Article

Evaluation of Three Biomaterials from Coconut Mesocarp for Use in Water Treatments Polluted with an Anionic Dye

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Abstract: Coconut consumption leads to the generation of a large number of fibrous residues such as epicarp and mesocarp. In this study, bioadsorbents were prepared from coconut shells (CS), coconut cellulose (CC) and treated coconut cellulose (MCC) with cetyl trimethyl ammonium chloride (CTAC) for the elimination of Congo red (CR) in a watery solution. The impact of the adsorbent quantity (15, 25 and 35 mg) and initial concentration (40, 70 and 100 mg/L) were evaluated. Fourier transform infrared spectra (FTIR) confirmed the existence of OH[−], C=O, COOH and CH₂ groups in the adsorbents as well as the deformation of the bands between 3400 and 3800 cm^{−1} after the adsorption of CR, which was attributed to its capture in the bioadsorbent. From the bromatological analysis, a content of 48.94% lignin, 35.99% cellulose and 10.51% hemicellulose was found. SEM images showed a lignocellulosic essential surface origin for all adsorbents with presence of folds, roughness of an irregular exposed area and fibrous filaments. The average particle size was 0.45 mm and adsorbents had a mean porosity of 0.58. Increasing the initial concentration had a beneficial influence on the removal efficiency of CR, achieving a 99.9% removal with MCC. CS showed slow kinetics in the initial stages whereas CC and MCC achieved 78% and 99.98% removal at 120 min, respectively; an equilibrium was reached at 480 and 20 min, respectively. MCC, CC and CS achieved a maximum *q_e* of 256.12 mg/g, 121.62 mg/g and 17.76 mg/g, respectively.

Keywords: adsorption; bioadsorbent; cellulose; dye removal; isotherms

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1. Introduction

Various activities can cause pollution of water resources, mainly anthropogenic activities such as those carried out in industries and their release of waste effluents [1]. Industrial effluents hold in many synthetic toxic colorings generated by pulp, paint, paper, cosmetic, plastic, textile, leather and carpet industries [2]. Congo red is a dye with the presence of azo and sulfonate groups with an aromatic ring and is a widely used damaging dye. This dye has been reported to cause cancer, cellular mutations, teratogenesis, respiratory damage and allergies [3]. Therefore, it is mandatory to remove this highly harmful pollutant from sewage before its final disposal into the water bodies [4].

In order to reduce and remove CR from effluents, several physicochemical methods have been employed such as reverse osmosis [5], adsorption, ion exchange [6], photodegradation [7], coagulation–flocculation [8], sedimentation and ultrafiltration [9]. Adsorption technology has obtained an enormous value for effluent treatment due to its various benefits such as a small expense, a straightforward design, an uncomplicated operation and changeableness over other methods similar to catalytic ozonation [10], Fenton oxidation and photocatalysis [11]. The success of the adsorption technique depends on many operating variables, including the contaminant concentration, adsorbent dosage, pH, contact time, adsorbate–adsorbent interaction and type of adsorbent [12]. Thus, the concern arises

to produce new adsorbents that are highly available, reusable and economical. Among them, lignocellulosic-based biomasses have received careful interest to prepare workable materials due to its clean, biodegradable and revolving properties [13]. Coconut is a globally distributed and widely consumed food and its mesocarp represents about 50% of the dry matter generated after coconut harvesting. Although alternative uses have been found, a great quantity of these residues are still considered to be rubbish or are in the open [14].

Cellulose molecules are composed of many hydroxyl groups attributed to their adsorption ability. Nevertheless, cellulose is used raw in the removal of contaminants; its adsorption capacity is lower as well as its selectivity in comparison with modified cellulose. To improve the adsorption capacity of the original cellulose, many cellulose-based adsorbents have been synthesized by chemical modification by adding protons to the surface area [15,16] to increase the electrostatic interactions as well as other interactions between the adsorbent and the contaminant [17]. For removing dyes in an aqueous solution, the adsorbent must have a positive charge. Cationized cellulose is a material in which positive functional groups are added onto its active centers; it shows cationic qualities at different pH values that favor the adsorption of anionic contaminants.

