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Improved Dye Removal Ability of Modified Rice Husk with Effluent from Alkaline Scouring Based on the Circular Economy Concept

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Abstract: To improve the ability of the rice husk to purify colored wastewater, effluent from the alkaline scouring of cotton yarn was used immediately after the scouring (without cooling and additionally added chemicals) in order to remove the non-cellulosic silicon-lignin shield from the rice husk's surface. This rice husk, with 93.8 mg/g adsorption capacity, behaves similarly as the rice husk treated with an optimized alkaline scouring recipe consisting of 20 g/L NaOH, 2 mL/L Cotoblanc HTD-N and 1 mL/L Kemonecer NI at 70 °C for 30 min with an adsorption capacity of 88.9 mg/g of direct Congo red dye. Treating one form of waste (rice husk) with another (effluent from the alkaline scouring of cellulosic plant fibers), in an effort to produce a material able to purify colored effluent, is an elegant environment-friendly concept based on the circular economy strategy. This will result in a closed-loop energy-efficient process of the pre-treatment of cotton (alkaline scouring), modification of rice husk using effluent from the alkaline scouring, dyeing cotton fabrics and cleaning its colored effluents with modified rice husk without adding chemicals and energy for heating.

Keywords: biosorbent; activation of rice husk; waste; colored effluent purifying; low-cost treatment; closed-loop process

1. Introduction

Colored wastewater (effluent) from the textile dyeing industry contains dye, surfactants and various organic and inorganic hazardous chemical pollutants that must be removed before the effluent is discharged into the environment [1,2]. Many of the recently developed techniques for purifying colored effluent are effective, but costly and require additional examination [3]. Sorption of dye molecules is an easily applicable method based on using a substrate (adsorbent) that has to be highly effective, cheap and ecologically friendly. Activated carbon, as a material that exhibits a large surface area, microporous structure and high adsorption capacity, is rated as one of the most used adsorbents for wastewater treatment [4,5]. Despite its numerous advantages, a commercially available form is very expensive because its fabrication incurs high-cost processes [6]. Low-cost adsorbents from agricultural waste are used as a cheap alternative for activated carbon [7–13]. The rice husk with its chemical composition [14] is the most promising adsorbent for the removal of many chemicals, including dyes [15–19]. Although the adsorption capacity of the raw rice husk was more apparent for basic [20] rather than direct [6,21] dyes, the adsorption was still low. The outer surface of the rice husk in the form of a hydrophobic silicon–cellulose membrane and the inner lignin-containing part are responsible for the lack of adsorption [22]. Several chemical and physical processes have been reported to modify rice husk. Namely, rice husk was physically grounded [20], chemically treated with ethylenediamine [23], acids [6], bases [24–27] and used as a precursor for producing activated carbon [28–30]. However, despite the obvious effective approach, such rice husk modifications are highly energy-dependent and require special expensive equipment that is capable of withstanding and operating at high pressure and elevated temperature.

Based on the chemical composition comprising 32.2% cellulose, 21.3% hemicellulose, 21.4% lignin, 1.8% extractives, 8.1% water and 15.1% SiO_2 [14], rice husk has similar chemistry as natural cellulosic fibers like linen, hemp and cotton [13] and theoretically is expected to demonstrate a strong potential for dye adsorption and colored effluent purifying. Traditionally, excellent dyeability of these fibers is achieved by removal of non-cellulosic hydrophobic lignin, waxes and pectins using alkaline scouring [13]. The procedure is carried out by 1–4% solution of sodium hydroxide (NaOH) in the presence of surfactants at boiling temperature for one to two hours [31]. Similar chemical composition of the natural cellulosic fibers and the rice husk indicates that the alkaline scouring or effluent from this process have the potential to modify rice husk. Thus, treating one waste (rice husk) with another (effluent from the alkaline scouring of plant fibers) is an elegant concept for the production of a material able to clean colored effluent from cotton dyeing. Moreover, the process is cheap, effective and avoids the use of chemicals for modification, energy for carbonization or grounding of the rice husk and investment in a new machinery system. In the present study, a modification of the rice husk with effluent from an alkaline scouring of cotton fiber for improved adsorption of the direct Congo red dye is proposed. The closed-loop process which consisted of: alkaline scouring of cotton, modification of the rice husk using the alkaline scouring effluent, dyeing cotton fabrics and purifying the colored effluents with modified rice husk, was tested. The adsorption capacity of this rice husk was compared with the alkaline scoured rice husk using an optimized recipe (the optimization of the concentration of sodium hydroxide, temperature and treatment time was done) following the kinetics of adsorption of Congo red, while the characterization of this rice husk was monitored by scanning electron microscopy-energy dispersive X-ray (SEM-EDX), attenuated total reflectance-infrared spectroscopy (ATR-IR), and ζ-potential measurements. Modification of the rice husk with effluent from alkaline scouring is a new concept that corresponds to a circular economy strategy that will end up creating an industrial closed-loop energy-efficient process for cleaning colored effluents.

2. Materials and Methods

2.1. Substrate and Chemicals

The rice husk (RH) collected from local rice mills, was sieved to remove the small particles with a size smaller than 1.25 mm, dried at 105 °C for 2 h and weighed before modification. Direct Congo red dye (C.I. 20120 or CI Direct red 28), with the structure given in Figure 1, was purchased from Sinochem Hebei Company, Shijiazhuang, China and used without further purification. Stock solution with 1 g/L was prepared by dissolving the dye in deionized (DI) water. The experimental dye solution with different concentrations was prepared by diluting the stock solution with a suitable volume of DI water. Sodium hydroxide pellets (NaOH) and sodium chloride (NaCl) were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Anionic washing surfactant Cotoblanc HTD-N was supplied by CHT Switzerland AG, Oberriet, Switzerland, while nonionic wetting surfactant Kemonecer NI by Kemo, Zagreb, Croatia. All aqueous solutions were prepared with DI water with a resistivity of 18.2 MΩ·cm (conductivity of 0.055 $\mu S \cdot cm^{-1}$).

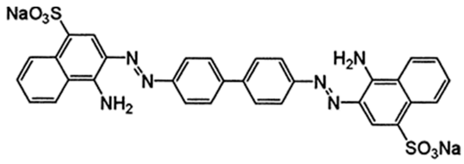


Figure 1. Structural formula of Congo Red.

