Article

Adsorption–Desorption Process to Separate Dyes from Tanning Wastewaters

Paolo Trucillo *, Amedeo Lancia and Francesco Di Natale

Department of Chemical, Material and Industrial Production Engineering, University of Naples Federico II, Piazzale V. Tecchio, 80, 80125 Napoli, Italy; lancia@unina.it (A.L.); fdinatal@unina.it (F.D.N.)
* Correspondence: paolo.trucillo@unina.it; Tel.: +39-329-65-66-043

Abstract: Wastewater production is a major environmental issue for the leather and textile industries: in a modern plant, several synthetic dyes are used in separated coloring batches whose wastewaters are usually mixed, diluted with other process water streams, and sent to a unique wastewater treatment plant. This includes specific physical and biochemical tertiary treatments to remove dyes efficiently. One of the main difficulties of these processes is the presence of multiple dyes, which cannot be treated with the same efficiency as a "wide-spectrum" process. This work explores the possibility of using conventional granular activated carbon (GAC) and a new polyurethane foam (PUF) for the adsorption of an acid red dye in the wastewater of a specific coloring batch of the tanning industry. The aim of this work is twofold: on the one hand, we aim to explore the performance of the new PUF sorbent; on the other hand, we aim to explore the possibility of using adsorption as an optimized pre-treatment for single-dye batches, which may take advantage of the presence of a single type of target dye and its higher concentration. The effluent is then sent to the wastewater treatment plant for further depuration.

Keywords: granular activated carbon; polyurethane foam; adsorption; tanning; wastewaters; dyes

1. Introduction

The fashion and related industries such as garments, footwear, and accessories have been significantly affected by globalization [1–3]; therefore, hundreds of companies and brands all over the world have emerged thanks to the work of thousands of valuable designers and numerous prestigious design schools [4]. However, while design is predominant in Western countries [5,6], textile production is still considered an Asiatic domain [7,8] due to the cheapest manufacturing cost [9,10].

According to the Annual Fashion Talk released by Mediobanca, in 2019, the world fashion industry was worth USD 471 billion, summing up the revenues of the 80 biggest manufacturing industries worldwide. Among these, Italy was the most represented country with the 10 most famous brands [11–13]. Recently, the Global Fashion Industry (source: https://fashionunited.com, accessed on 15 December 2019), estimated the overall value of brands, and assets of the global fashion industry to be around USD 3 trillion. Despite this high value and economic yearly income, the fashion sector generated significant environmental issues due to the intense use of toxic chemicals [14,15], with a subsequent necessity to modify processes within sustainable and environmentally friendly limits [16,17]. It was estimated that in 2017, about 80 thousand million garments were sold worldwide; this substantial increase in consumption resulted in a 75% increase in used clothes disposal, which without a specific recycling process, was destined for landfill disposal or thermal incineration [18]. This caused manufacturing industries to adjust dramatically to the increased request of the market. Nowadays, the estimated yearly consumption of dyes is around 10,000 tons in textile industries [19], thus resulting in an even higher environmental impact [20].

The fashion industry distinguishes itself with the use of diverse production methods and technological advancements [21,22]; among those, dyeing and weaving produce the largest number of pollutants [23,24], which increase the level of toxicity and non-recyclability during disposal [25,26]. Nowadays, the production of 1 kg of fabric requires an average amount of 200 L water and an amount of chemicals between 100 g to 1 kg (i.e., up to 100% of fabric weight, on a mass basis) [27–30]. This inhomogeneity in wastewater composition is also due to different worldwide regulations [31–33] and the high diversity of textile wastes [34,35]. Since the dye binding process is not particularly efficient, this results in the loss of between 10% and 50% of dyes, but also other substances such as formaldehyde, chlorine, and heavy metals. The disposal of these compounds in rivers and lakes creates further negative effects on living organisms, which can be quantified only with specific eco-toxicological measurements [36,37]. Focusing on the dyeing process, 1 kg of produced fabric generates from 20 to 100 kg of spent dyes, thus resulting in several washing post-processing steps [38–42]. Therefore, the textile dyeing and finishing industry created a huge pollution problem, as it is one of the most-discussed secondary pollutants of textile wastewater in applications related to agricultural irrigations [43–45].

In the late 1990s, dye removal methods included only preliminary water purification processes such as equalization and sedimentation [46–48] due to the absence of clearly defined boundaries regarding the release of dye effluents into the environment. After the definition of the permissible dye effluent release standards, more effective dye removal methods were introduced, such as chemical–physical or biological plants with activated sludge [49–52]. Moreover, the necessity to remove high percentages of dyes and surfactants led companies to try to improve the purification yields of these traditional processes by adding specific products. Among the proposed techniques, separation using polymeric porous membranes or composites provided several advantages such as high selectivity, low energy consumption, and moderate cost [53–56]. Additionally, oxidation, electrocoagulation, and biofilm techniques were utilized to degrade or separate contaminants found in industrial wastewater [57–59]. The results obtained using this system are encouraging, but a complementary treatment process is needed to remove residual impurities; moreover, these methods are expensive and do not guarantee a high and selective removal of dyes [60–62].

Among the separation processes, several adsorption methods have been developed for the treatment of contaminants in diverse environmental applications, with activated carbon emerging as a widely favored choice. Nevertheless, it is worth delving into a comparative exploration of various adsorption techniques aimed at purifying wastewater and mitigating the impacts of these contaminants [63]. Activated carbon, renowned for its exceptional adsorption properties, plays a pivotal role in wastewater treatment plants. Its porous structure and high surface area make it an effective adsorbent for a wide spectrum of contaminants. However, activated carbon is not the sole contender in the arena of adsorption processes. Other materials such as polyurethanes, zeolites, clay minerals, and metal oxides also exhibit remarkable adsorption capacities. Furthermore, adsorption processes can be customized based on the specific wastewater composition and the target contaminants. Factors such as pH, temperature, and contact time can be adjusted to optimize adsorption efficiency. Additionally, advancements in adsorbent modification techniques, including surface functionalization or the use of nanostructured materials, have expanded the toolkit for wastewater treatment. This work represented a first attempt to create a method for the use of alternative materials in a single or combined use to depurate wastewater from contaminants.

Adsorption separates dyes from textile wastewaters with the selective deposition of the dye's molecules on the surface of an adsorbent material. This type of treatment is particularly suitable for organic substances, such as solvents, surfactants, and pesticides, as well as dyes [64,65]. The method for adsorption dye removal could be considered an outstanding process in the case that it selectively separates one dye or a mixture of dyes. In general, for the adsorption of organic compounds, adsorption can also be repeated several

times, after the regeneration and reuse of the adsorbent material, until it becomes spent. This also permits a reduction in process costs in terms of fresh materials involved.

However, the number of regeneration cycles depends on various factors, including the nature and concentration of pollutants and the adsorption energy bonds. It is well-established that some dyes can be deposited on the adsorbent through physical adsorption pathways including the formation of a "condensed" phase on its surface, while in some other cases, chemisorption mechanisms involving site-specific interactions occur.

In this work, we report the first experimental data on the use of a new sorbent, namely, a polyurethane foam (PUF) for the treatment of a specific water-based solution produced during tanning processes. The use of foams in the treatment of wastewater is a promising option in the field of environmental protection and sustainable water management. Foams play a crucial role in facilitating the removal of contaminants and pollutants from wastewater streams [66]. These foam-based treatment methods are highly effective in separating suspended solids, oils, grease, and even certain dissolved contaminants from water, thus contributing to the purification of wastewater [67].

In particular, the use of polyurethanes in wastewater treatment represents an innovative and versatile approach to addressing environmental challenges. Polyurethanes, with their exceptional uptake capacities, have proven to be valuable materials in various stages of wastewater treatment processes. They are used for the fabrication of membranes and adsorbents with tailored properties, which are capable of selectively removing pollutants such as dyes, heavy metals, organic compounds, and microorganisms from wastewater streams [68,69].

This work (performed in collaboration with the company DMD S.p.A., Solofra, Avellino, Italy) concerns the use of new (the PUF) and conventional (the GAC) adsorbent materials to depurate the wastewater produced by a single-dye coloring batch to allow a more targeted pre-treatment of the dye. The aim is to provide a selective recovery of dyes and to reduce the amount of dye that is sent to the company's wastewater treatment plants. In fact, the presence of multiple dye streams, each with specific chemical composition and characteristics, and their overall dilution with the other process waters makes the tertiary treatment of these wastewaters particularly complex and expensive. The idea behind this approach is that it can be easier to treat the wastewater of each dyeing process separately, targeting the treatment to its specific chemistry. This work focused on the adsorption of dyes on two types of adsorbent materials: activated carbons [70–73], already studied and used in traditional purification processes, and polyurethane foams (PUF) [74], explored as an alternative adsorbent. The preparation of the model dyeing solution used in the tanning process was replicated in our laboratory. Starting from this, adsorption tests at 20 °C and 40 °C were performed, also investigating the effect of chemical additives generally used in the dyeing step (ammonia, fats, formic acid). In addition to the adsorption process, the desorption reverse process was also analyzed, with the final aim of understanding whether and how to dispose of the adsorbent material or to regenerate and reuse it in a subsequent adsorption cycle.

