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Evaluation of Original and Enzyme-Modified Fique Fibers as an Azo Dye Biosorbent Material

Oscar Muñoz-Blandón [1], Margarita Ramírez-Carmona [1], Beatriz Cuartas-Uribe [2] and José Antonio Mendoza-Roca [2,*]

[1] Centro de Estudios y de Investigación en Biotecnología-CIBIOT, Universidad Pontificia Bolivariana, Medellin 50004, Colombia; oscaralexis.munoz@upb.edu.co (O.M.-B.); margarita.ramirez@upb.edu.co (M.R.-C.)
[2] Instituto de Seguridad Industrial, Radiofísica y Medioambiental, Universitat Politècnica de València, 46022 Valencia, Spain; beacuau1@iqn.upv.es
* Correspondence: jamendoz@iqn.upv.es

Abstract: As natural fibers, low-cost biosorbents have proven to be an effective and clean tool to remove textile dyes from wastewater. In this research, the Reactive Black 5 removal ability of original and enzyme-modified natural fibers were assessed. A fiber extracted from a Colombian fique plant (*Furcraea* sp.) was employed. The effects of fique fiber protonation with different solvents and dye solution pH on RB5 removal were evaluated. The biosorbent chemical composition was modified using the commercial enzymes pectinase, ligninase, and xylanase. The point of zero charge (PZC) of the original and modified material was measured, and the dye removal capacity of the three enzyme-modified fibers was determined. Fiber protonation with 0.1 M HCl and a dye solution with pH of 2.4 increased the RB5 elimination to 49.1%. The change in the fiber chemical composition led to a reduction in the PZC from 5.5 to a 4.7–4.9 range. Pectinase-pretreated fique fibers presented the highest dye removal of 66.29%, representing a 36% increase in RB5 dye removal. Although the original fique fiber showed RB5 dye removal ability, its enzymatic modification changed the charge distribution on the fiber surface, improving the capture of dye molecules. Enzyme modification can be applied to obtain new functionalities for plant fibers as biosorbent materials.

Keywords: plant fiber; textile dyes; dye removal; point of zero charge; bioprocesses; lignocellulolytic enzymes

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1. Introduction

Every year, 7×10^5 tons of dyes are manufactured worldwide, corresponding to 1000 different chemical substances [1–3]. The world textile dye market was valued at $9.4 billion in 2018, and its projection is $15.5 billion by 2026 [4].

Azoic dyes are one of the most commonly used types, representing 60% of the production of total dyes and providing different color intensities and variations in industries such as textile, paper, pharmaceutical, cosmetic, and food [5–7]. Azo dyes have at least one azo group as a chromophore in the molecule [8,9] and have complex aromatic structures that are resistant to biological degradation and stable to light, high temperatures, and some oxidants [9,10].

Not all of the dye is taken up by fibers in the dyeing process. Nonfixed dye and some other chemicals are released in the effluent [11]. The management of textile wastewater containing dyes is a challenge for the industry. It causes health hazards to communities, and these substances produce significant harmful effects on aquatic systems because the increase in molecular weight decreases the degradation rate [5,12–14]. In the textile industry, the manufacture of 1 kg of textile material requires around 200 L of water, and concentrations of dye in effluents from textile mills can range between 10 and 7000 mg/L [11].

In recent decades, different chemical and physical treatments have been developed for dye removal from textile wastewater [1,15–17]. The adsorption process using biological materials has also proven to be effective for removal of pollutants, such as heavy metals, organic dyes, and oily substances, from wastewater [18–22]. Moreover, high-quality treated effluents can be obtained by bioadsorption, offering a relevant alternative for the treatment of some types of effluents [6,23,24].

In the literature, several biosorbents have been used for dye removal. They can be microorganisms [25–27] or agroindustrial wastes, such as cane bagasse and biomass from peanut shells [17,28,29].

Plant fibers can be used for dye removal. They mainly consist of cellulose, hemicellulose, lignin, and pectin. Plant fibers are renewable and low-cost biopolymers with significant ion exchange properties [30–33]. Fique fiber (*Furcraea* sp.) has also been used as a biosorbent, with a previous research proving its removal capacity for chlorothalonil pesticide [34], orange II dye [35], and caffeine and diclofenac [36]. Moreover, fique fiber (*Furcraea* sp.) has been reported as a promising material with adsorption ability in wastewater treatment once its surface has been modified [37–39].

Several natural fibers obtained from kapok, hemp, agave bagasse, or kenaf have been modified to optimize their capacity as a biosorbent [40–43]. Modification of plant fibers by controlled depolymerization of one of their components has been investigated and applied due to its relevance in producing new added-value products for different industrial uses [44–46]. Biological methods employing enzymes to modify the chemical composition of fibers have also gained importance in recent years [47–50]. In this case, fiber from a native plant of Colombia can become a new alternative biosorbent for azo dye removal through surface modification with lignocellulolytic enzymes.

In this study, the Reactive Black 5 dye removal capacity of the original fique fiber was improved by protonation of the fiber with an HCL solution. The effect of varying dye solution pH on the biosorbent capacity was evaluated. Then, fique fiber was modified by treatment with different lignocellulose-degrading enzymes. The point of zero charge (PZC) and dye removal ability of the original and enzyme-modified fibers were determined. This study can help find new and promising applications for the fique fiber, such as use as filtration material.

2. Materials and Methods

2.1. Bioadsorbent and Dye Solution

For this study, fique fiber (*Furcraea* sp., var. Uña de Águila), was provided by Compañía de Empaques de Medellín. Fibers were cut into 2 mm fragments.

The Reactive Black 5 (55%, Sigma-Aldrich, Steinheim am Albuch, Germany) dye was used for the adsorption experiments. Its molecular formula is $C_{26}H_{21}N_5Na_4O_{19}S_6$. The wavelength of the maximal absorbance was 598 nm. Solutions of 20 ppm of dye were prepared for all the tests.