2.2. Modification of Rice Husk

The modification of the RH was undertaken using the optimized recipe for alkaline scouring of natural cellulosic fibers (Section 2.2.1) or effluent from the alkaline scouring of cotton yarn (Section 2.2.2). The adsorption capacity of these rice husks was examined according to the procedure explained in the Section 2.3.

2.2.1. Optimization of Alkaline Scouring of Rice Husk

The optimization of the alkaline scouring of rice husk was conducted in two steps. First, the concentration of sodium hydroxide was defined by treating the rice husk in a bath with 20:1 liquor ratio using 5, 10, 20 and 40 g/L of NaOH in the presence of 2 mL/L Cotoblanc HTD-N and 1 mL/L Kemonecer NI at 90 °C for 30 min (the labels of this samples are shown in Table 1). Second, the optimal temperature and treatment time were determined by treating the rice husk in a bath with a 20:1 liquor ratio using 20 g/L sodium hydroxide in a presence of 2 mL/L Cotoblanc HTD-N and 1 mL/L Kemonecer NI at 50, 70 and 90 °C for 30 and 60 min (the labels of this samples are shown in Table 2).

Table 1. Sample label and summary of alkaline scoured rice husk treated with different concentrations of sodium hydroxide at 90 °C for 30 min.

Label.	Treatment of Rice Husk	NaOH (g/L)
R	Raw (untreated)	
S5	Scoured	5
S10	Scoured	10
S20	Scoured	20
S40	Scoured	40

Table 2. Sample label and summary of alkaline scoured rice husk treated with 20 g/L sodium hydroxide under different temperature and treatment time.

Label	Treatment of Rice Husk	Conditions	
		Temperature (°C)	Time (min)
R	Raw (untreated)		
S20_50/30	Scoured	50	30
S20_50/60	Scoured	50	60
S20_70/30	Scoured	70	30
S20_70/60	Scoured	70	60
S20_90/30	Scoured	90	30
S20_90/60	Scoured	90	60

The influences of temperature and treatment time of the alkaline scouring efficiency were analyzed using ANOVA analysis of variance (STATISTICA, Data Analysis Software System, Version 6, Inc., 2001). A two-factor (3 × 2) design was used to structure the experiment, wherein the factors (independent) variables were the temperature of scouring in 3 levels (50, 70 and 90 °C) and treatment time of scouring in 2 levels (30 and 60 min). The response (dependent) variable was the percent of dye removal for 120 min adsorption time.

2.2.2. Closed-Loop Process of Alkaline Scouring of Cotton, Modification of the Rice Husk Using Effluent from the Alkaline Scouring, Dyeing Cotton Fabrics and Purifying Its Colored Effluents by Modified Rice Husk

The effluent from the alkaline scouring was created by using the recipe for industrial alkaline scouring of the cotton yarn carried out in a bath with a 50:1 liquor ratio using 25 g/L of NaOH in the presence of 2 mL/L Cotoblanc HTD-N and 1 mL/L Kemonecer NI at 100 °C for 60 min in Ahiba Turbomat TM-6 apparatus, Datacolor, Gentbrugge, Belgium This effluent, which contains NaOH, surfactants and a negligible amount of waxes and pectin, was then used for modification of the rice husk in a bath with a 20:1 liquor ratio for 30 min without heating and adding chemicals in a Lintiest apparatus. In 30 min, the temperature of the effluent decreased from 100 °C to 40 °C with an average temperature of 70 °C which corresponds to the temperature of S20_70/30 treated rice husk. The scoured cotton yarn was rinsed twice at 90 °C for 15 min and twice at 25 °C temperature for 15 min. The effluent from the rinsing of the cotton was used for rinsing the rice husk too. Scoured cotton was dyed with 1%, 2%, and 4% overweight of the fabric (owf) Congo red in a bath with a 50:1 liquor ratio using 20 g/L NaCl at 90 °C for 60 min in Ahiba Turbomat TM-6 apparatus. The schematic of rice husk modification and purifying colored effluent is given in Figure 2. The adsorption ability of this rice husk was tested on the effluent from dyeing cotton yarn according to the procedure explained below.

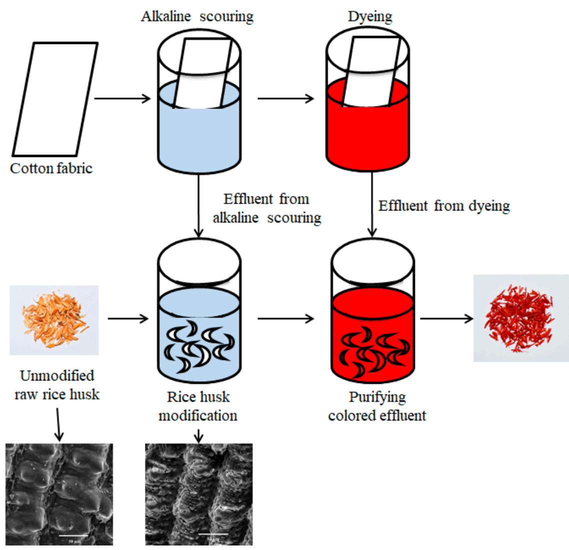


Figure 2. Schematic of rice husk modification and purifying colored effluent.

2.3. Adsorption Studies

The adsorption ability of the RH treated under optimized conditions of alkaline scouring (S20_70/30) and the RH modified with the effluent from the alkaline scouring of cotton yarn (ERH) was explored employing a batch adsorption method. A total of 2 g of rice husk was added to 200 mL of colored solution in a glass stoppered Erlenmeyer flask that was agitated at a constant speed of 60 min^{-1} for 120 min in a GLF-shaking water bath 1083 (EURO lux GmbH & Co. KG Karlstadt-Karlburg, Karlstadt, Germany).

The adsorption ability of S20_70/30 rice husk was tested at 25 °C using 0.1, 0.2, 0.3, 0.4 and 0.5 g/L initial dye concentration, while ERH was tested on effluent from cotton dyeing at the initial temperature of 90 °C that decreased to 25 °C for 60 min.