2. Materials and Methods

2.1. Materials

In this work, adsorption experiments were performed either in aqueous solutions or in model dyeing solutions containing fat-liquoring agents, as used in industrial tanning processes. "Acid red 97" (obtained by DMD Solofra S.p.A., Avellino, Italy) was used as a dyeing agent for this work. This kind of dye is particularly suitable for chrome-tanned leather. The authors only received its commercial nomenclature; therefore, it was not possible to report specific and detailed information about the formulation, but a UV-Vis spectrum obtained on the dye was provided, working in collaboration with DMD S.p.A, Solofra (AV), Italy. For the preparation of the aqueous solutions, the dye was simply dissolved in distilled water. In contrast, the preparation of the model tanning solution required several additional chemicals, such as Lipoderm N, ammonia, Coripol DX 1202,

formic acid, and distilled water. Sorbents utilized for adsorption tests were Filtercarb GCC 1240 and polyurethane. The characteristics of each used compound are reported in the following paragraphs.

"Lipoderm N" (BASF, Ludwigshafen, Germany) is an anionic emulsifier with a fat-liquoring action; its effect is considered necessary since animal skin loses most of its natural fats and oils during the tanning stage. Therefore, this emulsifier is put in contact with the leather matrix, preventing the adhesion of fibers [75,76] and favoring the penetration of dye into the leather. According to the BASF datasheet, the liquid form of Lipoderm N is characterized by a yellowish-brown color and pH of 8; moreover, it has an active content of approximately 50% on a mass basis, and its suggested stocking conditions are between 0 °C and 35 °C. This compound can be easily diluted in water, and its solutions are generally resistant to acids, alkalis, and salts.

Ammonia (Sigma Aldrich, Milan, Italy) is one of the auxiliaries used during the dyeing process to adjust the pH from acid to basic. In fact, at the beginning of the process, the leather that is obtained from the previous tanning steps has a pH of 3–4; then, with the addition of ammonia, the pH becomes close to 8. When the solution is basic, the dye is conveyed into the fiber. Indeed, in this step, the fiber allows the dye to penetrate within the cross-section of the leather.

Coripol DX 1202 (TFL, Rheinfelden, Germany) was used as a synthetic fat-liquoring agent. This white/yellowish anionic compound appears as an emulsion and is based on sulfated high molecular hydrocarbons. One of the properties of Coripol is its high heat resistance and good stability in mineral tanning floats. It is possible to dilute it in water under stirring at 60 °C. By combining it properly with the individual components of the fat-liquoring mixture, it is possible to reach practically any kind of softness or surface effects. Its pH is approximately 8, which is the same as the compound whose commercial name is Lipoderm N.

Formic acid (Thermo Fisher Scientific, Waltham, MA, USA), 85% w/w in water, was used as a reactive to adjust the acidity at the end of the dyeing protocol and to further improve the color penetration into fibers. Formic acid is used in the dyeing process to fix the color of the leather; in particular, it has an inverse role with respect to ammonia. After addition, the pH of the solution becomes acid again, and the fibers close, entrapping the dye inside the pores and the section of leather.

Two adsorbent materials were used to perform and compare adsorption experiments: granular activated carbon and polyurethane foam [77,78]. The activated carbon used in this work is FILTERCARB GCC 1240, which is used in granules of 1–2 mm diameter. It is generally used for water filtration processes and was obtained by Carbonitalia S.r.l. (Vezzano Ligure, Italy). This material is produced from coconut charcoal, physically activated with water vapor to develop a large active surface, which makes it suitable for the purification of water and organic liquids of the chemical and food industry (oil, liqueurs, glycerin, acids). Filtercarb GCC 1240 is an adsorbent characterized by a large specific surface and finds applications in numerous fields, such as pharmaceutical, food, catalysis, gas storage, and electrode materials, and also in the removal of odor from liquid and gaseous phases and the elimination of organic pollutants from drinking water and wastewaters [79,80]. The granular activated carbon was pre-washed before adding it to colored solutions.

Polyurethane is a leading member of the wide-ranging and highly diverse family of polymers or plastics. In this work, polyurethane was used in slices of cubic shape (about 1×1 cm). Its cellular-like structure is expanded by adding to the formation reaction a blowing agent that volatilizes because of the heat generated during the polymerization reaction. Polyurethane (PUF) has been used as an adsorbent in the treatment of contaminated water and effluent because of its low cost and the possibility of using it without pre-treatments [81,82]. In addition, PUF belongs to classes of substances characterized by both polar and nonpolar groups. Chemical and physical properties of the material used in this work has been reported in Table 1.

Table 1. Chemical and physical properties of used materials.

Material	Molecular Weight [g/mol]	Color	CAS Number	Bulk Density [kg/m^3]	Water Solubility
Acid Red 97	699	red-yellowish	10169-02-5	1579	8.85 g/L
Lipoderm N	*	opaque white	*	*	*
Ammonia	17	colorless	7664-41-7	0.73	31% *w/w*
Formic acid	46	colorless	64-18-6	1.22	Highly miscible
Filtercarb GCC 1240	*	black	*	530	Not miscible
Polyurethane	312	red-yellowish	25036-33-3	870	Not miscible
Coripol DX 1202	*	opaque white	*	*	*

* Information not provided by the manufacturer.

2.2. Methods

The experimental work was preceded by the preparation of either water-dyeing or fat-liquoring model dyeing solutions. Then, the experiments were divided into two macro-steps: adsorption experiments of dye with granular activated carbon and polyurethane, using the previously prepared dyeing solutions; secondly, desorption of dye from spent sorbents was performed. A sketch of the methodology is provided in Figure 1. A further description of the methodology is reported in the following sub-sections.
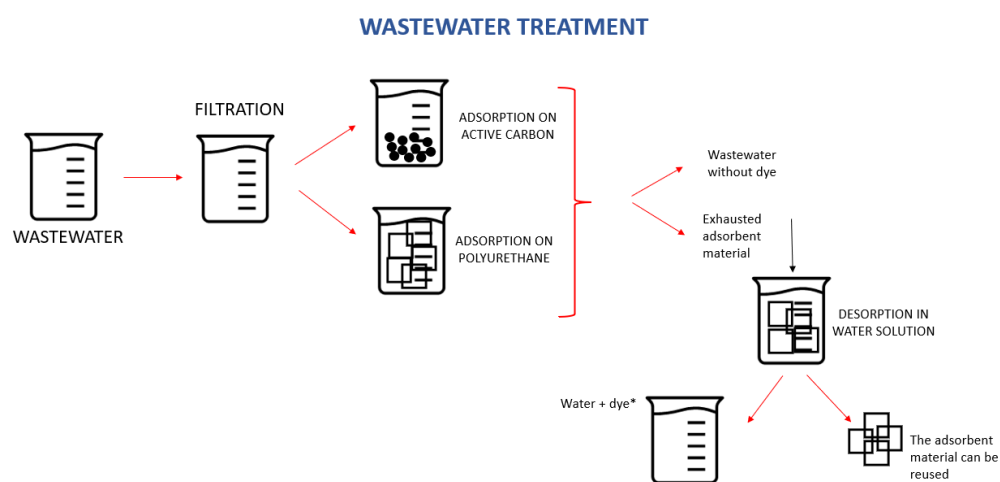

Figure 1. Description of the procedure used in this work for the treatment of wastewater, from preliminary filtration to adsorption and desorption process units. * On the basis of the selective capacity of the adsorbent material, here we may have other compounds reported in Table 1.

2.2.1. Dye Preparation Solutions

We followed a simplified protocol of a typical dyeing recipe provided to us by DMD Solofra S.p.A. and replicated it to simulate the composition of a typical tanning solution. In Table 2, a description of the four main steps involved in leather dyeing preparation is reported. However, in this study, we prepared dyeing solutions, as indicated in Table 2, but we did not use any leather scraps since the goal of this work was to adsorb dyes on active carbons and try to regenerate sorbents using desorption processes. In Table 2, all the percentages reported theoretically refer to the mass of leather, which, for simplicity, is set to a reference value of 5 g. We decided to work in the worst conditions, meaning that we considered the case in which it is possible to find all the chemical additives used in the dyeing phase in the simulated wastewater.