2.2. Biosorption Tests in Laboratory Packed Column

The removal of the Reactive Black 5 (RB5) dye was performed with a laboratory packed column of 2 cm diameter and 7 cm height. For this, 0.5 g of fique fiber was packed into 2 cm (packing height), so 5 cm was used for the solution reservoir. The feed flow rate was 0.016 L/min. For each biosorption test, the filtered volume (25 mL) was recirculated 9 times (9 cycles). The initial feed concentration was 20 ppm. The dye concentration at the end of each cycle was measured at 598 nm using Hewlett Packard HP-84-53 (Hewlett Packard, Waldbronn, Germany) type spectrophotometer. Each assay in this study was repeated twice, and the results were approximated through an exponential decay model. The model was fitted using the following equation:

$$C = a\ X\ e^{-br} + d \quad (1)$$

where C is the dye concentration (ppm), r is the number of recirculations, a is the total dye concentration change due to its removal, b is the decay constant, and d is the minimum dye concentration achievable at an infinite number of recirculations r. The model was fitted using the minimum square of the residuals as objective function in MS Excel.

2.3. Effect of Fiber Activation on Dye Adsorption

The effect of the activation of the original fique fibers by protonation was assessed. For this, HCl (pH 3), NaOH (pH 10), ethanol (96%), and osmotized water were used. First, 0.5 g of fique fiber was submerged into 50 mL of each solution. After a contact time of 24 h, the fibers were filtered and packed for the tests in the biosorption columns. The activating solution that yielded the highest dye removal was selected for the protonation of the modified fibers in the following trials.

2.4. Effect of Solution pH on Adsorption

The effect of the RB5 solution pH on removal capacity was assessed for a pH range between 2.4 and 4. The pH of RB5 solutions was adjusted to pH values of 2.4, 2.8, 3.2, and 3.8 with 0.1 M HCl solution. For this study, nonmodified fique fiber after activation with HCl solution (pH = 3) was used. The pH value with the highest RB5 removal was used for the following tests.

2.5. Fiber Enzymatic Modification

The fique fiber surface was modified using the commercial enzymes pectinase (Sigma-Aldrich Inc., Burlington, MA, USA), ligninase and xylanase (Novozymes, Bagsvaerd, Denmark). They were provided by the Centro de Estudios y de Investigación en biotecnología (CIBIOT) from Universidad Pontificia Bolivariana in Medellín, Colombia.

The enzymatic modification of the fibers was carried out by preparing 100 mL of solutions of ligninase (0.4 U/mL), pectinase (0.6 U/mL), and xylanase (0.6 U/mL). Fique fibers were submerged in the enzymatic solutions at pH 4.5, 45 °C, and continuous stirring at 150 rpm for 45 min. These conditions were the same for the three enzymatic solutions. After treatment, fibers were dried in a laboratory oven (1DIES, VCA115) until constant weight.

The lignocellulose composition in the original and modified fique fibers was determined. Cellulose and hemicellulose were determined according to Sun and Hughes (1998) in consecutive treatments with ethylenediaminetetraacetic acid (EDTA, 1%), sodium chlorite ($NaClO_2$, 1%), and sodium hydroxide (NaOH, 17.5%) [51]. The cellulose content was obtained by the dry weight of the residue present in the precipitate after treatment. Hemicellulose was determined by difference.

The lignin content was determined by the Klasson technique (H_2SO_4 at 72%) as indicated by the TAPPI Standard T222 om-02 (acid-insoluble fraction in wood and pulp). The determination of pectin was performed using the method used by Devia (2003) for citrus albedo fiber. It consisted of acid hydrolysis of pectin using ethylenediaminetetraacetic acid (EDTA) 1% at pH 4.5, 85 °C, for 60 min. The pectin content was obtained by dry weight difference before and after acid hydrolysis.

The morphology of the fiber surface was observed before and after the modification process. For the observation, fibers were prepared on aluminum stubs, fixed with carbon tape, and sputtered and coated with platinum for 15 s using Leica MED020 (Leica Microsystems, Buffalo Grove, IL, USA). Then, the samples were examined using the field emission microscope Auriga Compact from Zeiss (Orsay Physics Kleindiek Oxford Instruments, Oxford, UK). Imaging parameters were 1.5 kV accelerating voltage, 5.5 mm working distance, and SE detector to obtain topography information.

2.6. Point of Zero Charge Determination

The point of zero charge (PZC) was measured for the fique fibers before and after enzymatic modification. The PZC was determined following the pH drift method [52]. As the first step, 8 solutions between pH 3 and 10 were prepared. For this, 0.1 M HCl and

0.1 M NaOH solutions were used by adding the needed volume to 50 mL of distilled water. Then, 0.5 g of fiber was submerged into the solutions, and the mixture was subjected to orbital shaking for 48 h at room temperature. The final pH values of the solutions were measured. If initial and final pH values are known, the PZC corresponds to the point where the final pH curve intersects the diagonal straight of the figure. In other words, the PZC is found where the difference between the initial and final pH is equal to zero.

2.7. Effect of Enzymatic Modification on Dye Removal

The biosorption test was carried out with nonmodified fiber (NMF) and with fibers modified with pectinase (Pec), ligninase (Lig), and xylanase (Xyl).

The fibers were activated by protonation in HCl solution (pH 3), filtrated, and packed in the laboratory column. In the tests, the RB5 solution (adjusted at pH 2.4 with 0.1 M HCl solution) was recirculated nine times, with the final concentration of RB5 measured after each time. The surface morphology of the fiber yielding the best results in terms of dye removal was examined.

3. Results and Discussion

3.1. Effect of Fiber Activation on Dye Removal

The effect of the original fique fiber activation on RB5 removal was assessed. For this, four pretreatments were tested using HCl, NaOH, CH_3CH_2OH, and H_2O. Figure 1 shows the variation in dye concentration (ppm) for each recirculation.