Quaternary ammonium salts have generally been used to cationize the cellulose surface. Thus, due to the cationic compound in the structure, it can interact with negatively charged materials on the surface. Epichlorohydrin [18], trimethylamine [19], cetyl trimethyl ammonium bromide [20] and tetramethylethylenediamine [21] have all been used as modifier factors for the synthesis of protoned cellulose. Previously, a rice cellulose-based bioadsorbent was made by using hydroxy propyl octadecyl dimethyl ammonium as a modifier, achieving an adsorption capacity of 580.09 mg/g [17].

In this study, coconut mesocarps were used as precursor for separating cellulose by an alkaline treatment and a bleaching treatment. Cellulose from coconut shells was modified with CTAC to prepare cationized cellulose. The adsorption properties of diazo-anionic dye Congo red (CR) on coconut shells, coconut cellulose and cationized coconut cellulose were studied. The effect of adsorbent dosage, initial concentration and contact time was studied. The equilibrium adsorption behavior was analyzed to understand the adsorption mechanism. It is noteworthy that no studies on the use of this biomass modified with CTAC for dye removal have been reported in the literature; therefore, the contributions of the present study are considered to be essential for filling this gap.

2. Materials and Methods

Congo red, analytical grade, was implemented for the preparation of the stock solution. The pH was measured with HCl and NaOH solutions at 0.1 M. The measurement of the dyes was performed in a Shimadzu UV/Vis Spectrophotometer (UV 1700 Hach DR 2700). The removal efficiency (%) was considered to be a response variable and the adsorbent dose (mg), initial contaminant concentration (mg L^{-1}) and contact time (min) as independent variables. The experiments were conducted according to a multilevel factorial design of experiments with three levels of adsorbent dose (5, 8 and 12 mg L^{-1}) and three variations of contaminant concentration (40, 70 and 100 mg L^{-1}).

2.1. Biomass Pretreatment

Coconut shells were collected from street vendors in Cartagena (Colombia) and those in the best condition were selected to take advantage of a longer shelf life and to avoid decomposition. The precursor was rinsed with deionized water, dried at 60°C until it was a steady mass and reduced in size in a blade mill. A size classification was performed by using stainless steel sieves with opening sizes ranging from 0.8 mm to 0.355 mm [22].

2.2. Cellulose Extraction and Modification

For the cellulose extraction, the prepared coconut shell was submerged in 500 mL of NaOH at 4% wt. with agitation at 200 rpm and 80°C for 2 h; 20 g of the precursor was submerged in 500 mL of an NaOH solution at 4% wt. with agitation at 200 rpm at 80°C for

2 h [23]. The resulting subproduct was washed with distilled water. It was placed in contact with 50 g of NaClO₂ dissolved in 500 mL of distilled water and 50 mL of CH₃COOH with mechanical agitation at room temperature for 24 h. The sediment was then washed with distilled water and dried at 50 °C to obtain a constant weight.

The cellulose obtained was quaternized using 25% CTAC. For each 1 g of cellulose, the volume ratio was 10 mL of CTAC. The mixture was placed in contact with mechanical agitation at 300 rpm for 24 h at 25 °C. The resulting sample was washed with distilled water to obtain a pH of 7.

The bioadsorbents were characterized by an FTIR analysis before and after CR removal using a Perkin Elmer model 1600 series spectrophotometer in the range of 500 to 4500 cm^{−1} to establish the functional groups involved in the anion adsorption process. The zero charge point pH (pH_{PZC}) was determined to analyze the charge distribution on the adsorbent surface and its effect on the adsorption capacity [24]. The points of zero charge for the bioadsorbents from the coconut coir were determined by the solid addition method. A total of 50 mL of water with a pH varying from 2 to 12 was transferred to a series of 100 mL conical Erlenmeyers. The pH of the solutions was adjusted by adding HCl or NaOH 0.1 M. The solutions were put under contact with 0.5 g of each bioadsorbent and immediately securely capped. The suspensions were shaken at 250 rpm for 24 h; after that, the pH of the supernatant for each Erlenmeyer was noted [25].