According to the recipe reported above, the first step consists of the addition of the fat-liquoring agent and ammonia to the water in order theoretically to prepare the leather (not used in this study) for the addition of dye. To reproduce the stirring occurring on a large scale in tanning drums, the solutions are stirred for 60 min. In the second step, the addition of dye occurs, with a continuous magnetic rotating plate for 30 min. In the third

step, the fattening agent is added during another 30 min stirring. In the fourth and final step, formic acid is added to the solution; this has the function of narrowing the fibers and, consequently, fixing the dye deeply. According to this recipe, 3% of dye on a mass basis is added to the solution.

Table 2. Simplified model dyeing solution preparation (mass percentages per unit leather mass).

Mass Ratio	Steps of Preparation	Role of Additive
	1st step—60 min stirring at 200 rpm *	
600% *w/w*	Distilled water	Diluent
1% *w/w*	Lipoderm N	Emulsifier
3% *w/w*	Ammonia	pH corrector
	2nd step—addition of dye with 30 min stirring at 200 rpm	
3% *w/w*	Acid Red 97	Coloring agent
	3rd step—pre-fixing with 30 min stirring at 200 rpm	
3% *w/w*	Coripol DX 1202	Emulsifier
	4th step—fixing with 60 min stirring at 200 rpm	
5% *w/w*	Formic acid diluted in water 1:1 *v/v*	pH corrector

* Note that this first step is also characterized by the addition of 5 g leather; however, in this study, leather is not involved since the authors focused on the recovery and eventual reuse of the model solution.

2.2.2. Adsorption Experiments

The adsorption experiments are batch tests carried out in a PID-controlled oven at a fixed temperature. A fixed volume of the target solutions is placed in contact with a given mass of sorbent. For the kinetic tests, the experiments were performed setting the mass of GAC at 0.5 g and the mass of PUF at 0.1 g. In contrast, the initial dye concentration within the solution was varied according to the following indications: setting a volume of 30 mL of distilled water, different samples were prepared at 6 different dye concentrations, corresponding to dye concentration between 10 and 200 mg/kg. For the adsorption isotherms, the dosage and the concentration of the dye were varied to cover a representative concentration range.

Dye concentration measurements (in mg per kg of solutions) were performed using a spectrophotometer HACH (Loveland, CO, USA) mod. DR/2010 operating in the visible region, equipped with square-based glass cuvettes for blank and sample absolute absorbance measurement. As it is possible to see in Figure 2a, Acid Red 97's maximum absorbance peak was detected at 500 nm. Calibration lines were obtained on diluted Acid Red 97 solutions (Figure 2b), whose starting concentrations were known. In particular, the dye was dissolved first in water (round dots) and then in the model solution including tanning additives (square dots). These solutions were diluted 1:10 *v/v* in distilled water before absorbance measurements.
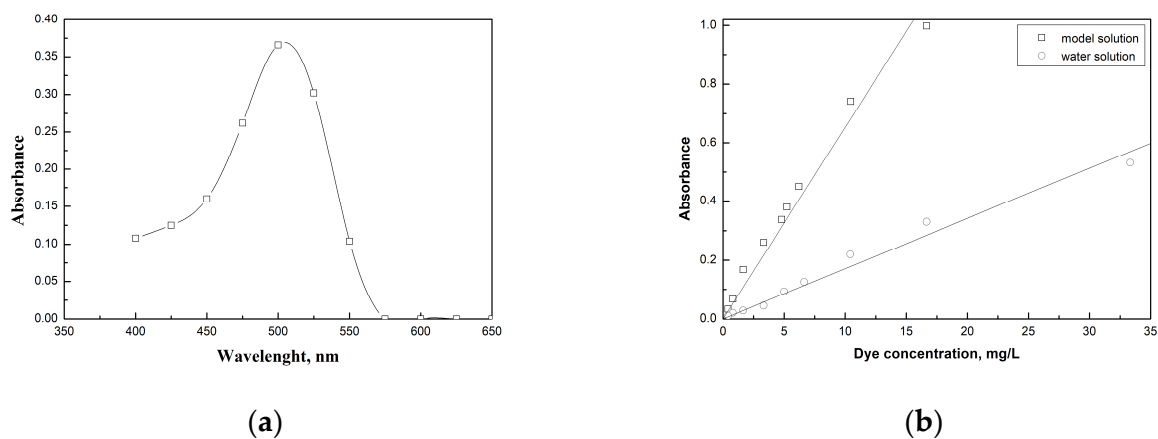

(**a**)   (**b**)

Figure 2. (**a**) UV-Vis spectrum of Acid Red 97. (**b**) Calibration curves of dye concentrations in water and model solutions.

The dye concentration and adsorption uptake expressed in these experiments were correlated by the following equation:

$$q(t) = \frac{V_a}{m} \left(C_0 - C(t) \right) \tag{1}$$

where $q(t)$ is the amount of dye adsorbed at time t, m is the mass of the sorbent, V_a is the volume of the solution, C_0 is the initial dye concentration, and $C(t)$ is the concentration of dye at time t. Adsorption isotherms were fitted using the Henry model as follows:

$$q_e = K \; C_e \tag{2}$$

where C_e is the dye concentration at equilibrium and q_e is the dye adsorption uptake at equilibrium.

2.2.3. Desorption Experiments

In this work, desorption tests were performed both in clean distilled water and in the clean solution obtained following the recipe described above, where "clean" refers to a total absence of the dye in the starting solutions. These tests were aimed at studying the possibility of reusing the solution in a new cycle of the tanning process, thus reducing fresh reagent consumption. In detail, a solution with a dye concentration of 70 mg/kg was put in contact with a given mass of sorbent until reaching uptake equilibrium conditions. Then, the adsorbent was separated from the solution and inserted into a newly prepared clean model solution. Then, the behavior of the adsorbent materials was investigated by changing the volume of this solution (6 mL, 9 mL, and 12 mL, respectively) at the temperature of 40 °C. While higher temperatures can be surely more effective for desorption, this temperature has been considered to contain the energy costs and the evaporative losses. The amount of dye desorbed from GAC to the receiving liquid medium was determined as a function of time, using the following equation:

$$q_d(t) = q_a - \frac{V_r}{m} \; C_a(t) \tag{3}$$

where $q_d(t)$ is the residual amount of dye on the sorbent at time t (mg/g), V_r is the volume of the receiving liquid medium, and $C_a(t)$ is the desorbed dye concentration in the liquid phase at time t (mg/kg). PUF was separated from the dyeing solutions after the adsorption experiments and was observed using a stereomicroscope, model SZX-T, Optika, Ponteranica, Italy.

During the experiments, we noted the presence of very fine PUF particles in the final solutions after centrifugation. Therefore, the solution was further filtered to be sure to remove these residues.

3. Results and Discussion

This first section concerns the adsorption of Acid Red 97 on activated carbon (GAC) and polyurethane foam (PUF), as reported in Figures 3 and 4.