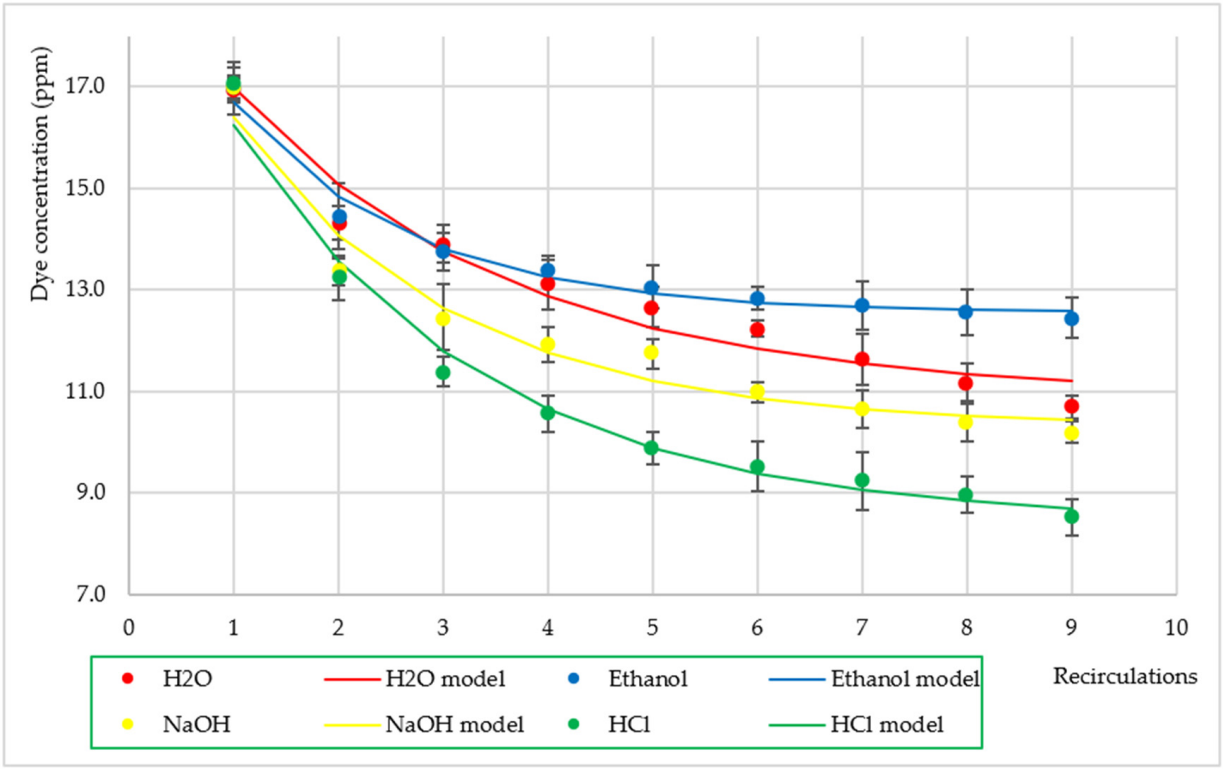

Figure 1. Variation of RB5 concentration (ppm) after dye removal test for different pretreatments. Values adjusted by exponential decay model.

In the biosorption test, dye adsorption occurred for the four tested pretreatments, achieving RB5 removal efficiencies higher than 35% in all the tests. The fiber pretreated with HCl yielded the highest removal efficiency (57.4% in the last recirculation). Meanwhile, the removal efficiency of the fique fiber after pretreatment with NaOH was 49%.

Concerning the modeling of dye removal for this assay, the correlation coefficient obtained for the model fitting was 95% or higher, demonstrating the robustness of the

mathematical model. The behavior of RB5 dye removal by fique fibers with different protonation treatments followed an exponential decay model (Table 1). The parameter *a*, which predicts the total change in the dye concentration due to its removal as explained above, showed the highest decrease with HCl treatment (59.35%). According to this, the fibers pretreated with HCl would remove azo dye down to a concentration of 8.4 ppm. This was the lowest dye concentration compared to other treatments, where the values were higher than 10 ppm, as shown in Table 1.

Table 1. Parameters of the exponential decay model for RB5 dye removal by original fique fibers with different protonation treatments.

Parameters	H_2O	Ethanol	NaOH	HCl
a	8.8671	7.5169	9.7960	11.8700
d	10.923	12.540	10.316	8.425
R^2	0.957	0.983	0.965	0.985

The best results for the HCl solution can be explained by the protonation of the fique fiber. HCl dissociates, providing protons that will bind to oxygen with nonshared pairs of electrons of the cellulose, hemicellulose, and lignin molecules present in the fique fiber. This increases the positive charges in the fiber and makes the surface more reactive for dye adsorption.

Other authors have also reported that protonation of adsorbents with HCl improves adsorption capacity. Lakshmipathy and Sarada (2014) pointed out that the adsorption of dyes onto watermelon rinds was enhanced by protonation with HCl due to the removal of K^+, Mg^{2+}, Na^+, and Ca^{2+} ions of the material. These ions have a high influence on the adsorption process as they compete for active sites in the surface [53].

Huang et al. explained the high removal efficiency (almost 100%) of methyl orange dye on chitosan fibers using a four-hour protonation process with HCl. The study by Rosique Hueso showed more than 34% increase in adsorption capacity of *Opuntia* biomass in the treatment of Cd(II) following protonation with 0.1 M HCl [54,55].

3.2. Effect of Dye Solution pH

The effect of the RB5 solution pH on the adsorption process was assessed. As RB5 is an anionic dye, the adsorption process was performed at pH values between 2.4 and 3.8, which are values below the PZC of the fiber [56,57]. In this way, the presence of positive charges on the adsorbent surface was ensured, thus enhancing the electrostatic interaction between the dye and fiber. Figure 2 shows the variation in dye concentration in the solutions after adsorption at different pH values.

According to Figure 2, the adsorption capacity of the fique fiber increased with reduction in the RB5 solution pH. For pH values between 3.8 and 2.8, the RB5 removal efficiency ranged between 21 and 35%, whereas at pH 2.4, the RB5 elimination increased up to 49.1% in the last recirculation. This showed the presence of more positive charges on the surface, which led to higher dye removal.

