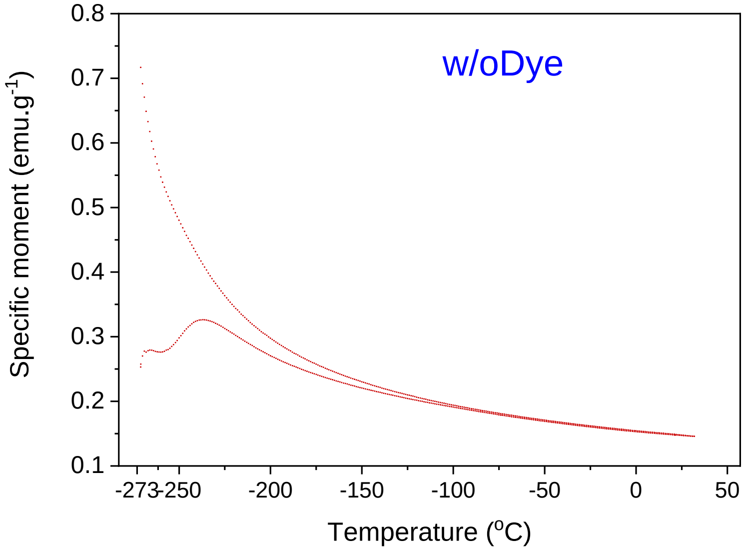



| Sample | AC_Fe0.07 | AC_Fe0.14 | AC_Fe0.07+Dye | AC_Fe0.14+Dye |
|---|---|---|---|---|
| **Theoretical** | 18.4 | 27.4 | < 14.2 | < 24.8 |
| **ICP** | 36.4 | 74.4 | 33.1 | 61.5 |
| **WDXRF Solid Phase** | 11.7 | n.a. | 12.7 | n.a. |
| **WDXRF Liquid Cell** | 17.7 | 27.0 | 14.7 | 31.0 |
| **WDXRF UltraCarry®** | 11.1 | 22.6 | 10.4 | 20.5 |
| **SEM-EDS** | 3.0 | 4.3 | 3.2 | 12.0 |
| **XPS** | 2.9 | n.a. | 1.47 | n.a. |

n.a.: not analyzed

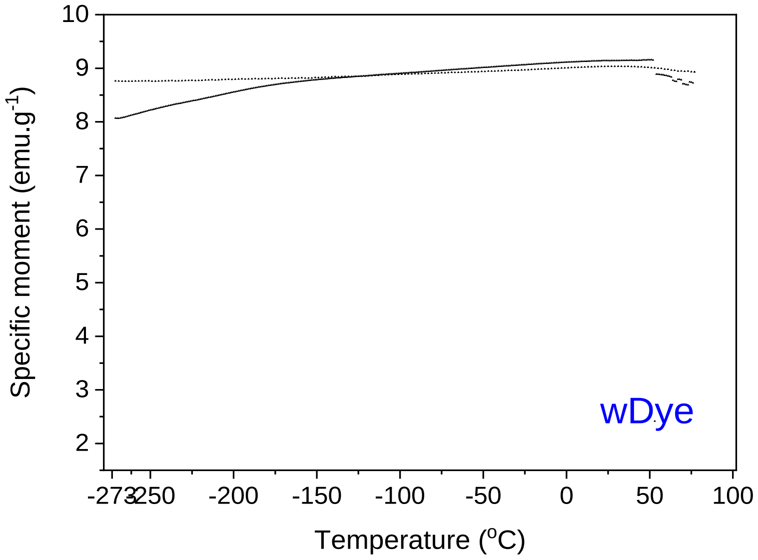
# MAC WhiteCotton.Fe7 – Magnetic properties