The constant aliquot of dye solution was pipetted at 5, 10, 15, 20, 30, 40, 60, 90 and 120 min and the concentration in the supernatant solution was analyzed using UV/VIS spectrophotometer (Model Hitachi-2800, United Kingdom) at a maximum wavelength for Congo red at 507 nm. The presented results are the mean values of 3 measurements. The dye removal efficiency or % of dye removal was calculated using the equation:

$$\text{Dye removal (\%)} = \left[\frac{C_0 - C_t}{C_0}\right] \times 100\ (\%), \tag{1}$$

where C_0 is the initial concentration of the dye in g/L and C_t is the concentration of the dye after sorption at any time in g/L.

The amount of the adsorbed dye onto the rice husk Q_e (g/g) was calculated according to the mass balance equation:

$$Qe = \frac{(C_0 - C_e) \times V}{W}, \tag{2}$$

where C_0 and Ce are the initial and concentration of dye at equilibrium in g/L, respectively, V is the volume of the solution in L and W is the weight of the sorbent used in g.

2.4. Characterization of the Rice Husk

Scanning electron microscope (SEM) images were collected using the VEGA3 LMU, Tescan instrument (Brno, Czech Republic) coupled with energy-dispersive X-ray (EDX) spectroscopy (INCA Energy 250 Microanalysis System, Oxford Instruments, High Wycombe, UK) to quantitatively analyze the chemical composition of the products. The voltage of the SE detector was set to 20 kV. Prior to scanning, a 5 nm gold coating was applied to the surface of the rice husk to minimize charging. Attenuated total reflectance infrared (ATR-IR) spectra of the unmodified and modified rice husk were collected on room temperature employing FT-IR Perkin Elmer 2000 interferometer and coupling a Golden Gate ATR Mk II system (Specac™, Orpington, UK), which consists of optics unit with ZnSe lenses and a diamond ATR top-plate. A sapphire anvil was mounted to the micrometre clamp. The spectra were collected in the 4000–550 cm^{-1} region (resolution 4 cm^{-1}, 16 scans per spectrum). Electrokinetic ζ-potential versus pH was measured by the streaming potential method using cylindrical cell on the SurPASS electrokinetic analyzer (Anton Paar GmbH, Graz, Austria) and calculated according to Helmholtz-Smoluchowsky equation [32]. All ζ-potential measurements were done in 3 replicates, and each point was averages of 4 potential measurements, which means that 12 measurements for each point at specific pH were collected.

3. Results

3.1. Optimization of the Alkaline Scouring of Rice Husk

Raw and alkaline scoured rice husk with 5 g/L NaOH (S5) at 90 °C for 30 min are employed as a first trial to explore their ability to clean 0.1 g/L water solution of direct Congo red dye. The adsorption curves in Figure 3, continuously lead to the saturation of both rice husks. The percentage of dye removal increases as the contact time rises, showing a rapid removal in the initial phase and slow rate after 60 min when an approximate constant is attained. In this study, 120 min was chosen as the time to attain an equilibrium, because the changes in dye removal from 2 to 24 h were only a few percent. Surprisingly, unmodified raw rice husk shows higher adsorption ability relative to S5. Similar to cellulosic plant fibers, alkaline scouring removes the non-cellulosic components from the rice husk, making it more hydrophilic with increased negative ζ-potential [32]. This phenomenon of the rice husk is examined and explained below in this paper. Since most direct dyes are sulfonated, they have a negative charge in a water solution that acts as an electrostatic barrier [33] making the dye adsorption onto the S5 modified rice husk less feasible.

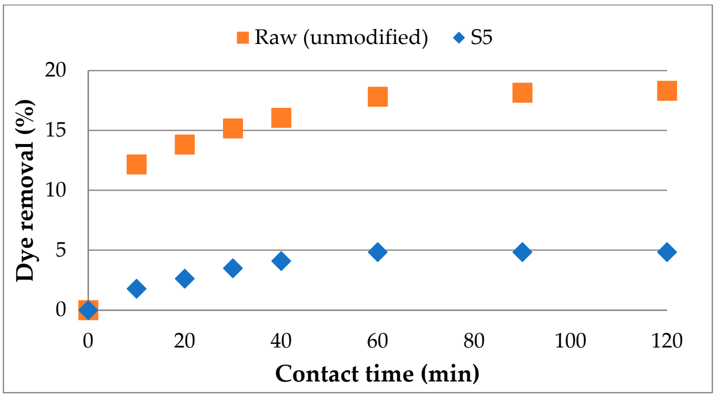


Figure 3. Effect of contact time on dye removal on: (red squares) raw-unmodified and (blue diamonds) S5 rice husks (adsorption conditions are 0.1 g/L Congo red, 25 °C, 10 g/L rice husk).

To overcome this, the dyeing of the natural cellulosic plant fibers with direct dyes is conducted by adding large quantities of sodium chloride (NaCl) or sodium sulfate (Na_2SO_4) [33], usually performed with 20 g/L salt. The results of the dye removal using 0.1 g/L dye solution with 0 to 20 g/L sodium chloride (Figure 4) emphasize the enhanced ability of modified S5 rice husk to adsorb Congo red as the concentration of the sodium chloride increases to 20 g/L. Assuming that half of the salt is consumed during the dyeing of the fibers, the constant concentration of 10 g/L sodium chloride, together with the previously defined 0.1 g/L initial dye concentration at 25 °C in the presence of 10 g/L rice husk as an adsorbent are used in the further adsorption experiments.

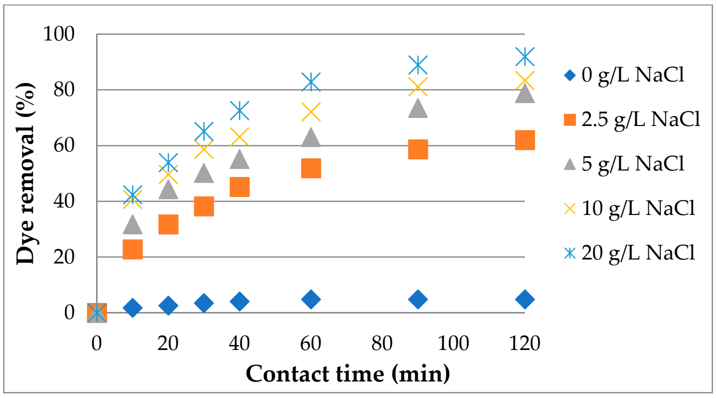


Figure 4. Influence of concentration of sodium chloride (NaCl) on dye removal on S5 rice husk (adsorption conditions are 0.1 g/L Congo red, 25 °C, 10 g/L rice husk).