Concerning the modeling of dye removal for this assay, the correlation coefficient (R^2) obtained for the model fitting ranged between 95 and 96%, demonstrating the robustness of the mathematical model. The trend of RB5 dye removal by fique fiber using different solution pH values followed an exponential decay model (Table 2). The parameter *a* showed the highest decrease (59%) at pH 2.4, meaning fibers in an RB5 solution at pH 2.4 would remove the azo dye down to a concentration of 10.02 ppm. This concentration was lower than those achieved by the other treatments, which were all higher than 13 ppm, as shown in Table 2.

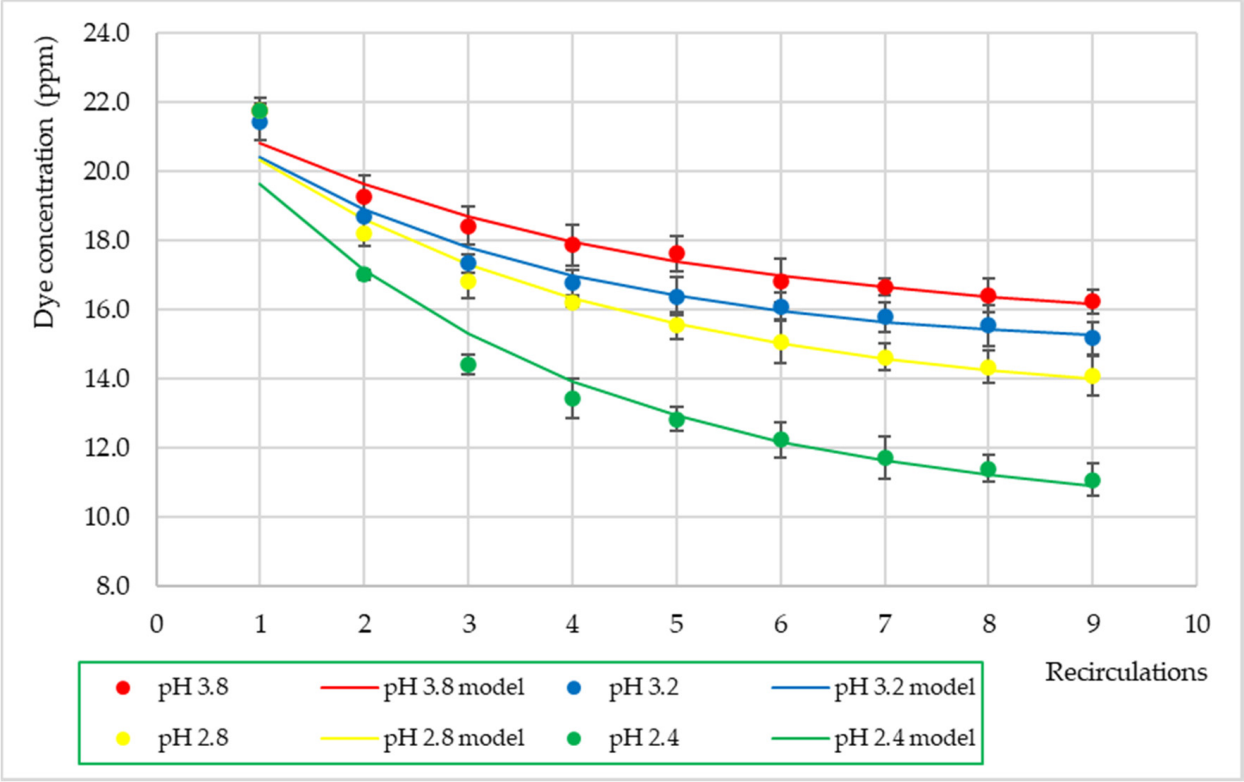

Figure 2. Variation in RB5 concentration (ppm) at different pH values (adjusted with 0.1 M HCl solution). Values adjusted by exponential decay model.

Table 2. Parameters of the exponential decay model for RB5 dye removal by original fique fibers using different solution pH values.

Parameters	pH 3.80	pH 3.20	pH 2.80	pH 2.40
a	6.9197	7.6630	9.3656	12.9879
d	15.473	14.784	13.248	10.024
R^2	0.960	0.962	0.958	0.954

The results in this assay were similar to those reported by other authors regarding RB5 adsorption. For instance, tests using chitosan and carbon nanotubes as adsorbents yielded the highest RB5 elimination at pH 4 [58,59]. Shaheed and Hussein (2014) reported the highest RB5 removal using titan nanoparticles at pH 2. The same pH was reported as the optimal one by Begun et al. (2012) when testing chitin extracted from shrimp shells [60,61]. Lee et al. (2016) reported a similar pH value (2.0) as the best result (97%) on biosorption of another anionic dye, Acid Blue 113, using overripe *Cucumis sativus* peel as absorbent [7].

In summary, the pH of textile wastewater has a significant influence on the bioadsorption process due to adsorption sites in the adsorbent surface also being modified, which affects the ionization process of the adsorbate molecule [10,62,63].

3.3. Fiber Enzymatic Modification

The fique fiber surface was modified employing lignocellulolytic enzymes. Table 3 shows the chemical composition of fique fiber after treatment with different enzymes. As can be observed, different enzymatic treatments altered the chemical composition of the fiber, decreasing or increasing the content of pectin, hemicellulose, and lignin, with subsequent increase in the percentage content of cellulose.

Table 3. Chemical composition of fique fiber after treatment with lignocellulolytic enzymes.

Treatment	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Pectin (%)
NMF	55.78 ± 1.45	18.58 ± 1.03	14.23 ± 0.42	6.15 ± 1.71
Pec	59.45 ± 1.56	19.73 ± 1.14	15.11 ± 0.64	1.19 ± 0.62
Xil	63.29 ± 2.13	9.04 ± 1.47	16.14 ± 1.28	6.66 ± 1.12
Lig	61.78 ± 3.25	21.58 ± 2.61	6.14 ± 1.96	5.74 ± 0.98

The behavior of the fique fiber components reflected the nature of the enzymes used during treatment. The fiber treated with pectinase presented a decrease of 71.8% in pectin content. Similarly, the action of xylanase reduced hemicellulose content by 51.3%. The fibers treated with ligninase presented 56.8% lower lignin content than the original fiber.