(A) Low Temperature



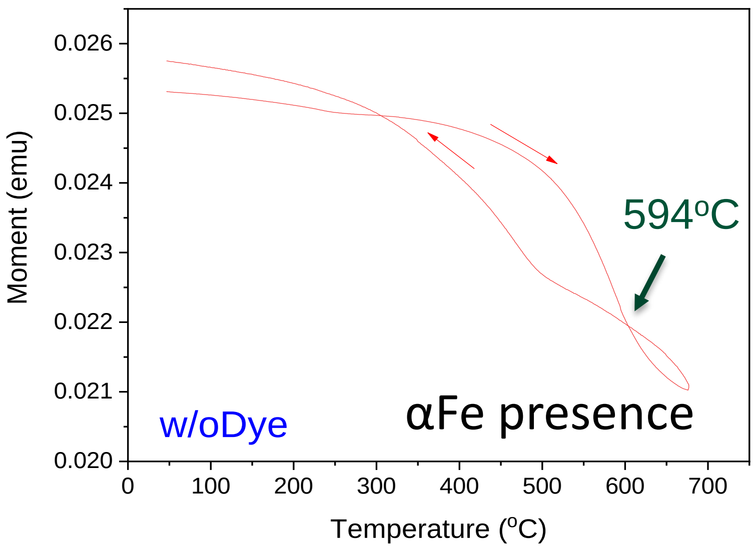

$Fe_3O_4$
Nanoparticle behavior

(B) Low Temperature




αFe
Bulk metal behavior

(C) High Temperature

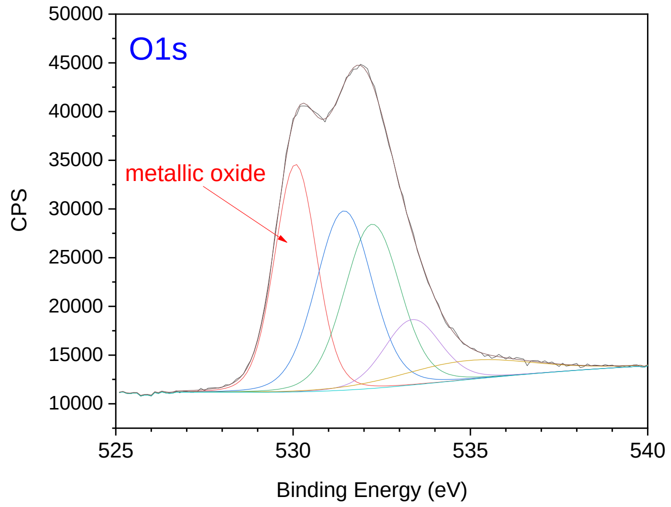


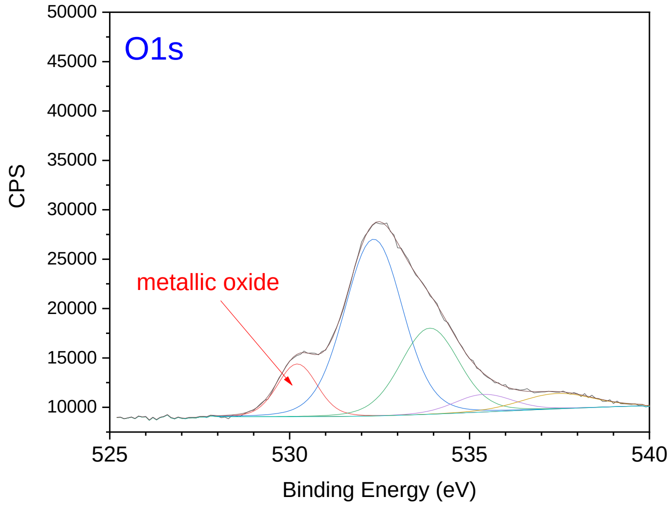

Curie temperature
$Fe_3O_4$ : 585 °C
αFe: 770 °C

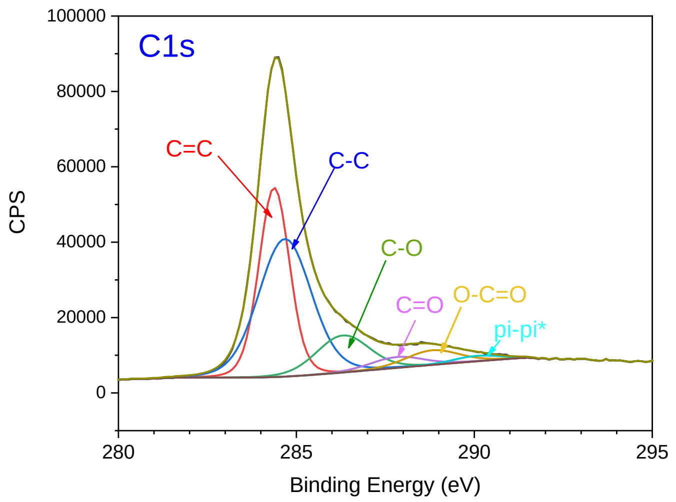