In the next step, the rice husk was alkaline scoured with 10, 20 and 40 g/L NaOH at 90 °C for 30 min. These samples, presented in Figure 5, show increased adsorption ability as the concentration of sodium hydroxide increases from 10 to 20 g/L and attain almost the same values as those after a further increase of the sodium hydroxide to 40 g/L.

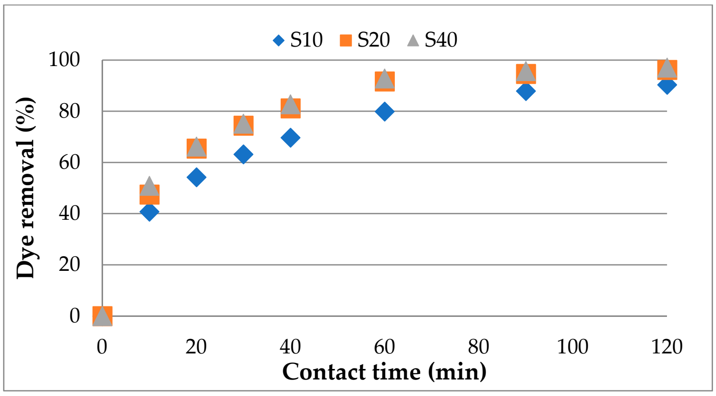


Figure 5. Dye removal vs. contact time of rice husk treated with 10, 20 and 40 g/L solution of sodium hydroxide (NaOH) at 90 °C for 30 min (adsorption conditions are 0.1 g/L Congo red, 25 °C, 10 g/L rice husk).

SEM images of these samples and quantitative elemental analyses measured by energy-dispersive X-ray (EDX) spectroscopy are shown in Figure 6 and Table 3, respectively. The silica–cellulose–lignin shield of the raw, untreated rice husk (Figure 6a) is largely removed after alkaline scouring (Figure 6b–d). SEM images of the S10 sample (Figure 6b) with 27.7% and the S20 (Figure 6c) with 29.4% weight loss have grainy cellulose structures embedded in the non-removed lignin matrix. The S40 rice husk (Figure 6d) with 34.5% weight loss depicts a grainy cellulose structure with many cracks, indicating a practically complete removal of the lignin from the rice husk.

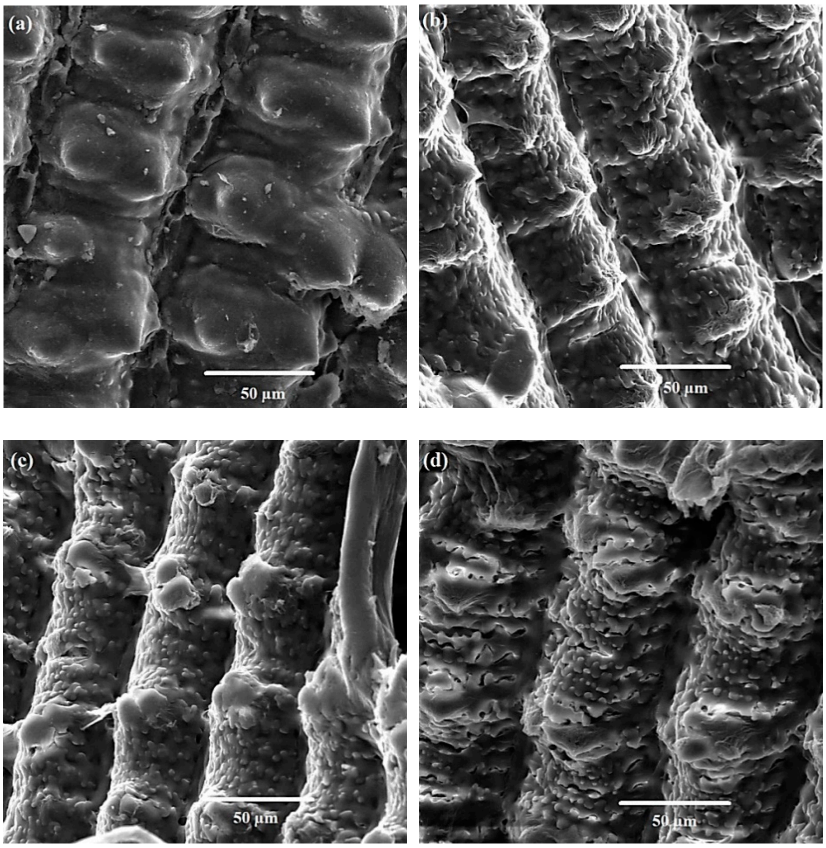


Figure 6. Scanning electron microscope (SEM) images of raw (**a**) and alkaline scoured S10 (**b**), S20 (**c**) and S40 (**d**) rice husk.

Table 3. SEM-energy dispersive X-ray spectroscopy (EDX) elemental chemical analysis from the surface of rice husks.

Element	Raw		S10		S20		S30	
	Wt.%	**O/C**	**Wt.%**	**O/C**	**Wt.%**	**O/C**	**Wt.%**	**O/C**
C	14.8		61.9		58.3		60.7	
O	61.9	4.19	37.8	0.61	39.3	0.65	41.6	0.71
Si	23.3		0.05		0.07		-	

The elemental chemical composition of the raw sample (Table 3), representing 23.3% silicon (Si) and 61.9% oxygen, indicates the presence of SiO_2 on the surface. The SEM-EDX results confirm the silica–cellulose–lignin shield structure on the outer part of the rice husk [22]. Alkaline scoured S10 and S20 samples revealed less than 0.1% Si, while S40 shows no Si presence. Obviously, the alkaline scouring removes SiO_2 and most of the lignin from the surface of the rice husk, resulting in a decrease of the O/C ratio (an indicator of the chemical composition of the rice husk) from 4.19 for raw to 0.61, 0.65 and 0.71 for S10, S20 and S40 samples, respectively. Based on the number of oxygen and carbon atoms in the structural unit of cellulose and lignin, the calculated O/C ratio for cellulose is 0.83 [34], whereas for lignin it is 0.3. The O/C ratio of the sodium hydroxide treated rice husks (S10, S20 and S30) increases as the concentration of sodium hydroxide rises (Table 3) indicating the removal of lignin and producing rice husks with enriched cellulose content. Calculated coefficients of correlation between O/C ratio of S10, S20 and S30 samples and dye removal after 30 and 120 min contact time are 0.804 and 0.786, respectively.

