

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

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This study aims to valorise the fabric wastes, solving another issue from the fashion industry: the coloured wastewater from the dyeing process, and still produce high added value product. Different types of fibers fabric (cotton, polyester, its mixture and mixture with elastane) were tested for reactive black dye adsorption, and subsequently carbonized to produce magnetic porous carbon. Magnetism is a hot topic in the development of new materials for use in adsorption and heterogeneous catalysis due to its easy to recover property, as well as for electrocatalyst support applied in supercapacitor and fuel cells (Thines, 2016). Nowadays, great focus is given to study the use of agro-industrial waste as feedstock for chemical transformations, neglecting the potential of municipal solid wastes (MSW). Among them, textile fabric waste is increasing worldwide, driven by the growth of the middle-class population, and the “Fast Fashion” phenomena, with more than 38 million ton being sent to landfill or incinerated in a year (Shepherd et al. 2017). In the other hand, there is a concern of material scarcity for activated carbon production (Market and Markets 2017) as its demand is increasing worldwide mainly due to more stringent environmental laws.

Method. Fabrics of four types of fibers (cotton, polyester, polyester50%/cotton50% and polyester/elastane(<10%)) and two different colours (white and red) were tested. *Adsorption.* Iron impregnation into the fabrics were made in two different ratios: for each 1 g of fabric, 0.5 g and 1.0 g of Fe(NO₃)₃·9H₂O was dissolved in 10 to 20 mL of distilled water, corresponding to 0.07 g_{Fe} and 0.14 g_{Fe} g_{fabric}⁻¹, (named Fe007 and Fe014 after fabric fiber name). Fabrics were cut in small pieces of about 1 cm x 1 cm, added to the iron nitrate solution and stirred for 1.5 h, removed from the solution and left to dry in an oven overnight at 60 °C. A stock solution of 5 g L⁻¹ of reactive black dye, and 15 g of NaCl to each 1 g of dye was prepared and kept under refrigeration until use. At the time of use, the stock solution was diluted to 100 mg L⁻¹ and the pH adjusted to 11 with 60% NaOH solution, and left in an oven at 60 °C for 1.5 h. Finally, the solution was diluted 1:1 with distilled water. Synthetic dye conditions were defined considering the wastewater characteristics in a jeans dyeing factory in Brazil. For the adsorption test 1 g of the iron impregnated fabric was used in 100 mL of 50 mg L⁻¹ dye solution, stirred for 2 h, under 40 °C. For colour removal it was considered the maximum absorption at 592 nm by UV-Vis spectrometer. Adsorption kinetics and isotherm study was performed for the white cotton fabric, and in this case, the iron impregnation was done without stirring, but only pouring a 5 mL water solution of 0.07 or 0.14 g_{Fe} g_{fabric}⁻¹ on the fabric. *Carbonization.* Carbonization and magnetization is performed together in an electrical tubular furnace with a heating rate of 10 °C min⁻¹, 700 °C for 2 hours in nitrogen flow, followed by natural cooling under nitrogen until temperature reaches 100 °C. No acid washing nor water rinsing is necessary after the pyrolysis.

Results. *Adsorption.* Iron impregnated white cotton (WhiteC+Fe) adsorption kinetics fitted better with Pseudo-second order model, with R² = 0.9990 and 0.9642, k₂ = 0.012 and 0.008 g mg⁻¹min⁻¹ for Fe007 and Fe014 respectively (Fig1). A fast colour removal occurs in the first 10 minutes immediately after the adsorbent is added to the dye solution, and then equilibrium is reached at 1 h for Fe007 and 4 h for Fe014. As the increase in the removal rate for the Fe014 from 2 h to 4 h is low (~32 % of the total removal capacity), we consider the energy and time increase is not worth. Therefore, the removal tests for the different fabrics were done with 2 h reaction time for both Fe007 and Fe014. Fe007 showed higher adsorption capacity than Fe014 despite the higher iron content, and higher acidic groups. This could be explained by the blockage of the active sites of the fabric by the high amount of Fe in its surface. Isotherm for WhiteC+Fe007 fitted well to the Langmuir model (Fig2) suggesting a monolayer adsorption mechanism, with R² = 0.9668, Q_{max}=31 mg g⁻¹, k_L=0.26 L mg⁻¹ and R_L (separation factor) = 0.025 to 0.45 indicating the adsorbate affinity to the solid adsorbent favoring the adsorption process.

Point of Zero Charge (PZC) of the cotton fabric is around pH 9 to 10, above which the cotton surface is negatively charged, (this is the pH range applied in textile dyeing process). Iron impregnation decreases the PZC proportionally to the Fe rate below pH 3, reaching a point that in all pH range, the surface is negatively charged. The iron also transferred acid groups on the fabric surface (1.9 mmol g⁻¹ for Fe007, and 2.6 mmol g⁻¹ for Fe014), therefore the dye solution firstly prepared in pH around 10, decreases to around 2.7 to 3.9 with the fabric, enhancing the dye adsorption by chemical process.

Among all fabrics types, the polyester/elastane fiber mixture showed the best colour removal (99.5%), while the polyester/cotton mixture showed the worst result (58.5%). Total Organic Carbon content confirmed that there was no chemical degradation of the dye, which would lead to a more toxic and dangerous compound in the environment.

