Fabric Waste Valorisation: a neglected material for application as dye adsorbent and magnetic mesoporous carbon precursor
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)
**DAI Program (Industrial Academic Doctorate program)**

**DAI**
Doutorado Acadêmico Industrial

- Academic Supervisor
- Industrial Supervisor
- Industry
- Project

**Pre-Doctorate**
2 to 6 months

**Industrial Academic Doctorate**
4 years

Start: 2013  UFABC + CNPq

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

http://dai.ufabc.edu.br/mapa.php
Research Context – Why Textile Fabrics?

Which is YOUR Environment?

OR

Brazil MSW Generation\textsuperscript{a}: 259,547 ton.day\textsuperscript{-1}

Textile

Latin America\textsuperscript{b}: 2.6 % (IPCC, 2006)
Brazil: 2.5 million ton.year\textsuperscript{-1}
World\textsuperscript{c}: 32 million ton.year\textsuperscript{-1}

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

<table>
<thead>
<tr>
<th>NATURAL FIBER</th>
<th>CHEMICAL FIBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>VEGETABLE</td>
<td>ANIMAL</td>
</tr>
<tr>
<td>SEEDS</td>
<td>SECREATION</td>
</tr>
<tr>
<td>Cotton</td>
<td>Silk</td>
</tr>
<tr>
<td>Kapok</td>
<td>HAIR/FUR</td>
</tr>
<tr>
<td>STALK</td>
<td>Alpaca</td>
</tr>
<tr>
<td>Hemp</td>
<td>Angora</td>
</tr>
<tr>
<td>Jute</td>
<td>Goat</td>
</tr>
<tr>
<td>Kenaf</td>
<td>Cashmere</td>
</tr>
<tr>
<td>Linen</td>
<td>Camel</td>
</tr>
<tr>
<td>Malva</td>
<td>Rabbit</td>
</tr>
<tr>
<td>Rami</td>
<td>Sheep (wool)</td>
</tr>
<tr>
<td>LEAF</td>
<td>Lhama</td>
</tr>
<tr>
<td>Abaca</td>
<td>Mohair</td>
</tr>
<tr>
<td>Caroa</td>
<td>Vicunha</td>
</tr>
<tr>
<td>Formio</td>
<td>Viscose</td>
</tr>
<tr>
<td>Sisal</td>
<td>FRUIT</td>
</tr>
<tr>
<td>Coconut</td>
<td>FABRIC WASTE</td>
</tr>
</tbody>
</table>

~15,000 colorants type (Ref1)

> 3150 additives listed in Industrial Guide (Ref2)


World Activated Carbon Market

WORLD PRODUCTION

- 0.4 million ton in 2000
- 5.7 million ton in 2015
- Projected 5.4 million ton in 2021

WIDE RANGE OF APPLICATIONS

- GAS
- WATER
- CATALYSIS

- Large Variety of applications
- Promoted mainly by environmental applications

BRAZIL FOREIGN TRADE

- Import
- Export

- Trade Amount (million $)

- Year


Precursor scarcity


Polyester/Cotton for Adsorption and MAC characterization

Cotton Fabric

Polyester Fabric

Iron Impregnation

Adsorbant

Reactive Black Dye

BET: 565 m² g⁻¹
Ms: 47.5 emu g⁻¹
CoreShell αFe or Fe₃O₄

Magnetic Activated Carbon

Carbonization

Activation

Magnetization
ACTIVATED CARBON  Conventional Process

Pyrolysis
Heat
Low Oxygen

Biomass
Wood
Agro-Industrial
Residues

Charcoal

Activation
Physical
(CO₂/Steam)
Or
Chemical
Process

Activated Carbon
Pore Development
ACTIVATED CARBON Chemical Activation

Chemical Activation:
biomass OR charcoal Imprergnation with a Chemical compound
\((\text{H}_3\text{PO}_4, \text{ZnCl}_2, \text{OH-},\text{etc})\)
+ pyrolysis at 500-1000°C, 2-4h (N\(_2\), Ar)
+ washing \(\rightarrow\) wastewater generation
A NEW PROPOSAL  Magnetic Activated Carbon from Textile

Textile Residue

Pyrolysis and Simultaneous Activation

Chemical Activation
impregnation with Fe(NO₃)₃.9H₂O
+ pyrolysis at 650-800°C, 2h (N₂)

MAGNETIC Activated Carbon

NO Washing

NO Effluent

UFABC

Rigaku
Leading With Innovation
A NEW PROPOSAL  Magnetic Activated Carbon from Textile

Alternative for Activated Carbon in Adsorption
Dye Destruction after adsorption
Increase C yield in the final AC
METHOD  Iron impregnation & Dye adsorption