Since the S40 sample with an almost lignin-free structure has nearly the same dye-adsorption capacity as the S20 rice husk (Figure 5), 20 g/L of NaOH was further chosen to inspect the significance of temperature and treatment time of alkaline scouring. The temperature was ramped up to 50, 70 and 90 °C for a period of 30 and 60 min in an attempt to obtain the optimal parameters (Figure 7). The results indisputably depict a surge in the rice husk's adsorption ability as a function of the temperature and treatment duration. The 30 min treatment revealed that the adsorption capacity of the S50 (around 40%) is less than a half, compared to the corresponding dye removal capacity of the S70 (nearly 80%) and S90 (around 95%) (Figure 7). Although 30 min scoured RH has a slightly lower ability to remove Congo red in contrast to the 60 min treated, ANOVA dispersion analysis (Table 4) indicates that the treatment time, with a p-value of 0.187 ($p < 0.05$ indicates significant influence), shows no significant influence on the dye removal after 120 mins contact time. On the other hand, the temperature of scouring with a p-value lower than 0.05 has a significant influence on dye removal. The output of these two experiments (Figures 5 and 7) build 20 g/L NaOH at 70 °C for 30 min as the optimal parameters for successful modification of the rice husk that, in addition, nicely corresponds with the chemical composition of the effluent from alkaline scouring. The optimal temperature and the duration derived from the following observation: it took 30 min to cool the effluent from 90 to 50 °C with an average temperature of 70 °C which corresponds to actual conditions for using effluent from alkaline scouring without heating and adding chemicals.

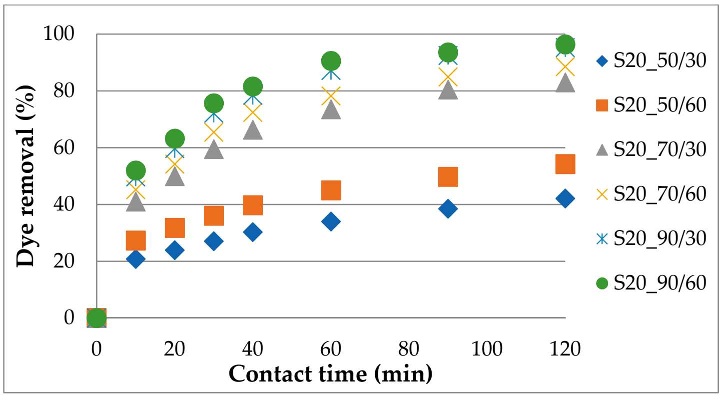


Figure 7. Dye removal vs contact time of rice husk treated with 20 g/L NaOH at 50, 70 and 90 °C for 30 and 60 min (adsorption conditions are 0.1 g/L Congo red, 25 °C, 10 g/L rice husk).

Table 4. Evaluated Fisher test (F-test) and *p*-values for temperature of scouring and treatment time for percent of removed Congo red for 120 mins.

Factors	F-Test	*p*-Values
Temperature of scouring	83.0 [1]	0.012
Treatment time	3.89	0.187

[1] Significant influence.

ATR-IR spectra and ζ-potential curves were an additional aid in characterising the raw-unmodified and S20_70/30 modified rice husks. The IR spectrum of the untreated rice husk exhibits considerable differences compared to the S20_70/30 sample counterpart (Figure 8). The major spectral discrepancies comprise the existence of two well-defined and sharp bands, positioned at 2917 and 2846 cm^{-1}, as well as the sole band at 1733 cm^{-1} (Figure 8a), that are not evidenced in the IR spectrum of the treated sample (Figure 8b). The former bands were assigned to the asymmetric and symmetric aliphatic C-H stretching vibrations from the methoxy groups, whereas the latter band was ascribed to the carbonyl C=O units within the lignin organic polymer structure. The band positions closely resemble the corresponding bands found in various pure lignin IR spectra [35], confirming the lignin presence in the untreated rice husk. On the other hand, the treatment of the rice husk has obviously stripped the lignin phase and the obtained spectrum closely matches the spectrum of cellulose [36], providing spectral evidence that the modified rice husk is practically lignin-free and cellulose-dominant.

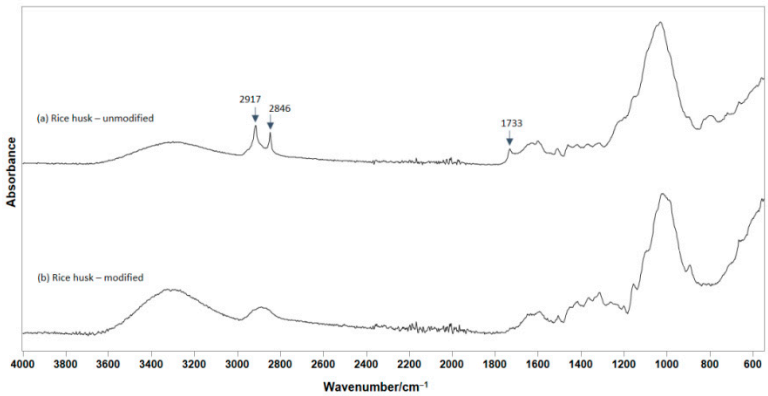


Figure 8. Attenuated total reflectance-infrared (ATR-IR) spectra of raw unmodified (**a**) and S20_70/30 modified (**b**) rice husk.