Acid Red 97 dissolved in distilled water (pH = 8) was adsorbed on Filtercarb GCC 12 × 40. The kinetic tests are reported in Figure 3a,b. Figure 3a shows the time courses of Acid Red 97 concentration, $c(t)$, while Figure 3b represents its uptake on the activated carbon, $q(t)$, in distilled water during the batch adsorption tests performed at 20 °C. The experiments revealed that adsorption takes place over a long time, reaching equilibrium conditions after about 11 days. The dye uptake is around 9 mg/g for a residual concentration of about 55 mg/kg. As a qualitative representation of the experiments performed, Figure 4 reports the time evolution of color intensities in the test samples at the beginning (upper figure, at $t = 0$) and end of the adsorption treatment (lower figure, at $t = 11$ days). The efficacy of adsorption on activated carbon is evident: after about 11 days, the most concentrated tests with, respectively, an initial dye concentration of 202 mg/kg, 150 mg/kg, and 70 mg/kg, become almost transparent, while the three less concentrated samples (41 mg/kg, 30 mg/kg and 18 mg/kg) become transparent.
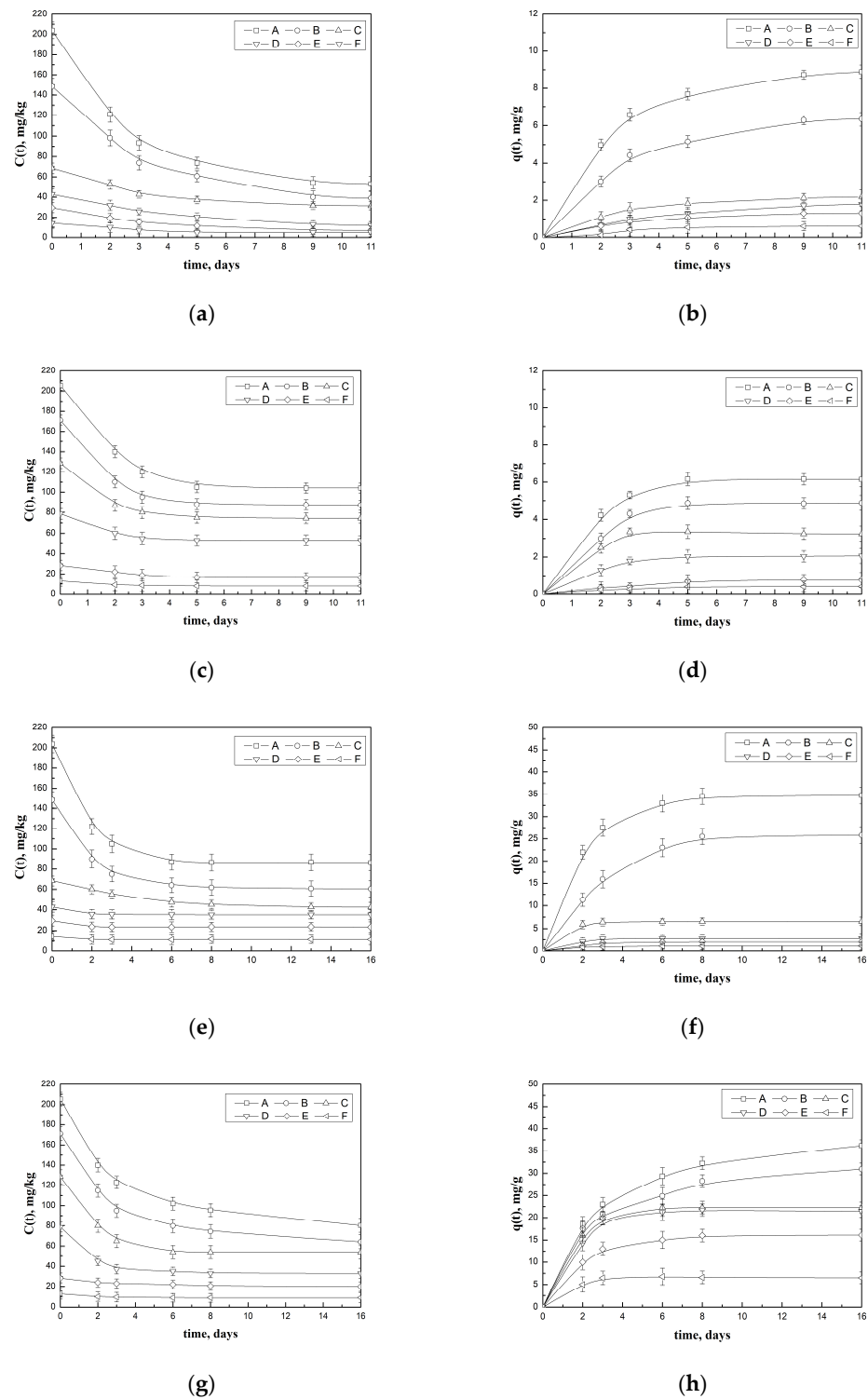
(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

Figure 3. Test performed at 20 °C with Acid Red 97: (**a**) residual concentration in the distilled water solution in contact with GAC vs. test time and (**b**) adsorption uptake on GAC in the distilled water solution vs. test time. Test performed at 20 °C with Acid Red 97: (**c**) residual concentration in the model dyeing solution in contact with GAC vs. test time and (**d**) adsorption uptake of residual Acid Red 97 on GAC in the model dyeing water solution vs. test time. Test performed at 20 °C with Acid Red 97: (**e**) residual concentration in the distilled water solution in contact with PUF vs. test time and (**f**) adsorption uptake on PUF in the distilled water solution vs. test time. Test performed at 20 °C with Acid Red 97: (**g**) residual concentration in the model dyeing solution in contact with PUF vs. test time and (**h**) uptake of residual Acid Red 97 on PUF in the model dyeing solution vs. test time.
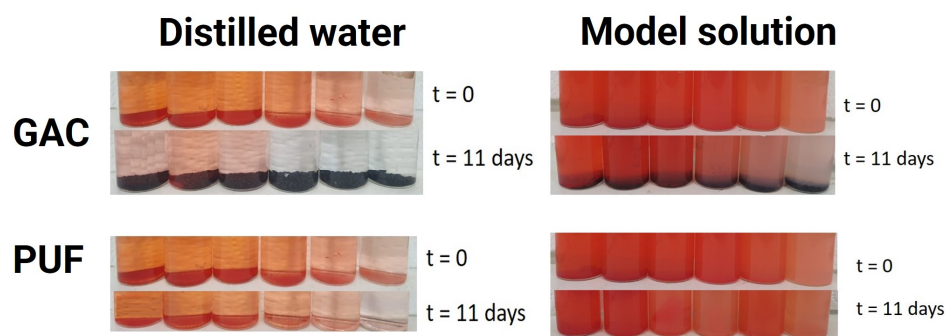
Figure 4. Test performed at 20 °C with Acid Red 97. Sample color intensity evolution intensities from the beginning ($t = 0$) to the end ($t = 11$ days) of the adsorption treatment using different adsorbent/solution couples.

Figure 3c,d shows the time courses of the Acid Red 97 concentration, $c(t)$, and its uptake on the activated carbon (GAC), $q(t)$, in the model dyeing solution during the batch adsorption tests performed at 20 °C. The mass of the sorbent was 0.5 g, the volume of the dyeing solution was 30 mL, and the pH was equal to 8, as in the previous set of experiments. The experimental results confirmed the general trend previously observed for the adsorption in the distilled water solution and indicated a lower adsorption efficiency, reaching, for the highest dye concentration, an uptake of around 6 mg/g for a residual concentration of about 100 mg/kg. In particular, the most concentrated starting solutions (205 mg/kg, 170 mg/kg, and 130 mg/kg, respectively) lost part of their color intensity without losing their opacity; the same behavior was encountered for the less concentrated samples. The experiments reported in Figure 3c,d revealed faster adsorption dynamics, with equilibrium conditions approached after around 5 days for all the samples, instead of 11 days, as observed in the case of distilled water. This result probably mirrors the competition between fats and dye on the surface of the activated carbon. The corresponding image in Figure 4 shows the time evolution of color intensities in the test samples at the beginning and end of the adsorption treatment. In this case, the solution color appears more opaque due to the presence of fattening agents: the color of the clean model solution is very close to the one shown for the lower dye concentration with GAC after 11 h.

In the following experiments, the granular activated carbon was substituted with PUF (Figure 3e–h) to compare the effect of another adsorbent material on distilled water plus dye solutions and on model dyeing solutions with fattening agents. The trend behavior of this new sorbent material was investigated. However, some differences arose from the use of a lower amount of PUF (0.1 g), which derived from the practical problem that it was not possible to set 0.5 g as the mass of PUF used in all the following experiments since the volume occupied by this material was much larger than 0.5 g GAC mass. A comparable mass of PUF would not have allowed a good bathing of the sorbent in the dyeing solution.

Figure 3e,f describes the time courses of the Acid Red 97 concentration and its uptake on the polyurethane foam (PUF) in distilled water during the batch adsorption tests performed at 20 °C in a total volume of 30 mL (pH was 7.8). As for the GAC, the experiments shown in Figure 4 revealed that adsorption took place over a long time, reaching equilibrium conditions after about 11 days. In these last experiments, the dye uptake is higher than that observed for the activated carbon, reaching up to 35 mg/g for a residual concentration of 85 mg/kg. Moreover, the corresponding image in Figure 4 shows the time evolution of color intensities in the test samples at the beginning ($t = 0$) and end ($t = 11$ days) of the adsorption treatment. Again, dye concentrations visibly decrease from left to right. In this case, due to the lower weight of PUF than GAC, the sorbent material is not immediately visible in the glass vial since it is floating on the upper part of the solution; however, it is still completely submerged.

Figure 3g,h shows the time courses of the Acid Red 97 concentration, $c(t)$, and of its uptake on the polyurethane foam (PUF), $q(t)$, in the model dyeing solution. The adsorption

data indicated that, differently from the activated carbon, the adsorption of Acid Red 97 on PUF is not affected by the presence of other species in the dyeing solution.

In all the cases, the adsorption kinetics appear quite slow. In this work, we used the Lagergren model with the experimental equilibrium data and fitting the experiments with the sole kinetic constant. Despite a good fitting capacity, we are not able to describe the dataset in a consistent way. The long characteristic time suggests that, for the GAC, the adsorption is limited by diffusion in the pore structure while, for the PUF, the large pore structure probably links the low adsorption rate with surface reaction kinetics. Further studies are needed to interpret this aspect.