IMPREGNATION
(fabric:Fe(NO₃)₃·H₂O)
1 g : 0.5 g
1 g : 1 g
(5 g fabric + 60-90 mL water)

DRYING
70 °C, Overnight

DYE ADSORPTION
2 g Fabric : 1 L dye solution
2 h stirring @ 40 °C

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

Reactive Black
50 mg L⁻¹
METHOD  Pyrolysis

- DYE ADSORPTION
- FILTERING
- DRYING 70 °C, Overnight

UV-Vis 592nm

Polyester based  Cotton based

Magnetic Mesoporous Activated Carbon

Heating:
5 °C.min⁻¹
700 °C
2 h
N₂
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 °C, 1.5 h (hydrolysis)
- Dilute 1:1 with water

**C) McKay-Poots intraparticle diffusion model**

Multilinear plot $\implies$ two steps occurring during color removal process

Linear Coef $\neq 0 \implies$ intraparticle diffusion is NOT the only rate-controlling step

Linear Coef $\propto$ 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.

**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.
C: Concentration of the Dye on Fabric Surface

Ce: Concentration of the Dye in the Solution

Diffusion Controlled
Cotton adsorption mechanism – isotherm models

**Langmuir:**
R\(^2\) = 0.967 (good Fit) monolayer adsorption mechanism
Q\(_{\text{max}}\) = 31 mg g\(^{-1}\)

(A)

**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\(^{-1}\)

**Figure 2.** Reactive Black Dye Adsorption Isotherms at 40 °C, 2 h contact.
(A) WCotFe7 in pH10
Cotton adsorption mechanism – isotherm models (2)

Fe(NO$_3$)$_3$·9H$_2$O

pH reduction
From ~10 to ~3

Fe(NO$_3$)$_3$·9H$_2$O

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric (low pH)</td>
<td>2.11</td>
</tr>
<tr>
<td>Fabric (high pH)</td>
<td>9.07</td>
</tr>
<tr>
<td>WhiteC+Fe007</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Figure 2. Reactive Black Dye Adsorption Isotherms at 40 ºC, 2 h contact.
(B) Pure Cotton in pH 2.5
1) HNO₃ from Fe(NO₃)₃·9H₂O
   reducing pH to PZC of Cotton

   Fe(NO₃)₃·9H₂O → Fe(OH)(NO₃)₂·H₂O + 7H₂O(g) + HNO₃

   During fabric/Fe drying at 60 ~ 70 °C (HNO₃ boiling point: 88 °C)

   Fe(OH)(NO₃)₂·H₂O + H₂O → Fe(OH)₃ + 2HNO₃

   During fabric/Fe pouring into the dye solution
2) Fe(OH)$_3$ forming (+) aquocomplex
agglomerating (-) dyes

\[
\text{Fe}^{3+} + 6\text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O)}_6]^{3+}
\]

\[
[\text{Fe(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe(H}_2\text{O)}_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+
\]

\[
[\text{Fe(H}_2\text{O)}_5(\text{OH})]^{2+} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Fe(H}_2\text{O)}_4(\text{OH})_2]^{1+} + \text{H}_3\text{O}^+
\]

(Adapted from Lima, Abreu, 2018 and Bratby, 2006)
Color removal mechanism - theory

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

![Diagram of dye adsorption and coagulation](image.png)
SEM images from Powder in Solution after adsorption
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/o Dye: 361 ± 80
- wDye: 483 ± 40
Conclusion

ADVANTAGES:

• 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 electrocatalysis applications
• New Income for the recycling agents in developing countries as Brazil.
Academic Supervisor
Prof Dr Wagner Carvalho

(Former) Industrial Supervisor
Dr. Akihiko Iwata

Industrial Supervisor
Pol de Pape

Sustainable Technology Nucleus (NuTS)
Catalysis and Organic Synthesis Group (GCaso)
THANK YOU FOR YOUR ATTENTION

Jenny Sayaka Komatsu
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Sustainable Technologies Nucleus
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
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)
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**
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
Figure. UV-visible absorption spectra of Fe(III) complexes in aqueous solutions. Fe 3+ corresponds to the hexa-aquo complex (ferric ion).