The ζ-potential versus pH of raw and S20_70/30 modified rice husks (Figure 9) indicates the similar negative ζ-potential of the untreated rice husk with raw cellulosic plant fibers in a range of pH 2–9 [37–39]. The alkaline scouring removes non-cellulosic compounds making the rice husk more hydrophilic and alters ζ-potential in both alkaline and acid conditions. At pH 9, ζ-potential changes from −11 mV for unmodified to −2 mV for S20_70/30 scoured rice husk. The plateau value of ζ-potential at pH 9 means that the charged surface groups are completely dissociated. The less negative ζ-potential of S20_70/30 scoured rice husk (−2 mV) demonstrates that charged surface groups may prevent the dissociation of neighboring groups by surface repulsing as well as inter-fibrillar swelling. These phenomena shift the shear plane into the liquid phase, causing a reduction of the ζ-potential [37–39]. In pH around 3, a noticeable increase in the negative value of the ζ-potential of S20_70/30 rice husk is observed after scouring. This behavior is more obvious for cellulose that contains carboxyl groups and early studies suggested that the ζ-potential of carboxyl-enriched cellulose strongly increases in the acid condition below pH 5, peaking at pH 3 [39,40].

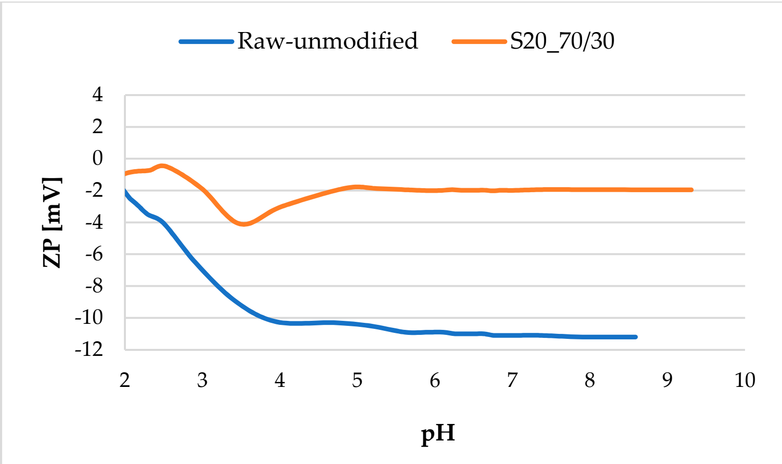


Figure 9. ζ-potential of raw unmodified and S20_70/30 rice husks plotted as a function of pH.

3.2. Adsorption Study

The analysis and design of the sorption process require relevant adsorption equilibria in order to provide fundamental physiochemical data for evaluating the applicability of the used sorbent. Langmuir (Equation (3)) and Freundlich (Equation (4)) isotherms were used to analyze equilibrium data of adsorption of Congo red onto S20_70/30 and ERH:

$$\mathrm{Qe} = \frac{\mathrm{Qm}\ \mathrm{K_L}\ \mathrm{Ce}}{1+\mathrm{K_L}\ \mathrm{Ce}}, \tag{3}$$

$$\mathrm{Qe} = \mathrm{K_F}\mathrm{Ce}^{1/\mathrm{n_F}}, \tag{4}$$

where Q_m and K_L are Langmuir and K_F and n_F Freundlich constants related to sorption capacity and sorption intensity of the adsorbents. The linearized form of Langmuir (Equation (5) and Freundlich (Equation (6) are written as follows:

$$\frac{\mathrm{Ce}}{\mathrm{Qe}} = \frac{\mathrm{Ce}}{\mathrm{Qm}} + \frac{1}{\mathrm{K_L}\ \mathrm{Qm}}, \tag{5}$$

$$\ln(\mathrm{Qe}) = \ln(\mathrm{K_F}) + \frac{1}{\mathrm{n_F}}\ln(\mathrm{Ce}), \tag{6}$$

The Langmuir's constants Q_m and K_L are calculated from the slope of the plot between Ce/Qe versus Ce, while the Freundlich's constants K_F and n_F are calculated from the intercept and slope of the plot between log Qe and log Ce.

The predicted Langmuir and Freundlich isotherm equations for adsorption of Congo red onto S20_70/30 rice husk, useful for design calculations, are given by Equations (7) and Equation (8), respectively, while the same isotherms for adsorption of Congo red onto ERH are given by Equation (9) and Equation (10), respectively.

$$Q_e = \frac{4.06C_e}{1+45.1C_e}, \quad (7)$$

$$Q_e = 0.0850\ C_e^{0.649}, \quad (8)$$

$$Q_e = \frac{0.168C_e}{1+1.77C_e}, \quad (9)$$

$$Q_e = 1.107\ C_e^{0.636}, \quad (10)$$

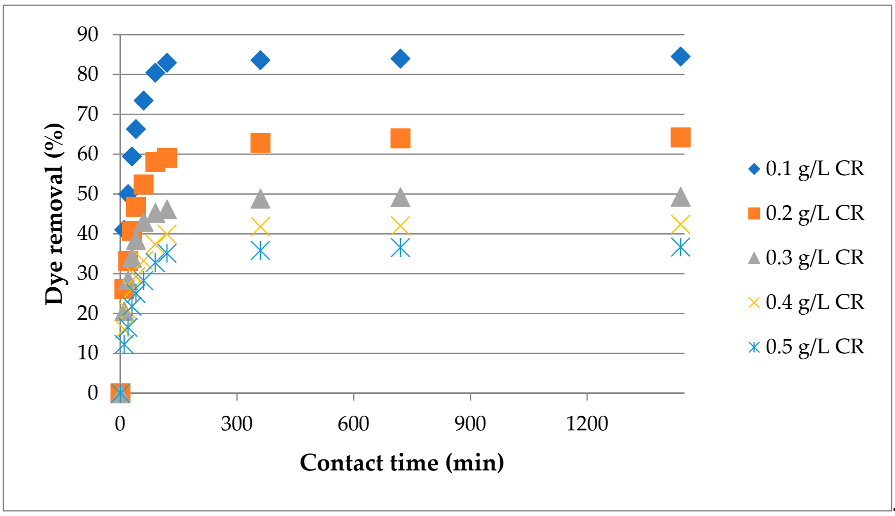
The adsorption curves of Congo red onto S20_70/30 and ERH as a function of contact time are shown in Figure 10. S20_70/30 rice husk is tested with 0.1 to 0.5 g/L dye solutions at 25 °C, while ERH is tested with effluents from dyeing cotton yarn dyed with an initial concentration of 1%, 2% and 4% (owf) dye. The Langmuir and Freundlich curves for S20_70/30 rice husk (Figure 11a), generated using the adsorption curves from Figure 10a and Equations (7) and (8), show that equilibrium data are better represented by the Langmuir ($R^2 = 0.981$) in comparison to the Freundlich ($R^2 = 0.653$) equation, confirming monolayer coverage of Congo red onto S20_70/30 rice husk with a maximum sorption capacity of 88.9 mg/g (Table 5). The Langmuir and Freundlich curves for ERH (Figure 11b), generated using the adsorption curves from Figure 10b and Equations (9) and (10), show that equilibrium data are better represented by the Freundlich in comparison to the Langmuir equation. This result was expected since the effluent from cotton dyeing contains low concertation of Congo red, and therefore at the maximum adsorption, the monolayer is not achieved. Even though the sorption equilibrium of S20_70/30 and ERH fit with different equilibrium equations the ERH with 93.8 mg/g and S20_70/30 with 88.9 mg/g have similar adsorption capacity of Congo red (Table 5). This is one of the better results achieved for chemically modified rice husk (Table 6). Moreover, calculated $1/n_F$ values of both rice husk samples are less than 1, giving the favorable sorption of Congo red onto both modified rice husk samples [24].