# MAC – XPS difference between $Fe_3O_4$ and αFe MAC

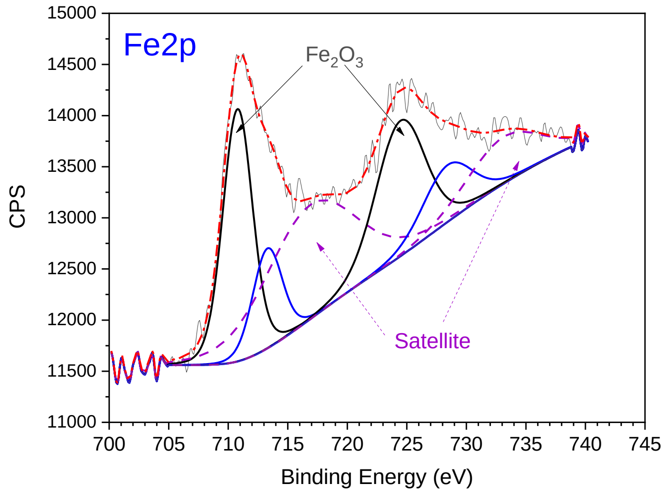
w/oDye WhitePoly/Elast ($Fe_3O_4$)

wDye RedPoly/Elast (αFe)

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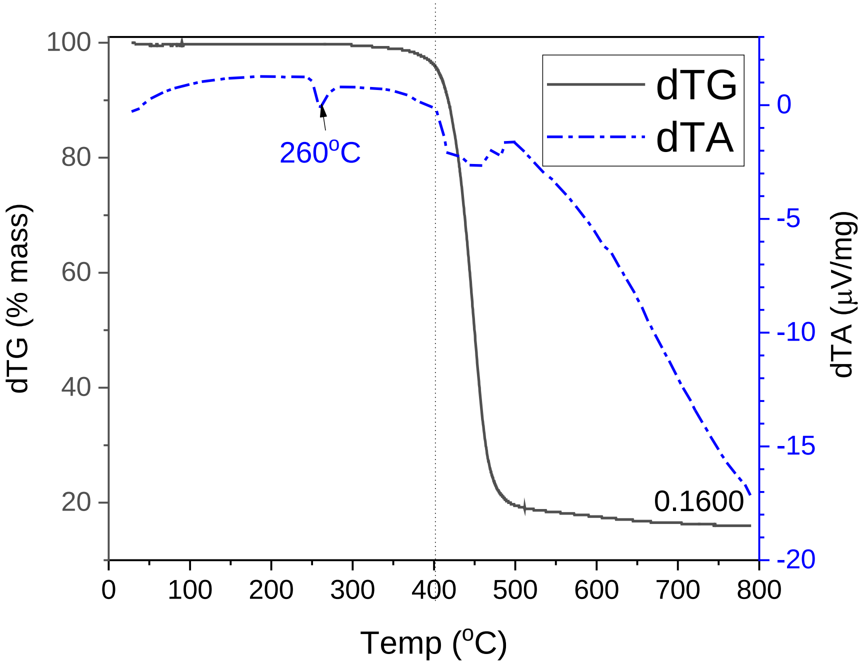
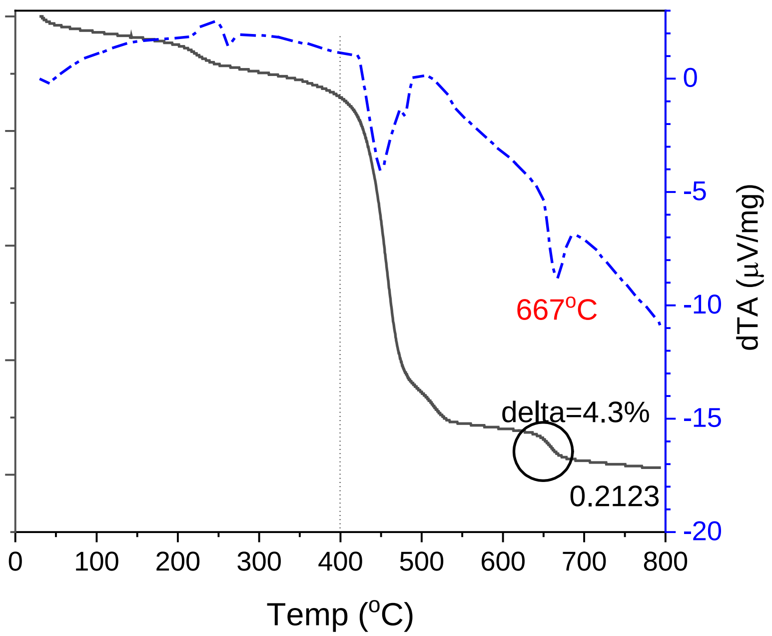
# TG under $N_2$ for Polyester/Elastane fabric