Lignocellulolytic enzymes are biological tools capable of catalyzing reactions with high stereo-, regio-, enantio-, and chemoselectivity. On specific substrates, their action almost exclusively produces the product of interest without unwanted by-product generation [64,65]. In this way, the enzyme hydrolyzes the component of the fiber that corresponds to it without affecting others.

The surface of the fique fiber before and after enzymatic modification was examined by field emission scanning microscopy (FSEM). Figure 3 shows fique fiber before treatment (a) and after modification treatment with Pec (b), Xyl (c), and Lig (d).

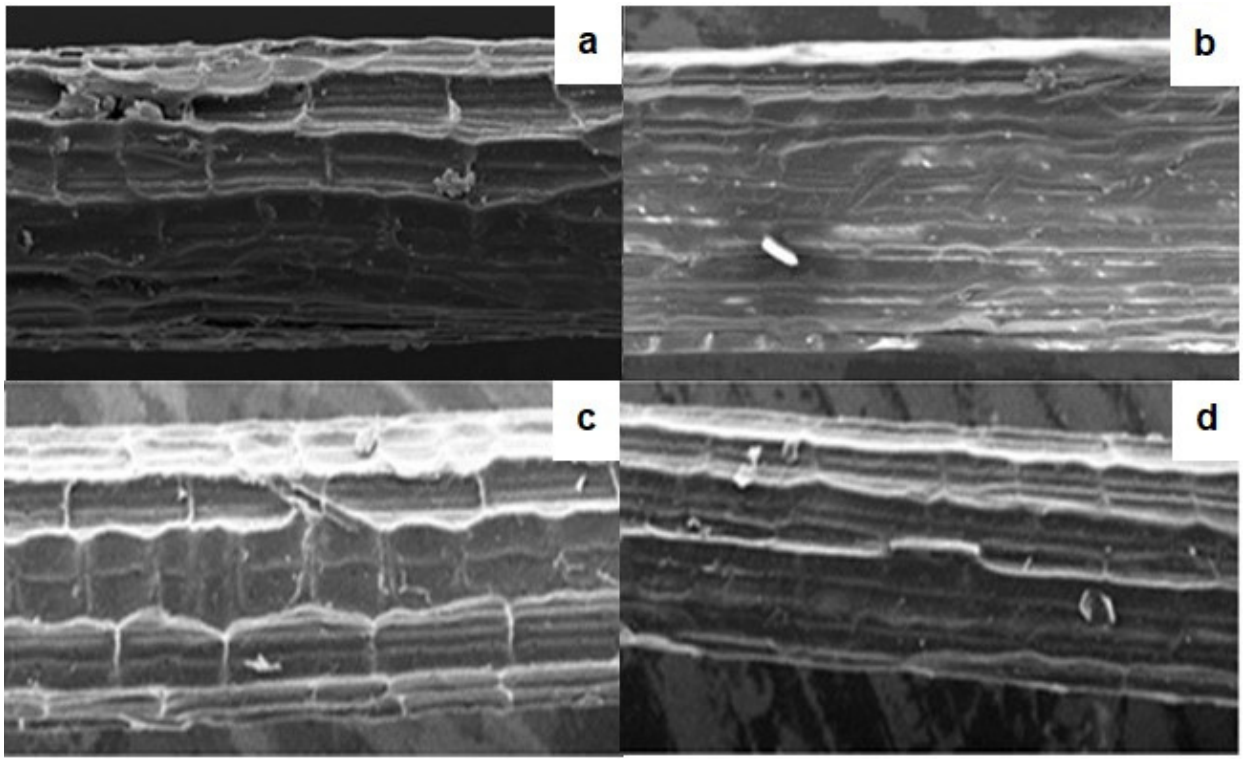

Figure 3. Surface morphology of the fique fiber before and after modification treatments: (**a**) non-modified fiber (Nmf), (**b**) fiber treated with pectinase (Pec), (**c**) fiber treated with xylanase (Xyl). (**d**), and fiber treated with ligninase (Lig).

The images obtained by SEM in the longitudinal axis of the untreated fique fiber show a surface with a series of undulations in a direction both parallel and perpendicular to the axis. These undulations formed a rectangular figure that was repeated along with the fiber (Figure 3a) and extended the surface of the fiber upwards. In this case, it was inferred that they could be responsible for the roughness to the touch of this type of fiber.

It was observed that after treatment with pectinase, the fiber exhibited a direct effect on the fiber surface (Figure 3b). The undulations, which were prominent in the unmodified fiber, could not be easily observed anymore. The images corresponding to the other enzymatic treatments (Xyl and Lig) (Figure 3c,d) did not show the effect produced by the pectinase. This suggests that the fiber surface may be determined by the characteristics of the primary cell wall and the middle layer, where pectin is one of the components. In this way, pectinase may play an important role in its modification.

3.4. Point of Zero Charge Measurement

The point of zero charge (PZC) was measured according to the method reported by Jiao et al. (2017) in a pH range between 2 and 10. The PZC was determined for the Nmf and the modified fibers (Pec, Xyl, and Lig).

PZC is an important factor that describes the effect of pH variation on the fiber surface, indicating the active sites of the adsorbent and consequently its adsorption capacity [66]. Therefore, PZC indicates the most suitable pH range to achieve efficient removal of the targeted pollutant according to its anionic or cationic charge [67]. Figure 4 shows the relationship between the initial and final pH of the solutions with fique fiber. The final pH values ranged between 2 and 6.