The adsorption isotherms for Acid Red 97 in distilled water and the model solution at 20 and 40 °C tested with GAC and PUF are shown in Figure 5. The isotherms show an almost linear trend, which is well-described by the Henry law presented in Section 2, whose parameters are reported in Table 3. Other models can be used, but the significance of the additional fitting parameters is questionable.
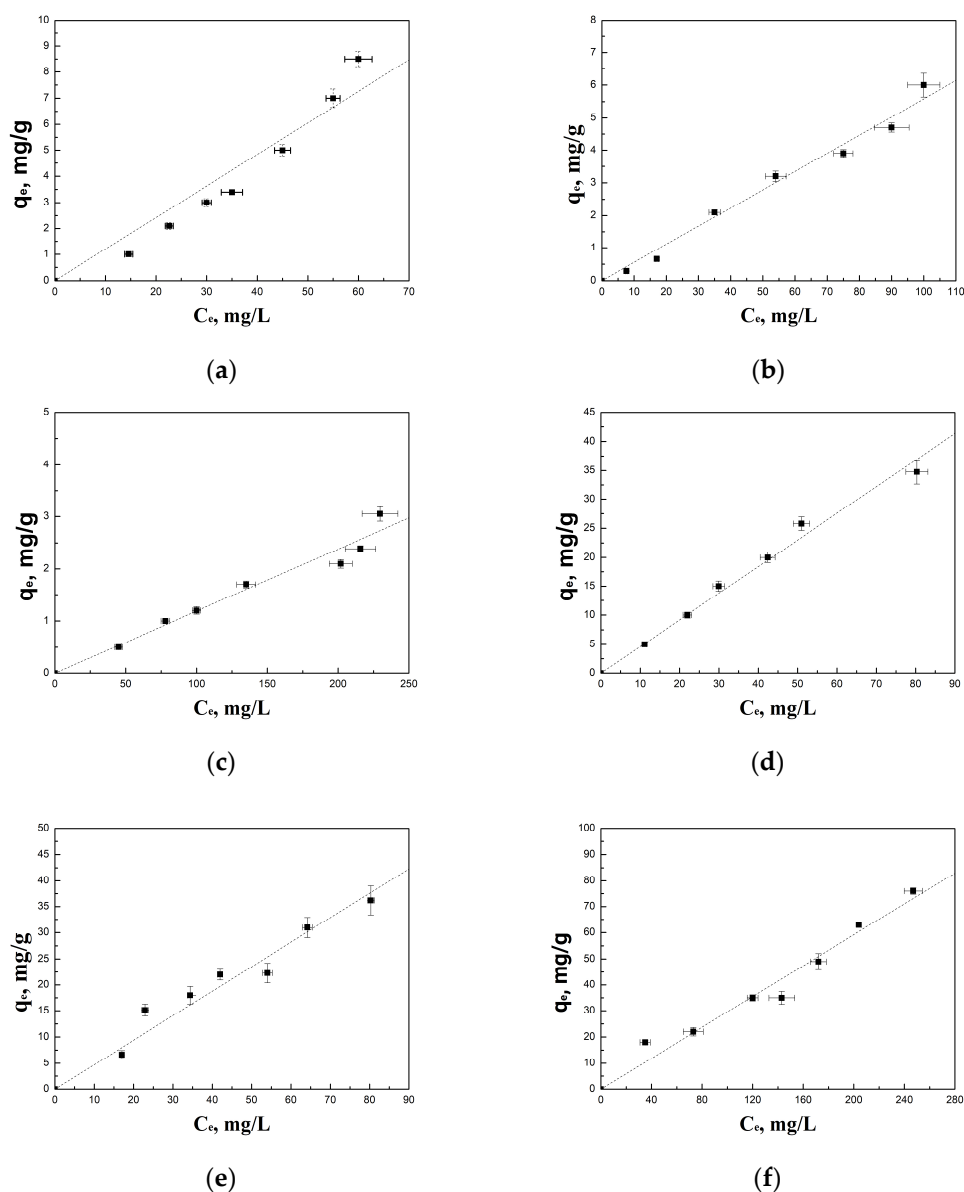

Figure 5. Adsorption isotherms of Acid Red 97 over (**a**) GAC in distilled water (DW) at 20 °C, (**b**) GAC in the model solution (MD) at 20 °C, (**c**) GAC in the model solution at 40 °C, (**d**) PUF in distilled water (DW) at 20 °C, (**e**) PUF in the model solution (MD) at 20 °C, and (**f**) PUF in the model solution at 40 °C.

Table 3. Henry model parameters obtained from fitting on isotherms.

Solution	Ads* Material	Temperature, °C	Henry Constant	R^2, %
Aqueous	GAC	20	0.121	93.4
Model	GAC	20	0.056	98.5
Model	GAC	40	0.012	96.7
Aqueous	PUF	20	0.459	98.6
Model	PUF	20	0.469	95.7
Model	PUF	40	0.296	96.9

*Ads: adsorbent material; R^2: mean squared error.

The experiments revealed that the adsorption isotherm at T = 20 °C with distilled water and the model solution have quite different behavior; however, the isotherm at 40 °C with the model solution is less favorable. As expected, due to the effect of temperature in an exothermic process, the adsorption capacity at 40 °C is far lower than that observed at 20 °C.

The same construction of isotherms is reported for the adsorption experiments performed with PUF at 20 °C in distilled water and using the model solution at 20 °C and 40 °C. At 20 °C, the use of PUF did not show a significant difference between the adsorption isotherm in distilled water and the same isotherm with the model solution. In this case, at a constant temperature, the adsorption is as favorable as using the model solution, without being affected by the presence of the additional species in the model dyeing solution. On the other hand, the adsorption isotherm for PUF at 40 °C in the model solution is less affected by a temperature change from 20 °C to 40 °C than the activated carbon.

The Henry law isotherm can be seen as the first portion of the Langmuir model:

$$\lim_{c \to 0} q = q_{max} \frac{Kc}{1 + Kc} \cong q_{max}Kc = Hc \tag{4}$$

where q_{max} is the maximum adsorption capacity of the sorbent. In the case of the adsorption of a specific compound, such as a specific molecule or an ion, on a single specific active site, the Langmuir constant (K) corresponds to the equilibrium constant for the adsorption reaction and can be written as:

$$K = exp\left(-\frac{\Delta G^\circ}{RT}\right) \tag{5}$$

Therefore, the relation between Henry constant and temperature can be written as:

$$H = q_{max} \, exp\left(-\frac{\Delta G^\circ}{RT}\right) \tag{6}$$

Therefore, if at least two values of the Henry constant (H_1 and H_2) at two temperatures (T_1 and T_2) are known, one can derive an estimation of the ΔG° and q_{max} as:

$$\Delta G^\circ = \frac{R ln\left(\frac{H_1}{H_2}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \tag{7}$$

$$q_{max} = H_1 exp\left(\frac{\Delta G^\circ}{RT_1}\right) = H_2 exp\left(\frac{\Delta G^\circ}{RT_2}\right) \tag{8}$$

While this method is rigorously valid for the case of adsorption of one compound on one active site, it may be able to describe the behavior of more complex systems if they do not deviate too much from the ideal behavior. When applied to our data, the model indicates, for PUF, a value of ΔG° of -17.55 kJ/mol and a q_{max} = 347.9 mg/g. For GAC, the values are inconsistent. This is expected because PUF tests for the model aqueous solution and for the model dying solution show similar results, indicating that PUF is selective toward the dye and it is not affected by the other species in the liquid phase. Furthermore,

due to the PUF chemical structure, the predominance of a single kind of active site is a reasonable assumption. On the other hand, the adsorption of the GAC reveals a high variability with the composition of the matrix and with the temperature, and several kinds of active surface sites can be expected. Therefore, the same inconsistencies of the $\Delta G°$ and q_{max} values further indicate that the dye adsorption process for GAC involves multiple active sites and that the interactions with the other components of the liquid solution cannot be neglected.

The limited variation in the adsorption capacity as a function of temperature suggests that the regeneration of the spent PUF is not feasible. To obtain an effective desorption, a significant reduction in the adsorption isotherm is needed.

Desorption tests on spent activated carbon were carried out, starting from a sample of GAC used for the adsorption of Acid Red 97 in the model dyeing solution.

We performed three desorption tests starting from the same adsorption test solution (same volume); however, the following desorption step occurred in three different volumes. To explain the experimental procedure, the following letters (reported in Figure 6) define the consequential steps of this process:

(A) A preliminary model solution of 30 mL containing an initial dye concentration of 80 mg/kg was prepared. In these conditions, without putting the solution in contact with GAC, the initial uptake capacity is referred to as 0 mg/kg. Then, 2 g of GAC (4 times larger than the previous adsorption experiments) was added to the solution in order to obtain a solid/liquid ratio of around 67 g/L.

(B) The equilibrium adsorption uptake was reached at 3.53 mg/g, at a concentration of 10.9 mg/kg at the temperature of 20 °C.