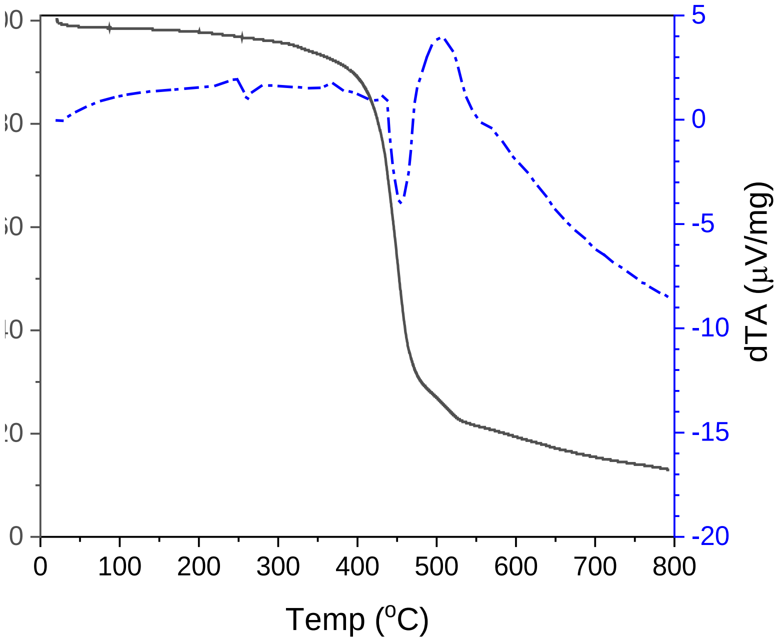
## no Fe




## Fe w/oDye




## Fe wDye

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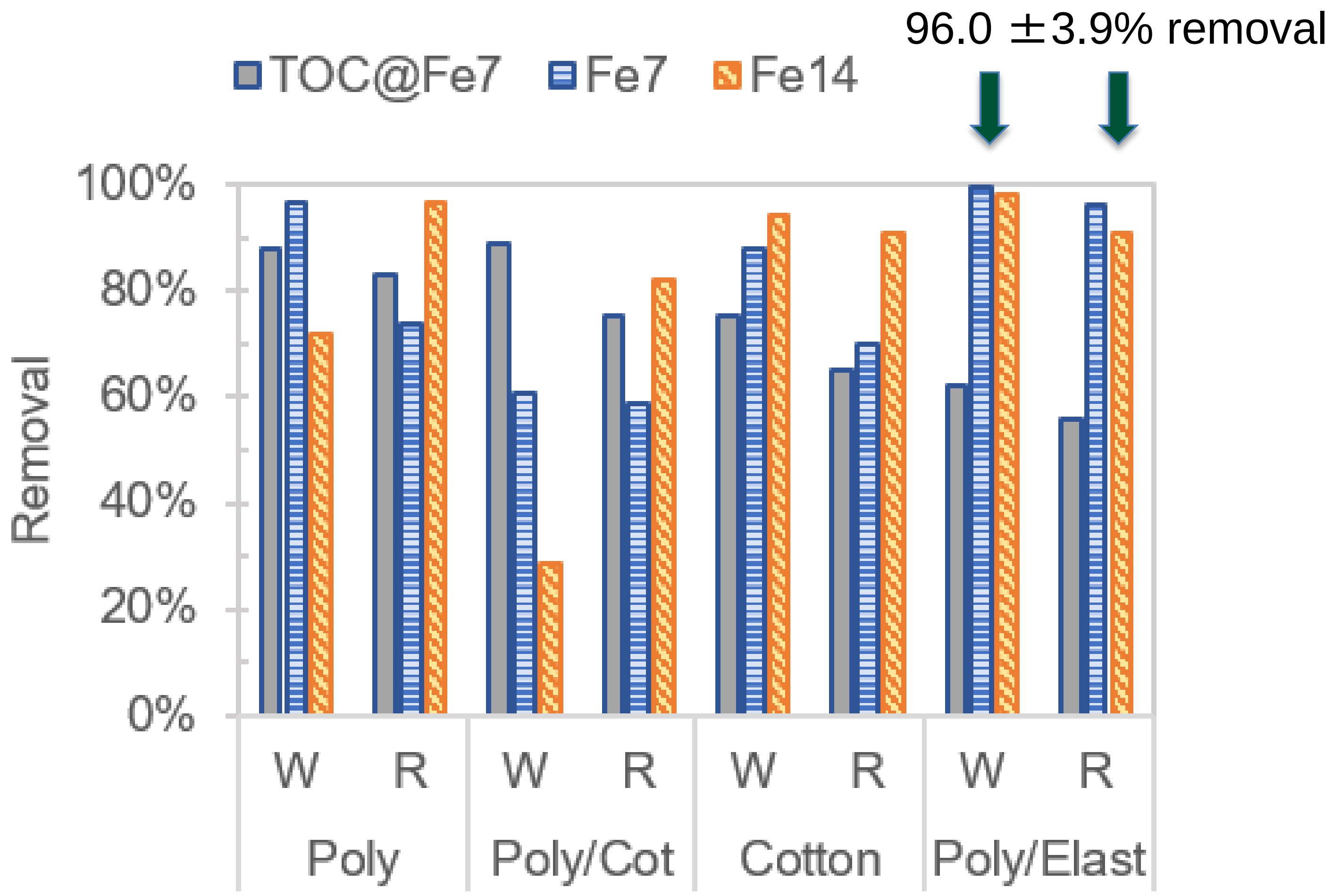
# Polyester mixed fabrics – adsorption capacity comparision




Experimental Conditions:

50 mg $L^{-1}$ synthetic Dye (NaCl pH~10)

1g Fabric to 100 mL solution

40 °C, 2h

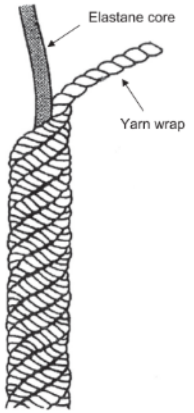
Fabrics:

Polyester
Poyester/Cotton 50%
Cotton
Polyester/Elastane 3%

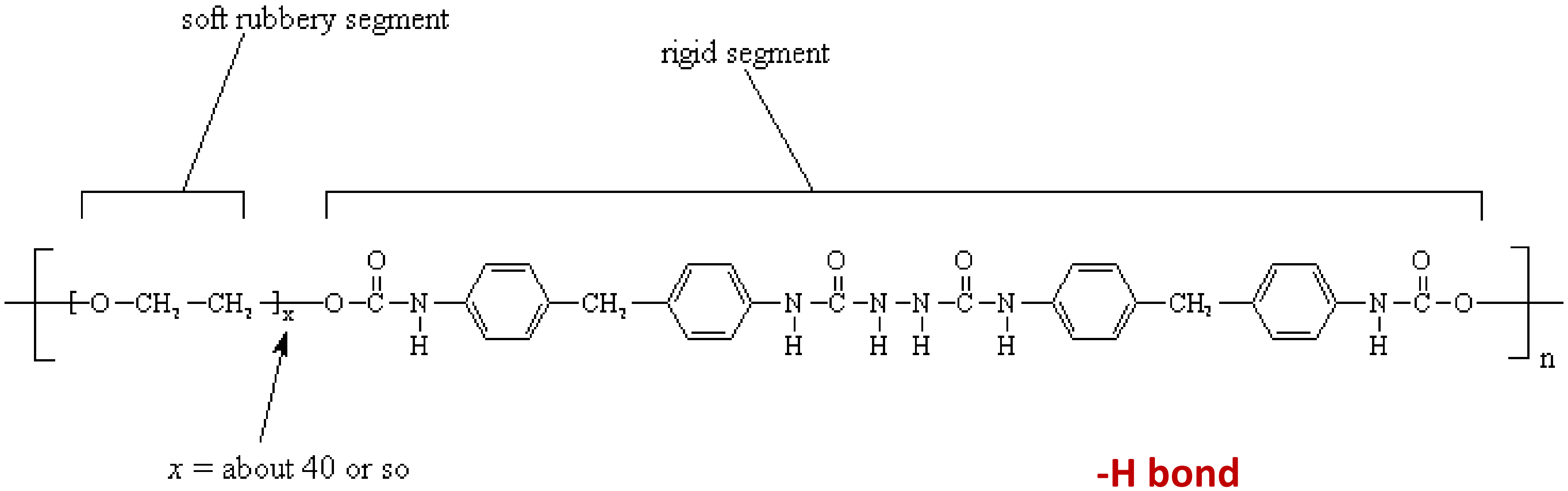
White and Red
Fe: 0.07 g $g^{-1}_{Fabric}$ and 0.014g $g^{-1}_{Fabric}$

# Elastane fiber

(A)



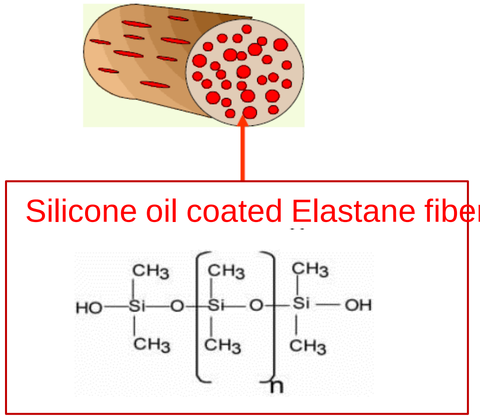

(B)