Table 5. Equilibrium constants for sorption of Congo red onto S20_70/30 and cotton yarn (ERH).

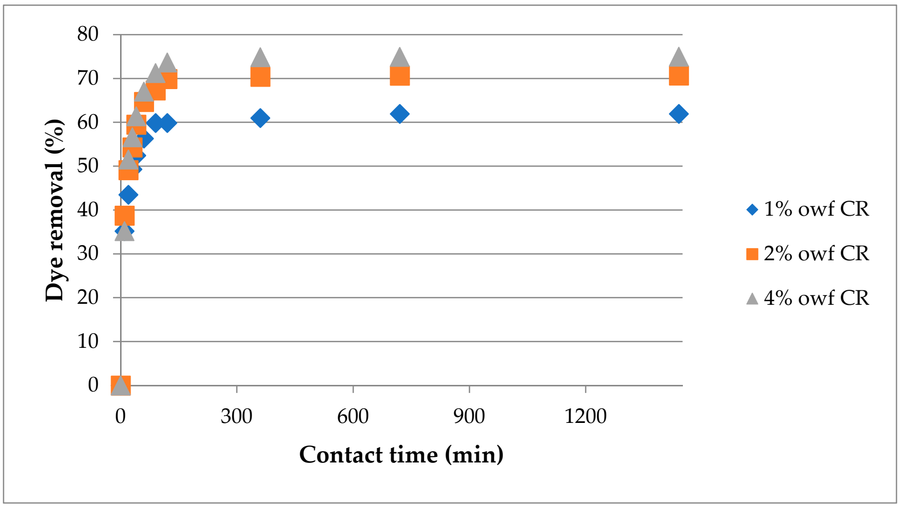
Isotherms	**Parameters**					
	S20_70/30			**ERH**		
Langmuir	K_L (L/g)	Qm (g/g)	R^2	K_L (L/g)	Qm (g/g)	R^2
	0.374	0.0889	0.981	1.84	0.0938	0.114
Freundlich	K_F (L/g)	n_F	R^2	K_F (L/g)	n_F	R^2
	0.352	1.53	0.653	1.11	1.58	0.952

Table 6. Adsorption capacity of chemically modified rice husks.

Chemical Modification	**Dye**	**Adsorption Capacity (mg/g)**	**Literature**
0.6 mol/L oxalic acid at 20 °C	Methylene blue	53.2	[41]
	Malachite green	54.0	[41]
5% NaOH at 10 psi (~120 °C) for 15 mins	Crystal violet	44.9	[25]
	Safranine	37.9	[26]
	Malachite green	12.6	[24]
0.5 g EDTA in 300 mL 0.1M NaOH at 70 °C for 30 mins	Methylene blue	46.3	[42]
	Reactive orange 16	7.68	[42]
0.1N HCl at 30 °C for 1 h	Everdirect Orange-3GL	29.9	[43]
	Direct Blue-67	37.9	[43]
0.02 mole of EDTA in water at 80 °C for 2 h	Basic blue 3	3.3	[23]
	Reactive orange 16	24.9	[23]

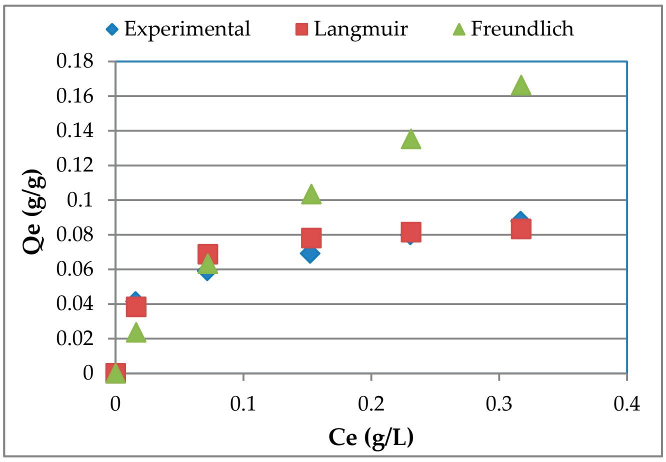


(**a**).