Estabilidade térmica do carvão, sob O₂
(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: 400°C (antes da degradação)
Temperatura de auto-ignição: 556°C (sem Fe: 468°C)
### Activating Agent

<table>
<thead>
<tr>
<th>Activating Agent</th>
<th>Fe(NO₃)₃·9H₂O</th>
<th>ZnCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nomenclature</td>
<td>C_FWC + Fe(0.07)</td>
<td>C_FWC + Zn(0.5)</td>
</tr>
<tr>
<td>BET area (m².g⁻¹)</td>
<td>183</td>
<td>1,543</td>
</tr>
<tr>
<td>Total Pore Volume (cm³.g⁻¹)</td>
<td>0.162</td>
<td>0.674</td>
</tr>
<tr>
<td>Micropore Volume (cm³.g⁻¹)</td>
<td>0.040</td>
<td>0.559</td>
</tr>
<tr>
<td>Mesopore Volume (cm³.g⁻¹)</td>
<td>0.122</td>
<td>0.115</td>
</tr>
<tr>
<td>% Micropore</td>
<td>43 %</td>
<td>83 %</td>
</tr>
<tr>
<td></td>
<td>Easy to handle, as a fabric. Possible to cut with scissors, although being very fragile, turning to powder very easily.</td>
<td>-Not possible to handle as fabric. -Keeps little fiber aspect. -Require maceration to make handling possible.</td>
</tr>
<tr>
<td></td>
<td>Do not keep fiber aspect, which is completely destroyed</td>
<td></td>
</tr>
<tr>
<td>Other observation</td>
<td>Magnetic specie: Fe₃C, Ms: 7.2 emu.g⁻¹</td>
<td>Magnetic specie: Fe0</td>
</tr>
<tr>
<td></td>
<td>Dye solution prepared only by dissolving in distilled water.</td>
<td>Mass loss during handling, due to its hardness, and low density</td>
</tr>
<tr>
<td></td>
<td>High mass loss due to repeated cycles of acid and water washing/filtering</td>
<td></td>
</tr>
</tbody>
</table>
### Fe quantification - ICP x WDXRF

<table>
<thead>
<tr>
<th>Sample</th>
<th>AC_Fe0.07</th>
<th>AC_Fe0.14</th>
<th>AC_Fe0.07+Dy</th>
<th>AC_Fe0.14+Dy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>18.4</td>
<td>27.4</td>
<td>&lt; 14.2</td>
<td>&lt; 24.8</td>
</tr>
<tr>
<td>ICP</td>
<td>36.4</td>
<td>74.4</td>
<td>33.1</td>
<td>61.5</td>
</tr>
<tr>
<td>WDXRF Solid Phase</td>
<td>11.7</td>
<td>n.a.</td>
<td>12.7</td>
<td>n.a.</td>
</tr>
<tr>
<td>WDXRF Liquid Cell</td>
<td>17.7</td>
<td>27.0</td>
<td>14.7</td>
<td>31.0</td>
</tr>
<tr>
<td>WDXRF UltraCarry®</td>
<td>11.1</td>
<td>22.6</td>
<td>10.4</td>
<td>20.5</td>
</tr>
<tr>
<td>SEM-EDS</td>
<td>3.0</td>
<td>4.3</td>
<td>3.2</td>
<td>12.0</td>
</tr>
<tr>
<td>XPS</td>
<td>2.9</td>
<td>n.a.</td>
<td>1.47</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a.: not analyzed

*Figure 33: WDXRF UltraCarry® x ICP*
MAC WhiteCotton.Fe7 – Magnetic properties

Fe₃O₄
Nanoparticle behavior

αFe
Bulk metal behavior

Curie temperature
Fe₃O₄: 585 °C
αFe: 770 °C

594°C
MAC – XPS difference between Fe$_3$O$_4$ and αFe MAC

w/o Dye White Poly/Elast (Fe$_3$O$_4$)

w/Dye Red Poly/Elast (αFe)

O$_1$s

metallic oxide

C$_1$s

C=C

C-C

C=O

O-C=O

C=π-C=π

C=π=C=π

Fe$_2$p

Fe$_2$O$_3$

Satellite
TG under N₂ for Polyester/Elastane fabric

- **no Fe**
  - 260°C
  - 0.1600

- **Fe w/oDye**
  - 667°C
  - delta=4.3%
  - 0.2123

- **Fe wDye**
  - 260°C
Experimental Conditions:
50 mg L\(^{-1}\) synthetic Dye (NaCl pH~10)
1g Fabric to 100 mL solution
40 °C, 2h

Fabrics:
Polyester
Polyester/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) Elastane core

(B) Soft rubbery segment

(C) Silicone oil coated Elastane fiber

H bond

\[
\text{Spandex has a complicated structure, with both urea and urethane linkages in the backbone chain.}
\]
Polyester mixed fabrics – adsorption capacity comparison

Experimental Conditions:
50 mg L⁻¹ synthetic Dye (NaCl pH~10)
1g Fabric to 100 mL solution
40 °C, 2h

Fabrics:
Polyester
Polyester/Cotton 50%
Cotton
Polyester/Elastane 3%

White and Red
Fe: 0.07 g g⁻¹ Fabric and 0.014g g⁻¹ Fabric
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