(C) The GAC adsorbent spent was then separated from the solution, dried, and put in contact with a fresh solution to perform the desorption step (in this case, the $c(t)$ becomes equal to zero).

(D) One-third of the spent GAC was added to the desorption liquid (volume of 6 mL), reaching a final concentration of 172 mg/kg, corresponding to about 1.47 mg/g residual uptake.

(E) One-third of the spent GAC was added to the desorption liquid (volume of 9 mL), reaching a final concentration of 174 mg/kg, corresponding to about 0.39 mg/g residual uptake.

(F) One-third of the spent GAC was added to the desorption liquid (volume of 12 mL), reaching a final concentration of 173 mg/kg, corresponding to almost no residual uptake.
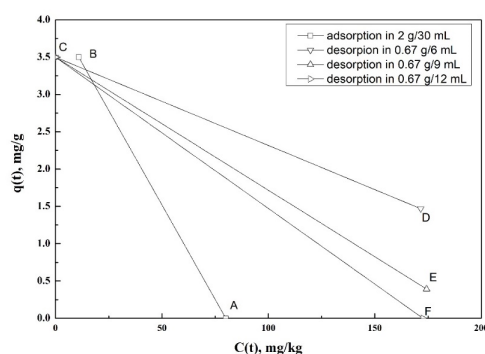

Figure 6. Adsorption and desorption test on Acid Red 97 adsorption on GAC using dye-free model dyeing solution at 40 °C as desorption media and using distiller water at 40 °C as desorption media (points D, E, and F overlap in terms of concentration).

Figure 6 shows the adsorption–desorption tests. In detail, the A to B segment is related to the adsorption process; the B to C segment is related to GAC addition to clean solution; the C to D segment is related to desorption in a new fresh volume of 6 mL; the C to E segment is related to desorption in a new fresh volume of 9 mL; and the C to F segment is related to desorption in a new fresh volume of 12 mL.

Figure 6 shows that the worst operating conditions are defined by the letter D, corresponding to about 1.5 mg/g residual uptake, while better performances are observed for E and F. When the tests were carried out with distilled water at 40 °C, all the points, D, E, and F, approached the Acid Red 97 isotherm. When the tests were carried out with the clean model solution, point D appeared very close to the corresponding 40 °C isotherm, but the E and F points were below the isotherm. Such behavior is unexpected and probably mirrors the existence of specific chemical interactions between the dye and the other components of the model solution, which enforce desorption efficiency thanks to complexation mechanisms. It is worth noting that the liquid produced by desorption in the clean model solution can be used to prepare a fresh batch for a new tanning process.

This experimental result indicates that, despite the lower adsorption capacity, the use of GAC can be a valuable option to reduce the content of Acid Red 97 in tannery wastewater plants while restoring other components that can be useful for the production process.

4. Conclusions

Considering the generally high cost of wastewater treatment [83–91], in this work, we investigated the possible on-site depuration of exhaust dye solutions used in the leather industry before discharging them to the traditional sewage system. This work aimed to study the adsorption treatment of the effluent of a specific coloring drum used in the leather industry in place of testing the mixture of diluted dyes transferred to a wastewater treatment plant. This approach gives the chance to reduce the concentration of the effluents before they reach the plant, which can simplify the treatment of the other process waters while taking benefits from the presence of a single dye at higher concentration levels. The coloring batch process unit only generates excess dye and fattening agents as wastes; therefore, it could be easier to recover those materials instead of sending them to general plant wastes. In the experiments, a real dyeing solution (dyes and fattening agents) was prepared following the coloring recipe provided by an Italian manufacturer.

The experiments use two sorbents, a polyurethane foam (PUF) and granular activated carbon (GAC). The experiments revealed slow adsorption kinetics: for GAC, the adsorption rate is probably limited by diffusion in the pores, and the foam kinetics is probably limited by the surface reaction rate. Further studies are needed to investigate this issue.

The experiments indicate that the PUF has a far larger adsorption capacity with respect to GAC, but GAC may be effectively desorbed, thus opening the possibility for a cyclic use of the sorbent and the reutilization of the solution for future tanning processes. Of course, this possibility requires new in-field investigations. It is finally worth comparing the performances of the PUF and GAC with those of other sorbents: despite the huge number of studies on dye adsorption, the large differences in dye typologies and wastewater solutions make the comparison cumbersome [92,93]. In the range of concentrations studied therein, the sorbent adsorption capacity ranks low with respect to other sorbents, but the linear trend of adsorption isotherms indicated that the attainment of saturation levels is still far, suggesting that there is room for further exploitation of the PUF and GAC in this specific treatment. Furthermore, this also suggests that other sorbents can be proficiently used to improve the single-dye batch treatment process.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Laing, R.M.; Sleivert, G.G. Clothing, textiles, and human performance. *Text. Prog.* **2002**, *32*, 1–122. [CrossRef]
2. Bonetti, E. Strategic groups in the fashion industry. *Int. J. Bus. Glob.* **2014**, *13*, 153–172. [CrossRef]
3. Mabeleng, L.B. An Assessment of the Role of the Textile and Clothing Industry in the South Africa Economy. Doctoral Dissertation, North-West University, Potchefstroom, South Africa, 2021.
4. Burns, L.D.; Mullet, K.K.; Bryant, N.O. *The Business of Fashion: Designing, Manufacturing, and Marketing*; Bloomsbury Publishing USA: New York, NY, USA, 2016.
5. Ledezma, V. Globalization and fashion: Too fast, too furious. *Laurier Undergrad. J. Arts* **2017**, *4*, 9.
6. Narumi, H. Fashion orientalism and the limits of counter culture. *Postcolonial Stud. Cult. Politics Econ.* **2000**, *3*, 311–330. [CrossRef]
7. Kim, J.O.; Traore, M.K.; Warfield, C. The textile and apparel industry in developing countries. *Text. Prog.* **2006**, *38*, 1–64. [CrossRef]
8. Yu, H.L.; Kim, C.; Lee, J.; Hong, N. An analysis of modern fashion designs as influenced by Asian ethnic dress. *Int. J. Consum. Stud.* **2001**, *25*, 309–321. [CrossRef]
9. Elson, D.; Pearson, R. 'Nimble fingers make cheap workers': An analysis of women's employment in third world export manufacturing. *Fem. Rev.* **1981**, *7*, 87–107. [CrossRef]
10. Pollin, R.; Burns, J.; Heintz, J. Global apparel production and sweatshop labour: Can raising retail prices finance living wages? *Camb. J. Econ.* **2004**, *28*, 153–171. [CrossRef]
11. Barbaresco, G.; Salerno, E. *Mid-Sized Companies According to Mediobanca-Unioncamere*; Mid-Sized Manufacturing Companies: The New Driver of Italian Competitiveness; Springer: Milano, Italy, 2013; pp. 13–40. [CrossRef]
12. Martina, M. How do we talk about fashion in Italy? The big players and independent publishers from 2000 to today: Transformations and orientations. *Film Fash. Consum.* **2016**, *5*, 83–102. [CrossRef]
13. Radwan, M.; Kamal, M.; Khavarinezhad, S.; Calandra, D. Influencing Factors on Modest Fashion Market: A Case Study. International. *J. Appl. Res. Manag. Econ.* **2019**, *2*, 12–22. [CrossRef]
14. Patti, A.; Cicala, G.; Acierno, D. Eco-sustainability of the textile production: Waste recovery and current recycling in the composites world. *Polymers* **2020**, *13*, 134. [CrossRef] [PubMed]
15. Zhou, Q.; Le, Q.V.; Meng, L.; Yang, H.; Gu, H.; Yang, Y.; Chen, X.; Lam, S.S.; Sonne, C.; Peng, W. Environmental perspectives of textile waste, environmental pollution and recycling. *Environ. Technol. Rev.* **2022**, *11*, 62–71. [CrossRef]
16. Dissanayake, D.G.K.; Sinha, P. Sustainable waste management strategies in the fashion industry sector. *Int. J. Environ. Sustain.* **2012**, *8*, 77–90. [CrossRef]
17. Targosz-Wrona, E. Ecolabelling as a Confirmation of the Application of Sustainable Materials in Textiles. *Fibres Text. East. Eur.* **2009**, *17*, 75.
18. Chavero, S.T. The unsustainability of fast fashion. *Datatèxtil* **2017**, *36*, 56–62.
19. Al-Tohamy, R.; Ali, S.S.; Li, F.; Okasha, K.M.; Mahmoud, Y.A.G.; Elsamahy, T.; Iiao, H.; Fu, Y.; Sun, J. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicol. Environ. Saf.* **2022**, *231*, 113160. [CrossRef]
20. Parmar, S.; Daki, S.; Bhattacharya, S.; Shrivastav, A. Microorganism: An ecofriendly tool for waste management and environmental safety. In *Development in Wastewater Treatment Research and Processes*; Elsevier: Amsterdam, The Netherlands, 2022; pp. 175–193. [CrossRef]
21. Bullon, J.; González Arrieta, A.; Hernández Encinas, A.; Queiruga Dios, A. Manufacturing processes in the textile industry. Expert Systems for fabrics production. *ADCAIJ Adv. Distrib. Comput. Articial Intell. J.* **2017**, *6*, 17–23.
22. Macchion, L.; Moretto, A.; Caniato, F.; Caridi, M.; Danese, P.; Vinelli, A. Production and supply network strategies within the fashion industry. *Int. J. Prod. Econ.* **2015**, *163*, 173–188. [CrossRef]
23. Hauser, P.J. Reducing Pollution and Energy Requirements in Cotton Dyeing. *Text. Chem. Color. Am. Dyest. Report.* **2000**, *32*, 44–48.
24. Mukherjee, S. Environmental and social impact of fashion: Towards an eco-friendly, ethical fashion. *Int. J. Interdiscip. Multidiscip. Stud.* **2015**, *2*, 22–35.
25. Correia, V.M.; Stephenson, T.; Judd, S.J. Characterisation of textile wastewaters—A review. *Environ. Technol.* **1994**, *15*, 917–929. [CrossRef]
26. Nidheesh, P.V.; Couras, C.; Karim, A.V.; Nadais, H. A review of integrated advanced oxidation processes and biological processes for organic pollutant removal. *Chem. Eng. Commun.* **2022**, *209*, 390–432. [CrossRef]
27. Madhav, S.; Ahamad, A.; Singh, P.; Mishra, P.K. A review of textile industry: Wet processing, environmental impacts, and effluent treatment methods. *Environ. Qual. Manag.* **2018**, *27*, 31–41. [CrossRef]