Our hypothesis for the dye removal is a two steps mechanism. First by coagulation due to the Fe (III) dissolved onto the solution producing hexaaquairon (III) Fe³⁺ + 6H₂O → [Fe(H₂O)₆]³⁺ that undergoes hydrolysis to produce other aquairons: [Fe(H₂O)₆]³⁺ + H₂O ⇌ Fe(H₂O)₅(OH)²⁺ + H₃O⁺, coagulating the dye and other pollutants. NaCl was detected

by XRD from the coagulated and filtered material. Multivalent metals as ferric chloride and ferrous sulphate have been widely used for decades as coagulant (Joo et al. 2007). Once all free iron ions are dissolved into the water solution, the adsorption mechanism becomes more relevant.

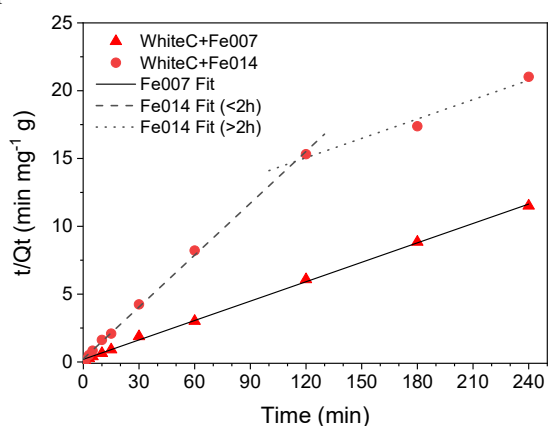


Fig 1. Adsorption Pseudo-second order kinetic model for White Cotton impregnated with Fe007 and Fe014

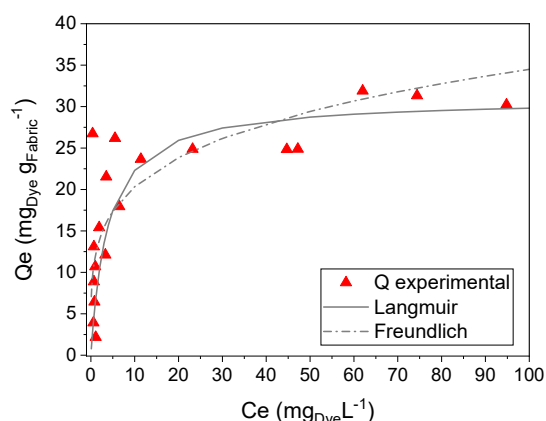


Fig 2. Adsorption isotherm @ 40 °C, by White Cotton impregnated with Fe007

Magnetic Activated Carbon (MAC). All carbons before or after the dye adsorption developed both micropores and mesopores up to 5 nm, with an average 428 m² g⁻¹ BET area and showed magnetic property with a magnetization saturation up to 47.5 emu g⁻¹. As observed from the author's previous work, it was confirmed that the dye adsorption process contributes to enhance the pore development. In all fiber types, except for the red cotton, the adsorption step increased the BET area. The increase in the Fe impregnation rate, decreased the BET in most of the fabrics, when the adsorption step is not performed. That was not the case for the after dye fabrics, where the difference in BET due to higher Fe rate was not so evident as for before dye. Therefore, some of the Fe007 fabrics were chosen for detailed characterization. The dye adsorption process also induced the reduction of the iron component in the MAC, leading to the formation of a metallic alpha-iron specie (Fig3), with higher magnetization saturation, instead of oxide specie of magnetite. This phenomenon could be due to the acidic characteristics of the iron nitrate. The dye adsorption process also enhances the development of micropores, without losing the mesoporous.

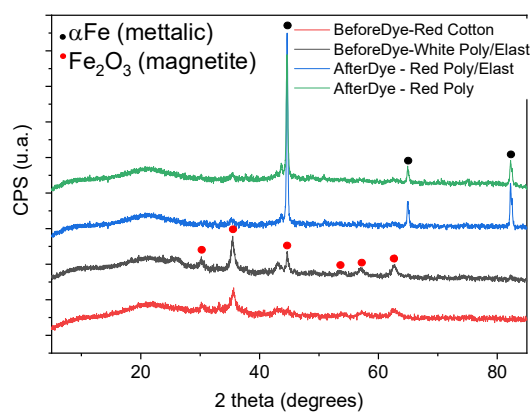


Fig3. XRD of MACs

Conclusions & Significance. This proposal gives important insights for two major environmental issues in the fashion industry: solid fabric wastes and dyeing wastewater. Fabric when combined with iron nitrate, enhances its adsorption capacity and lead to a micro and mesoporous MAC. Social impact is also relevant in countries like Brazil. Including the fabrics as a "recyclable" item, it will increase the income of recycling agents, decrease municipal solid waste collection costs and extend landfill lifetime. Textile could have many other applications as carbon source, for example for biorefinery. During carbonization, oil and syngas is formed, which also have others applications being studied worldwide. In the end, when carbon is all spent, and no regeneration possibility, it is always possible to burn and use as fuel for energy generation.

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