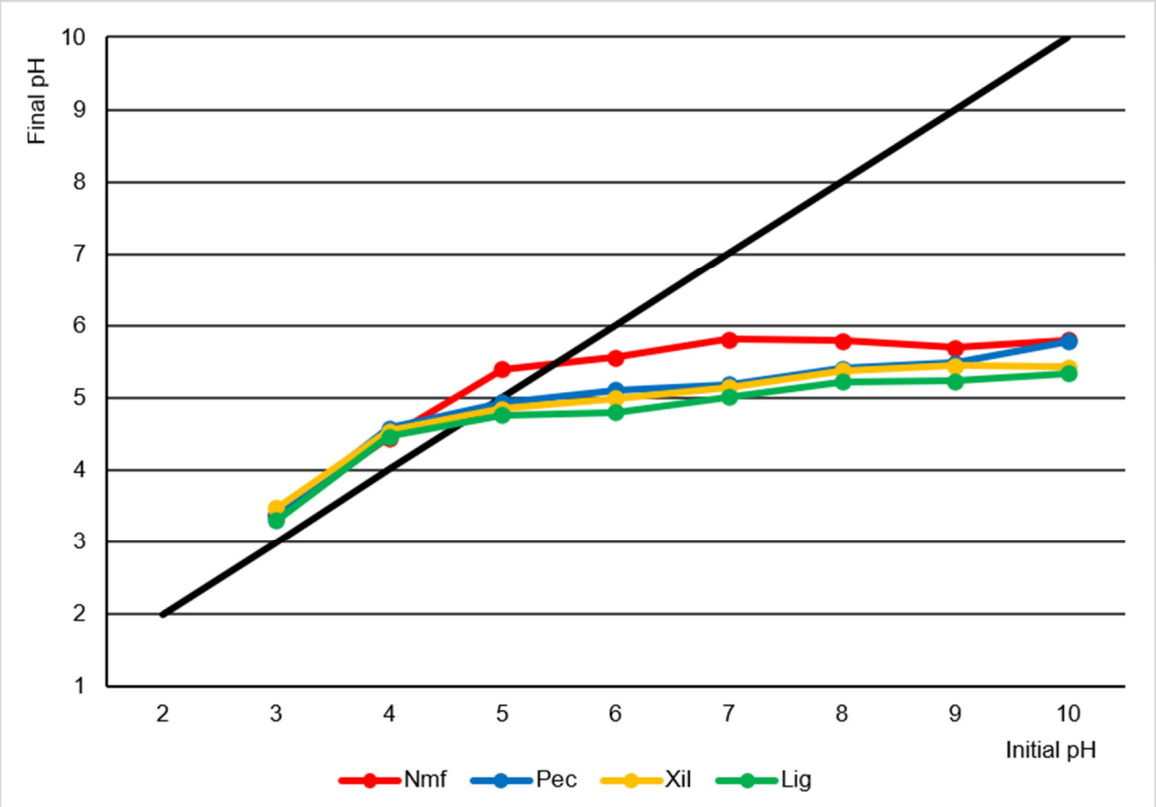

Figure 4. Point of zero charge for the fique fiber before and after modification: NMF: nonmodified fiber, Pec: fiber treated with pectinase, Xyl: fiber treated with xylanase, Lig: fiber treated with ligninase.

The PZC corresponds to the point at which the difference between the initial and final pH value is zero. The PZC for the unmodified fiber was 5.5. In other words, this is the pH value at which the surface of the fiber is neutral in terms of having no charge [67]. The fiber surface charge will be positive for pH values lower than the PZC, while the surface charge will be negative for pH values higher than the PZC [68–70].

These results are similar to those reported by Amaringo and Hormaza for other lignocellulosic materials. These authors measured the PZC of rice husk and coconut shell

and obtained values of 5.4 and 4.6, respectively. Khan and Sarwar reported PZC of 4.4 for corn stalk [67,71].

Although PZC is a relevant factor to study the capacity of a solid to retain ionic pollutants, only some authors have considered this property as a selection factor of the operating pH to reach optimal removal efficiency [3,72].

The fibers that were modified with enzymes showed PZC values lower than NMF. The PZC was 4.9, 4.8, and 4.7 after modification with pectinase, xylanase, and ligninase, respectively. These results prove that depolymerization of different lignocellulosic components on the fiber significantly changed the distribution of the surface charges. Thus, modified fique fibers required lower pH values than unmodified fiber in order for the surface to charge positively.

After the interaction between fique fibers and HCl and NaOH solutions, it was observed that at pH values lower than the PZC (where the fiber surface was charged positively), the final pH values were higher than the initial ones. For pH values higher than the PZC, the final pH values of the solutions were much lower than the initial ones. This difference was directly proportional to the pH value. This behavior can be explained by the release of protons from the acidic functional groups of the fiber (carboxyl, hydroxyl, and uronic acids) when the pH is higher than the PZC, which negatively charges the fiber surface and reduces the final pH value. At initial pH values lower than the PZC, alkaline functional groups capture protons from the solution, which positively charges the fiber surface and increases the final pH value of the solution [73–75].

According to the explanation above, the enzymatic treatment of the fiber altered the balance between acidic and alkaline functional groups, enhancing the predominance of the first ones. At pH values between 5.5 and 4.9, the original fique fiber had positive charge due to the protonation of the alkaline groups. However, after modification, negative charges appeared in this pH range, which were produced by the presence of acidic groups releasing protons from the solution.

This phenomenon may be due to oxidation reactions on the fique fiber surface by the enzymes. Some authors have reported the oxidation of Mn^{2+} to Mn^{3+} by the manganese peroxidase enzyme, which led to the oxidation of phenolic structures in lignin due to the diffusion and oxidation capacity of this ion [76,77]. On the other hand, it has been reported that xylanase enzymes hydrolyze the glycosidic bond (β-1,4) between xylan molecules in the hemicellulose polymer. This leads to the protonation of the oxygen in the glycosidic bond of one of the two xylan molecules acidifying it [78]. Finally, polygalactoronase enzymes catalyze the hydrolytic breakage of galacturonic acid chains by water diffusion through the hydrogen bonds [79].