28. Phillips, B.J.; McQuarrie, E.F. Contesting the social impact of marketing: A re-characterization of women's fashion advertising. *Mark. Theory* **2011**, *11*, 99–126. [CrossRef]

29. Karthik, T.; Gopalakrishnan, D. Environmental analysis of textile value chain: An overview. In *Roadmap to Sustainable Textiles and Clothing*; Springer: Singapore, 2014; pp. 153–188. [CrossRef]

30. Roy Choudhury, A.K. Environmental impacts of the textile industry and its assessment through life cycle assessment. In *Roadmap to Sustainable Textiles and Clothing*; Springer: Singapore, 2014; pp. 1–39. [CrossRef]

31. Li, X.; Wang, L.; Ding, X. Textile supply chain waste management in China. *J. Clean. Prod.* **2021**, *289*, 125147. [CrossRef]

32. Kamau, E.C. Pollution Control in Developing Countries with a case study on Kenya. A need for consistent and stable regimes. *Rev. Int. Direito Cid.* **2010**, *9*, 29–42.

33. Bhuiya, M.H. Upcycling the Garment Solid Waste in Bangladesh. Ph.D. Dissertation, Tallinn University of Technology, Tallinn, Estonia, 2017.

34. Zhang, Y.Q.; Lykaki, M.; Markiewicz, M.; Alrajoula, M.T.; Kraas, C.; Stolte, S. Environmental contamination by microplastics originating from textiles: Emission, transport, fate and toxicity. *J. Hazard. Mater.* **2022**, *430*, 128453. [CrossRef]

35. Khattab, T.A.; Abdelrahman, M.S.; Rehan, M. Textile dyeing industry: Environmental impacts and remediation. *Environ. Sci. Pollut. Res.* **2020**, *27*, 3803–3818. [CrossRef]

36. Atangana, E.; Oberholster, P.J. Using heavy metal pollution indices to assess water quality of surface and groundwater on catchment levels in South Africa. *J. Afr. Earth Sci.* **2021**, *182*, 104254. [CrossRef]

37. Hellawell, J.M. Toxic substances in rivers and streams. *Environ. Pollut.* **1988**, *50*, 61–85. [CrossRef]

38. Chequer, F.D.; De Oliveira, G.R.; Ferraz, E.A.; Cardoso, J.C.; Zanoni, M.B.; De Oliveira, D.P. Textile dyes: Dyeing process and environmental impact. *Eco-Friendly Text. Dye. Finish.* **2013**, *6*, 151–176. [CrossRef]

39. Chen, H.L.; Burns, L.D. Environmental analysis of textile products. *Cloth. Text. Res. J.* **2006**, *24*, 248–261. [CrossRef]

40. Hussain, T.; Wahab, A. A critical review of the current water conservation practices in textile wet processing. *J. Clean. Prod.* **2018**, *198*, 806–819. [CrossRef]

41. Thadepalli, S.; Roy, S. Implications of Sustainability on Textile Fibres and Wet Processing, Barriers in Implementation. In *Sustainable Approaches in Textiles and Fashion*; Springer: Singapore, 2018; pp. 133–156.

42. Singha, K.; Pandit, P.; Maity, S.; Sharma, S.R. Harmful environmental effects for textile chemical dyeing practice. In *Green Chemistry for Sustainable Textiles*; Woodhead Publishing: Cambridge, UK, 2021; pp. 153–164.

43. Verma, R.K.; Sankhla, M.S.; Rathod, N.V.; Sonone, S.S.; Parihar, K.; Singh, G.K. Eradication of fatal textile industrial dyes by wastewater treatment. *Biointerface Res. Appl. Chem.* **2021**, *12*, 567–587. [CrossRef]

44. Jolly, Y.N.; Islam, A.; Mustafa, A.I. Characterization of dye industry effluent and assessment of its suitability for irrigation purpose. *J. Bangladesh Acad. Sci.* **2009**, *33*, 99–106. [CrossRef]

45. Sen, S.K.; Patra, P.; Das, C.R.; Raut, S.; Raut, S. Pilot-scale evaluation of bio-decolorization and biodegradation of reactive textile wastewater: An impact on its use in irrigation of wheat crop. *Water Resour. Ind.* **2019**, *21*, 100106. [CrossRef]

46. Lin, S.H.; Peng, C.F. Treatment of textile wastewater by electrochemical method. *Water Res.* **1994**, *28*, 277–282. [CrossRef]

47. Malliaros, C.; Guitonas, A. Pre-treatment and elimination systems of toxic industrial waste and sludges. The case study of the department of Attika. *Water Sci. Technol.* **1997**, *36*, 91–100. [CrossRef]

48. Babu, B.R.; Parande, A.; Raghu, S.; Kumar, T.P. Textile technology. *Technology* **1995**, *11*, 110–122.

49. Saleh, I.A.; Zouari, N.; Al-Ghouti, M.A. Removal of pesticides from water and wastewater: Chemical, physical and biological treatment approaches. *Environ. Technol. Innov.* **2020**, *19*, 101026. [CrossRef]

50. Haddad, M.; Abid, S.; Hamdi, M.; Bouallagui, H. Reduction of adsorbed dyes content in the discharged sludge coming from an industrial textile wastewater treatment plant using aerobic activated sludge process. *J. Environ. Manag.* **2018**, *223*, 936–946. [CrossRef]

51. Ciardelli, G.; Corsi, L.; Marcucci, M. Membrane separation for wastewater reuse in the textile industry. *Resour. Conserv. Recycl.* **2001**, *31*, 189–197. [CrossRef]

52. Ciardelli, G.; Capannelli, G.; Bottino, A. Ozone treatment of textile wastewaters for reuse. *Water Sci. Technol.* **2001**, *44*, 61–67. [CrossRef] [PubMed]

53. Liu, X.; Wang, L.; Zhou, X.; He, X.; Zhou, M.; Jia, K.; Liu, X. Design of polymer composite-based porous membrane for in-situ photocatalytic degradation of adsorbed organic dyes. *J. Phys. Chem. Solids* **2021**, *154*, 110094. [CrossRef]

54. Hu, F.; Fang, C.; Wang, Z.; Liu, C.; Zhu, B.; Zhu, L. Poly (N-vinyl imidazole) gel composite porous membranes for rapid separation of dyes through permeating adsorption. *Sep. Purif. Technol.* **2017**, *188*, 1–10. [CrossRef]

55. Zirehpour, A.; Rahimpour, A. Membranes for wastewater treatment. *Nanostructured Polym. Membr.* **2016**, *2*, 159–208. [CrossRef]

56. Vatanpour, V.; Nekouhi, G.N.; Esmaeili, M. Preparation, characterization and performance evaluation of ZnO deposited polyethylene ultrafiltration membranes for dye and protein separation. *J. Taiwan Inst. Chem. Eng.* **2020**, *114*, 153–167. [CrossRef]