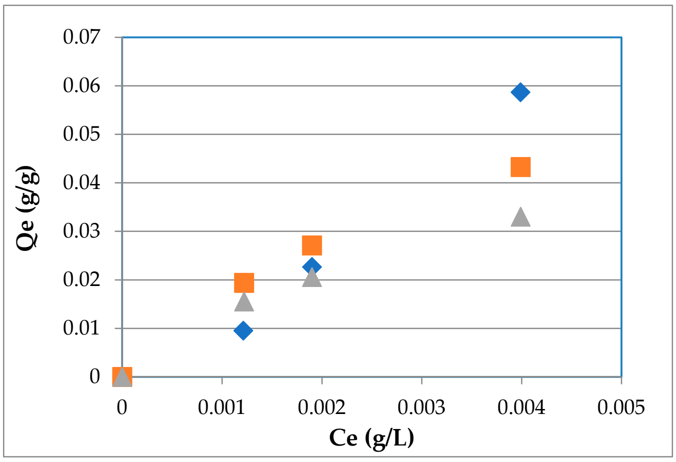


(**b**)

Figure 10. Dye removal vs. contact time of: (**a**) alkaline scoured S20_70/30 rice husk (adsorption conditions are 0.1 to 0.5 g/L Congo red (CR), 25 °C, 10 g/L rice husk) and (**b**) ERH (adsorption conditions are effluent from dyeing cotton with 1%, 2% and 4% (owf) initial concentration of CR, 90 °C initial temperature and 10 g/L rice husk).



(**a**)



(**b**)

Figure 11. Equilibrium curves for sorption of Congo red onto (**a**) S20_70/30 and (**b**) ERH.

The SEM image of ERH shown in Figure 12 has a similar structure as S10 and S20 alkaline scoured rice husk presented in Figures 6b, c. This is in line with the good adsorption ability of ERH that is close to the adsorption ability of S20_30/70 rice husk.

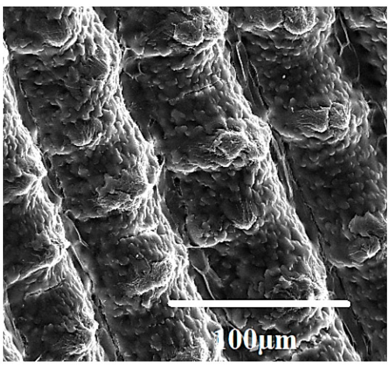


Figure 12. SEM image of ERH rice husk.

3.3. Kinetic Modeling

The adsorption curves of CR onto S20_70/30 and ERH as a function of contact time (Figure 10) were further used to evaluate the kinetics of the adsorption process. The pseudo-first-order

(Equation (11)) and pseudo-second-order (Equation (12)) kinetic models were tested to obtain the rate constants and equilibrium adsorption capacity at different initial concentrations [44].

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}\,t, \quad (11)$$

$$\frac{t}{Q_t} = \frac{1}{k_2\,Q_e^2} + \frac{1}{Q_e}t, \quad (12)$$

k_1 and k_2 are rate constants for pseudo-first and pseudo-second-order, respectively, Qe is adsorption capacity at equilibrium and Qt is adsorption capacity at t contact time.

k_1 and k_2, Qe and Qt and coefficients of correlation for tested models are listed in Table 7. The R^2 for the pseudo-second-order model is significantly better than for the pseudo-first-order model. Since theoretical and experimental values of adsorption capacity are very close to each other, the adsorption of CR onto both S20_30/70 and ERH rice husks can be described by the pseudo-second-order model. The k_2 decreases as the initial CR concentration increases. This phenomenon may be due to a lesser competition for the adsorption sites at lower initial CR concentration. At higher initial dye concentration, the competition for the sites will be stronger and the adsorption rates will consequently decrease [45].

Table 7. Kinetic parameters for adsorption of Congo red (CR) onto S20_70/30 and ERH rice husks.

Rice Husk	Initial Dye Concentration	$Q_{e,\,exp}$ (g/g)	Pseudo-First-Order Kinetic Model			Pseudo-Second-Order Kinetic Model		
			$Q_{e,\,cal}$ (g/g)	k_1 (1/min)	R^2	$Q_{e,\,cal}$ (g/g)	k_2 (g/g min)	R^2
S20_30/70	0.1 g/L CR	0.0423	0.00733	0.00484	0.535	0.0426	1.83	0.999
	0.2 g/L CR	0.0642	0.0157	0.00599	0.729	0.0650	1.15	1
	0.3 g/L CR	0.0740	0.0162	0.0122	0.913	0.0747	0.853	1
	0.4 g/L CR	0.0849	0.0221	0.00921	0.847	0.0859	0.563	0.999
	0.5 g/L CR	0.0917	0.0233	0.00852	0.786	0.0931	0.477	0.999
ERH	1% owf CR	0.00987	0.00129	0.0101	0.789	0.00993	15.2	1
	2% owf CR	0.0229	0.00281	0.0138	0.845	0.0231	6.79	1
	4% owf CR	0.0597	0.00744	0.0161	0.814	0.0601	2.26	1

All these results confirmed the possibility of using the effluent from the alkaline scouring of cotton as a cheap and effective technique that improves the ability of the rice husk to purify colored effluent. To keep the circular economy concept, reuse or safe disposal of the used rice husk has to be considered. The colored rice husk could be further used as a source of renewable energy [46], a source for nano-cellulose production [47,48], or as reinforcing material in the composite structure [49]. The waste solution contains lignin, silica and other non-cellulosic components from cotton and rice husk modification. These components, especially the lignin, could be used as flame retardants [50], as concrete plasticizers or lignin-based composites [51].

4. Conclusions

Effluent from the traditional alkaline scouring of cotton yarn was applied to improve the rice husk's capacity to remove direct Congo red dye from colored effluents. This rice husk (ERH), as well as rice husk treated with an optimized recipe for alkaline scouring of cotton yarn (S20_70/30) comprising 20 g/L NaOH in the presence of 2 mL/L Cotoblanc HTD-N and 1 mL/L Kemonecer NI at 70 °C for 30 min, have 93.8 and 88.9 mg/g adsorption capacity, respectively, which present one of the better results achieved for adsorbents from a renewable source. The sorption equilibrium data of ERH fit better with the Freundlich equation, while the S20_70/30 rice husk data fit the Langmuir one better. Moreover, calculated $1/n_F$ values of both rice husk samples are less than 1, giving the favorable sorption of Congo red onto both modified rice husks. This study, through implementing the circular economy concept, showed that treating one form of waste (rice husk) with another (effluent from the alkaline scouring of cellulosic plant fibers) in order to produce a material able to purify colored effluent from cotton dyeing, is an elegant concept to find a cheap and more effective alternative avoiding the use of chemicals and energy for carbonization and grounding of the rice husk and investment in a new machinery system.

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