Similar results can be found in research works performed with activated carbon. Diminution of the PZC has been performed with ozone [80] and nitric acid [81,82] due to an increase in the acidic group in the carbon surface because of oxidation.

3.5. Effect of Enzymatic Modification on Dye Removal

The effect of enzymatic modification of fique fiber on RB5 adsorption is shown in Figure 5, which presents the variation in RB5 concentration in the treated solution for each recirculation considering the three enzymatic modifications.

The three tests with modified fique fibers led to RB5 removal efficiencies higher than 40%. Enzymatic modification with xylanase (Xyl) and ligninase (Lig) did not improve the adsorption capacity of the fique fiber. In other words, the RB5 removal efficiency after these tests was very similar to that obtained with unmodified fibers.

However, fiber modification with pectinase (Pec) led to a reduction in RB5 concentration from 18.9 to 6.7 ppm, representing a removal efficiency of 66.29% or a 38% increase in adsorption capacity compared to unmodified fique fiber. This can be explained by elimination of pectin from the "middle lamella" of the cell wall of the fiber. With the removal of pectin, cavities are generated between monofilaments that allow greater access to the

longitudinal extension of the fiber and therefore to a greater number of active sites for adsorbate–adsorbent interaction, improving the retention of a greater quantity of dye.

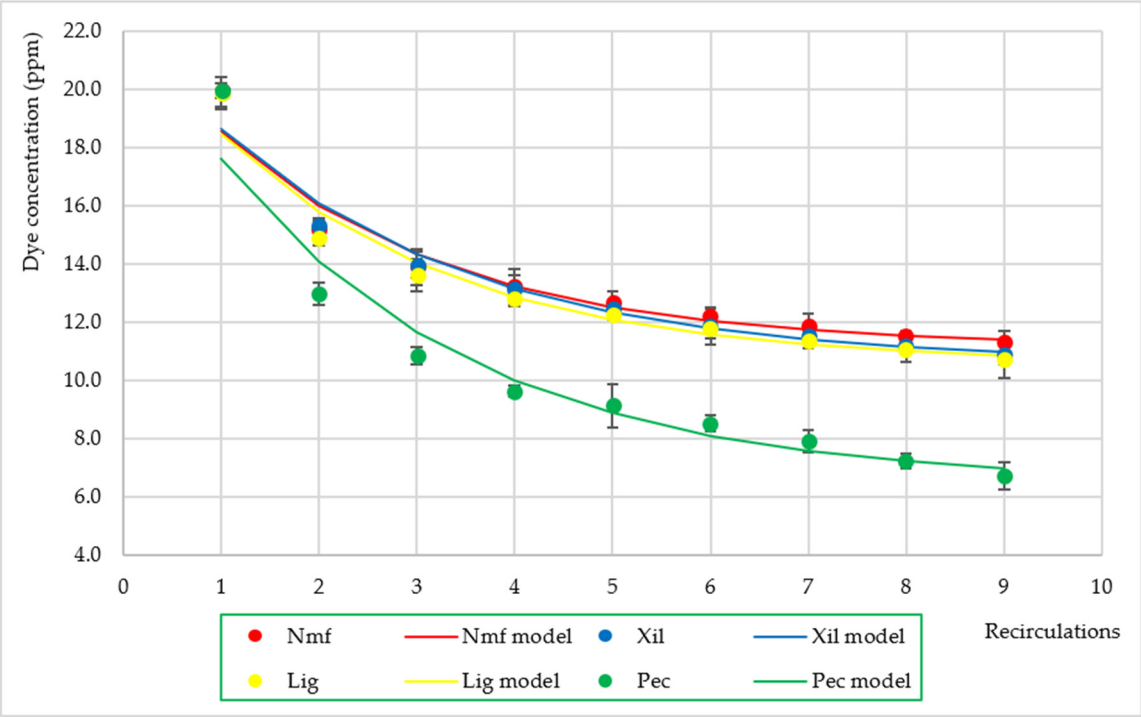

Figure 5. Variation in RB5 concentration using three enzymatic modifications of fique fiber: NMF: nonmodified fiber, Pec: fiber treated with pectinase, Xyl: fiber treated with xylanase, Lig: fiber treated with ligninase.

For these tests, the correlation coefficient (R^2) ranged between 94 and 96%, implying a high fit between the experimental and model data. The RB5 dye removal by fique fiber using nonmodified fiber (Nmf) and fibers treated with xilanase (Xil), ligninase (Lig), and pectinase (Pec) fitted an exponential decay model (Table 4). The parameter *a* showed the highest dye removal efficiency (74.4%) for the fibers treated with pectinase. Thus, the pectinase-modified fibers would remove azo dye down to a concentration of 6.45 ppm, representing the lowest concentration value obtained in the tests.

Table 4. Parameters of the exponential decay model for RB5 dye removal by nonmodified fiber (Nmf) and fibers treated with xilanase (Xil), ligninase (Lig), and pectinase (Pec).

Parameters	Nmf	Xil	Lig	Pec
a	11.2922	11.8036	11.8778	16.3732
d	11.162	10.622	10.586	6.456
R^2	0.958	0.968	0.958	0.949

Similar results for this assay were reported by Pejic et al. (2009) when modified hemp fibers were used for heavy metal adsorption. These authors attributed the increase in adsorption capacity to middle layer degradation and the consequent generation of cavities among fiber filaments [83].

Figure 6 shows the FSEM images corresponding to the fique fiber before treatment with pectinase (Figure 6a), after modification with pectinase (Figure 6b), and after the adsorption process for dye removal (Figure 6c,d).