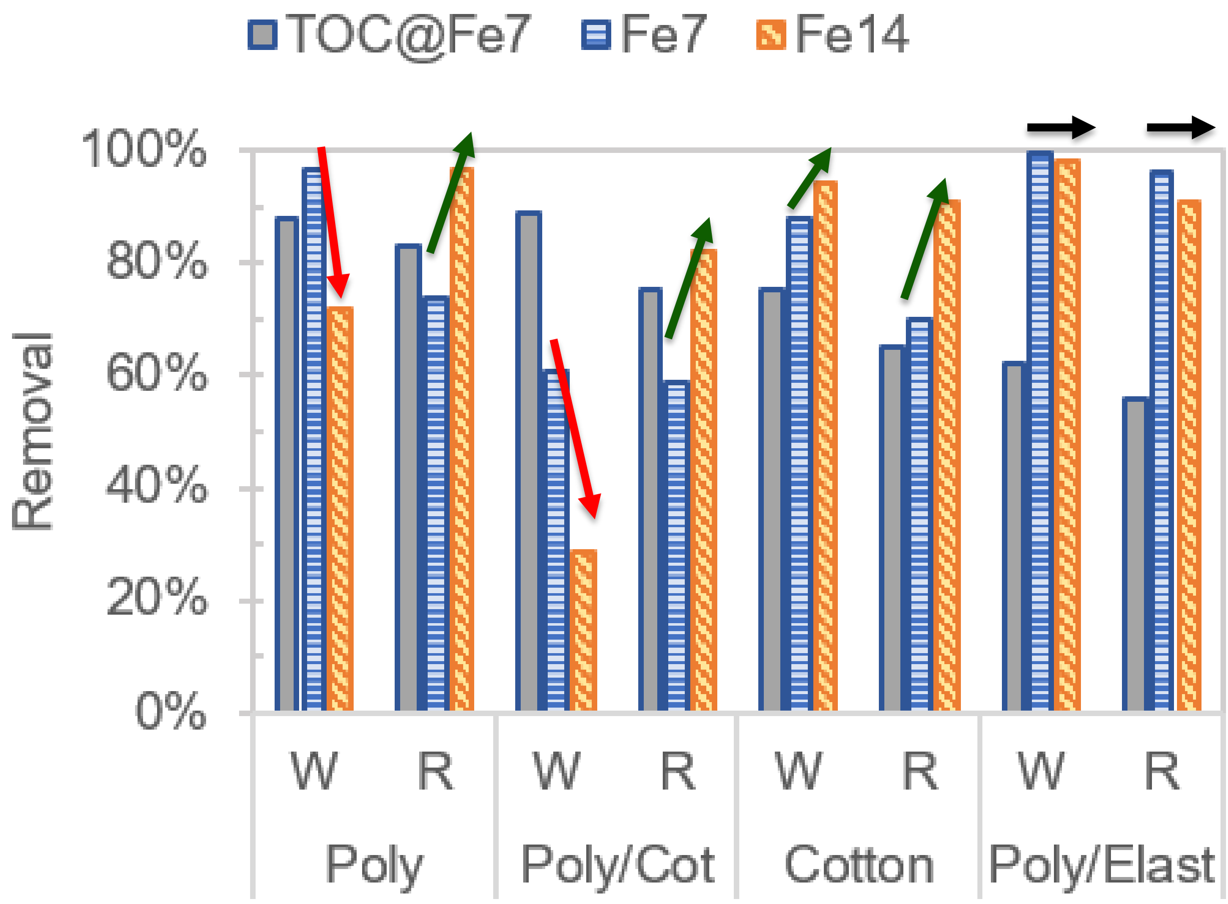

**-H bond**

Spandex has a complicated structure, with both urea and urethane linkages in the backbone chain.

(C)



# Polyester mixed fabrics – adsorption capacity comparision




Experimental Conditions:

50 mg $L^{-1}$ synthetic Dye (NaCl pH~10)

1g Fabric to 100 mL solution

40 $^{o}C$, 2h

Fabrics:

Polyester
Poyester/Cotton 50%
Cotton
Polyester/Elastane 3%

White and Red
Fe: 0.07 g $g^{-1}_{Fabric}$ and 0.014g $g^{-1}_{Fabric}$

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# Fabric Pictures – before and after adsorption


**SupFig 2.** WCotton pictures before (let) and after (rigth) dye adsorption
(A) Fe007 in pH10, (B) Fe014 in pH10, (C) Pure Cotton in pH 2.5