57. Chen, G. Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.* **2004**, *38*, 11–41. [CrossRef]

58. Wang, Z.; Xue, M.; Huang, K.; Liu, Z. Textile dyeing wastewater treatment. *Adv. Treat. Text. Effl.* **2011**, *5*, 91–116. [CrossRef]

59. Singh, K.; Arora, S. Removal of synthetic textile dyes from wastewaters: A critical review on present treatment technologies. *Crit. Rev. Environ. Sci. Technol.* **2011**, *41*, 807–878. [CrossRef]

60. Qasem, N.A.; Mohammed, R.H.; Lawal, D.U. Removal of heavy metal ions from wastewater: A comprehensive and critical review. *Npj Clean Water* **2021**, *4*, 36. [CrossRef]

61. Särkkä, H.; Vepsäläinen, M.; Sillanpää, M. Natural organic matter (NOM) removal by electrochemical methods—A review. *J. Electroanal. Chem.* **2015**, *755*, 100–108. [CrossRef]

62. Kobya, M.; Bayramoglu, M.; Eyvaz, M. Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections. *J. Hazard. Mater.* **2007**, *148*, 311–318. [CrossRef]

63. Suwannahong, K.; Wongcharee, S.; Kreetachart, T.; Sirilamduan, C.; Rioyo, J.; Wongphat, A. Evaluation of the Microsoft Excel Solver Spreadsheet-Based Program for nonlinear expressions of adsorption Isotherm models onto magnetic nanosorbent. *Appl. Sci.* **2021**, *11*, 7432. [CrossRef]

64. Russo, M.E.; Di Natale, F.; Prigione, V.; Tigini, V.; Marzocchella, A.; Varese, G.C. Adsorption of acid dyes on fungal biomass: Equilibrium and kinetics characterization. *Chem. Eng. J.* **2010**, *162*, 537–545. [CrossRef]

65. Russo, M.E.; Di Natale, F.; Marzocchella, A.; Varese, G. Dyes biosorption of textile wastewaters in a lab-scale fluidised bed. In Proceedings of the MFIP12: 12th International Conference on Multiphase Flow in Industrial Plants, Ischia, Italy, 21–23 September 2011.

66. Buckley, T.; Xu, X.; Rudolph, V.; Firouzi, M.; Shukla, P. Review of foam fractionation as a water treatment technology. *Sep. Sci. Technol.* **2022**, *57*, 929–958. [CrossRef]

67. Hailan, S.M.; Ponnamma, D.; Krupa, I. The separation of oil/water mixtures by modified melamine and polyurethane foams: A review. *Polymers* **2021**, *13*, 4142. [CrossRef]

68. Amin, M.T.; Alazba, A.A.; Manzoor, U. A review of removal of pollutants from water/wastewater using different types of nanomaterials. *Adv. Mater. Sci. Eng.* **2014**, 825910. [CrossRef]

69. Dasa, P.; Duttab, S. Sustainable membranes with FNs: Current and emerging research trends. In *Membranes with Functionalized Nanomaterials: Current and Emerging Research Trends in Membrane Technology*; Elsevier: Amsterdam, The Netherlands, 2022; p. 159. [CrossRef]

70. Mezohegyi, G.; van der Zee, F.P.; Font, J.; Fortuny, A.; Fabregat, A. Towards advanced aqueous dye removal processes: A short review on the versatile role of activated carbon. *J. Environ. Manag.* **2012**, *102*, 148–164. [CrossRef]

71. Simpson, D.R. Biofilm processes in biologically active carbon water purification. *Water Res.* **2018**, *42*, 2839–2848. [CrossRef]

72. Wang, H.; Ho, L.; Lewis, D.M.; Brookes, J.D.; Newcombe, G. Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. *Water Res.* **2007**, *41*, 4262–4270. [CrossRef]

73. Walker, G.M.; Weatherley, L.R. Biological activated carbon treatment of industrial wastewater in stirred tank reactors. *Chem. Eng. J.* **1999**, *75*, 201–206. [CrossRef]

74. Simón, D.; De Lucas, A.; Rodríguez, J.F.; Borreguero, A.M. Glycolysis of high resilience flexible polyurethane foams containing polyurethane dispersion polyol. *Polym. Degrad. Stab.* **2016**, *133*, 119–130. [CrossRef]

75. Cuq, M.H.; Benjelloun-Mlayah, B.; Delmas, M. Oil extracted from seal hides: Characterization and use as leather fat liquor. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1015–1019. [CrossRef]

76. Sardari, A.; Sabbagh Alvani, A.A.; Ghaffarian, S.R. Preparation of castor oil-based fatliquoring agent via a Pickering emulsion method for use in leather coating. *J. Coat. Technol. Res.* **2019**, *16*, 1765–1772. [CrossRef]

77. Elhadiri, N.; Benchanaa, M.; Chikri, R. Activated carbon for dyes removal: Modeling and understanding the adsorption process. *J. Chem.* **2020**, *2020*, 2096834. [CrossRef]

78. Maddalena, R.L.; McKone, T.E.; Kado, N.Y. Simple and rapid extraction of polycyclic aromatic hydrocarbons collected on polyurethane foam adsorbent. *Atmos. Environ.* **1998**, *32*, 2497–2503. [CrossRef]

79. Ferreiro, C.; Villota, N.; de Luis, A.; Lombraña, J.I. Analysis of the effect of the operational conditions in a combined adsorption–ozonation process with granular activated carbon for the treatment of phenol wastewater. *React. Chem. Eng.* **2020**, *5*, 760–778. [CrossRef]

80. Ying, W.C.; Zhang, W.; Chang, Q.G.; Jiang, W.X.; Li, G.H. Improved methods for carbon adsorption studies for water and wastewater treatment. *Environ. Prog.* **2006**, *25*, 110–120. [CrossRef]

81. Ozsoy, H.D.; van Leeuwen, J.H. Removal of color from fruit candy waste by activated carbon adsorption. *J. Food Eng.* **2010**, *101*, 106–112. [CrossRef]

82. Vona, A.; Di Martino, F.; Garcia-Ivars, J.; Picó, Y.; Mendoza-Roca, J.A.; Iborra-Clar, M.I. Comparison of different removal techniques for selected pharmaceuticals. *J. Water Process Eng.* **2015**, *5*, 48–57. [CrossRef]

83. Ahmad, A.; Jamil, S.N.A.M.; Shean Yaw Choong, T.; Abdullah, A.H.; Mastuli, M.S.; Othman, N.; Jiman, N. Green flexible polyurethane foam as a potent support for Fe-Si adsorbent. *Polymers* **2019**, *11*, 2011. [CrossRef]

84. Lefebvre, L.; Kelber, J.; Jierry, L.; Ritleng, V.; Edouard, D. Polydopamine-coated open cell polyurethane foam as an efficient and easy-to-regenerate soft structured catalytic support (S2CS) for the reduction of dye. *J. Environ. Chem. Eng.* **2017**, *5*, 79–85. [CrossRef]

85. Selvasembian, R.; Gwenzi, W.; Chaukura, N.; Mthembu, S. Recent advances in the polyurethane-based adsorbents for the decontamination of hazardous wastewater pollutants. *J. Hazard. Mater.* **2021**, *417*, 125960. [CrossRef]

86. Anglada, A.; Urtiaga, A.; Ortiz, I. Contributions of electrochemical oxidation to waste-water treatment: Fundamentals and review of applications. *J. Chem. Technol. Biotechnol.* **2019**, *84*, 1747–1755. [CrossRef]

87. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. *Environ. Chem. Lett.* **2019**, *17*, 195–213. Available online: https://hal.science/hal-02082916 (accessed on 1 January 2020). [CrossRef]

88. Crini, G. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.* **2006**, *97*, 1061–1085. [CrossRef]

89. Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* **2001**, *77*, 247–255. [CrossRef]

90. Suwannahong, K.; Sirilamduan, C.; Deepatana, A.; Kreetachat, T.; Wongcharee, S. Characterization and optimization of polymeric bispicolamine chelating resin: Performance evaluation via RSM using copper in acid liquors as a model substrate through ion exchange method. *Molecules* **2022**, *27*, 7210. [CrossRef]

91. Trucillo, P.; Lancia, A.; Di Natale, F. Recovery of platinum from diesel catalysts by combined use of H2O2/HCl leaching and adsorption. *J. Environ. Chem. Eng.* **2022**, *10*, 107730. [CrossRef]

92. Dutta, S.; Gupta, B.; Srivastava, S.K.; Gupta, A.K. Recent advances on the removal of dyes from wastewater using various adsorbents: A critical review. *Mater. Adv.* **2021**, *2*, 4497–4531. [CrossRef]

93. Agarwala, R.; Mulky, L. Adsorption of Dyes from Wastewater: A Comprehensive Review. *ChemBioEng Rev.* **2023**, *10*, 326–335. [CrossRef]