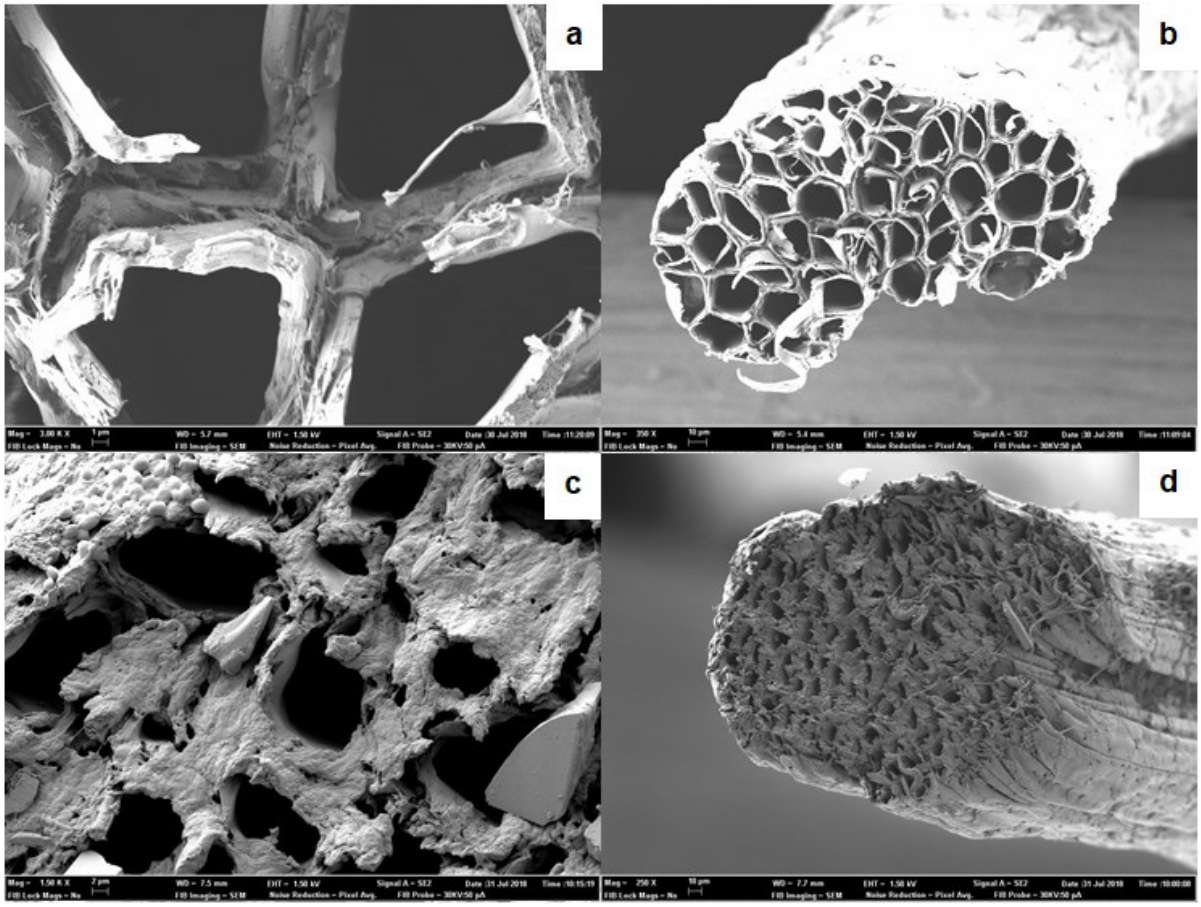

Figure 6. FSEM images of fique fiber showing the binding between monofilaments: (**a**) without enzymatic modification, (**b**) after enzymatic treatment with pectinase, and after biosorption of dye (previously modified with pectinase) (**c**,**d**).

As can be seen in Figure 6a, the secondary walls of the monofilaments were joined together, forming a fiber bundle. This was due to the pectin present in the middle layer, which allowed adhesion between monofilaments. After enzymatic treatment (Figure 6b), the adsorbent material showed separation between monofilaments within the fiber bundle, with the lumen of each monofilament being observed as additional cavities.

There was a 38% increase in adsorption capacity in the pectinase-modified fiber, which was associated with pectin elimination from the "middle lamella" of the cell wall. After RB5 absorption (Figure 6c,d), dye deposition was observed on the cavities generated on the secondary walls of the filaments. This showed that during the adsorption process, the dye solution entered the fiber through the lumen of the secondary wall and, in the case of fiber treated with pectinase, through the interstices generated by pectin degradation. However, dye retention happened inside the secondary wall.

There was an electrostatic interaction between the anionic molecules of the dye and the positively charged molecular components of the wall, such as cellulose, hemicellulose, and lignin. This might be due to the generation of interstices between the monofilaments by pectin degradation. The dye solution could access a higher specific surface on the fiber, making it susceptible to electrostatic interaction with the dye molecules.

Research carried out by Pakarinen et al. indicated that the location and structure of pectin hindered the accessibility of lignocellulolytic enzymes to the interior of the biomass. The researchers found that its elimination in traditional retting processes led to the separation of the fiber bundles in hemp and flax, improving further processing of the fiber [84].

4. Conclusions

The results of this work prove that original and enzyme-modified fique fiber can retain RB5 dye by adsorption. Activation with 0.1 M HCl as pretreatment achieved protonation of the fiber surface, increasing its positive charge. This led to an increase in the dye removal capacity. As RB5 is an anionic dye, the adsorption process is enhanced at acidic pH values. Hence, the highest RB5 retention was obtained at pH 2.4.

At a pH of 5.57, the original fique fiber surface had a neutral charge. Below this pH, the fiber surface charge was positive due to alkaline functional groups in their composition, which captured protons from the solution. Enzyme modification with lignocellulosic enzymes changed the chemical composition and the PZC of the fique fiber. Enzymatic treatment reduced the PZC value to 4.9, 4.8, and 4.7 for assays with pectinase, xylanase, and ligninase, respectively.

Enzymatic degradation of the fiber with pectinase produced degradation of the middle layer, generating cavities inside the fiber bundles. Fiber modification increased the RB5 removal efficiency by 38% due to the increase in active sites on the fiber surface.

With specific enzymatic treatments directed towards pectin removal in the chemical composition, fique fibers can become a promising biosorbent for azo dye removal through surface modification. They can be of particular significance for textile wastewater treatments in terms of improving the quality of the water before discharge.

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