2.3. Adsorption Assays

The removal assays were performed in a Thermo Scientific orbital shaker (model MAXQ 4450) (Waltham, EE.UU.); 5 mL of the solution was set in contact with the adsorbent at 250 rpm at room temperature for 24 h. The final RC concentration was measured by infrared spectrophotometry at 427 nm in a Biobase model BK-UV1900 UV/Vis spectrophotometer [26]. The removal efficiency (E) was determined according to Equation (1):

$$E [\%] = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1)$$

where $C_0 \left(\frac{mg}{L}\right)$ is the initial dye concentration in the solution and $C_f \left(\frac{mg}{L}\right)$ is the concentration of the ending of the adsorption tests.

An analysis of variance (ANOVA) was performed in Statgraphics Centurion XVIII.II software to determine the statistical significance of the evaluated variables on the dye removal efficiency of CR. The effect of time was evaluated at the best condition of the adsorbent dose and initial concentration. For this, the solution tinted with RC was laid in contact with the bioadsorbent material at 250 rpm; samples were collected at 5, 10, 20, 30, 60, 120, 240, 480, 720 and 1440 min and the remaining dye concentration was determined [27]. The experimental kinetic data were adjusted to the models shown in Table 1.

Table 1. Non-linear kinetic models.

Model	Equation	Parameter
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$ (2)	q_e and q_t (mg/g): adsorption capacities at an equilibrium and at a certain time. k_1 (min ⁻¹): Lagergren constant.
Pseudo-second order	$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$ (3)	k_2 (g ⁻¹ min ⁻¹): pseudo-second order adsorption constant.
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$ (4)	α (mg g ⁻¹ min ⁻¹): speed of adsorption at the beginning. β (g mg ⁻¹): desorption constant. q_t (mg/g): quantity of chemisorbed pollutant.
Intraparticle diffusion	$q_t = k_3 t^{0.5}$ (5)	q_t (mg/g): amount of contaminant adsorbed per mass unit of adsorbent in a time, t . t (min): time. k_3 (mg g ⁻¹ min ^{-1/2}): constant intraparticle diffusion.

2.4. Adsorption Isotherms

The adsorption equilibrium study was performed by varying the initial concentration of RC (25, 50, 75, 100, 125 and 150 mg/L). The top conditions found during the assays of the adsorbent dosage using the bioadsorbents prepared from coconut mesocarp were 24 h at 150 rpm and room temperature. The data were modelled by the Langmuir (2) and Freundlich (3) models [28].

The Langmuir model infer that the active sites on an adsorbent surface are similar to each other with an equal reaction energy towards the contaminant without interactions between the adsorbed pollutant and the remaining aquatic media [29].

$$q_e = q_{max} \frac{bC_e}{1 + bC_e} \quad (6)$$

where q_e (mg/g) is the concentration of the metal adsorbed on the bioadsorbent, C_e (mg L⁻¹) is the residual concentration of the metal in the solution, q_{max} (mg g⁻¹) is the maximum adsorption and b is the ratio between the adsorption/desorption rates.

The Freundlich model assumes that adsorption occurs on a heterogeneous surface with active sites having a different performance from each other and being capable of forming a multilayer [30].

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

where K_f (mg g⁻¹) is the Freundlich constant, n represents the adsorption intensity, q_e is the amount of metal adsorbed at an equilibrium and C_e (mg L⁻¹) is the residual concentration of metal in the solution.

3. Results

3.1. Characterization of the Bioadsorbents

3.1.1. FTIR Spectrum

Figure 1 shows the spectra of the bioadsorbents prepared from coconut shells before and after the adsorption of Congo red.

Figure 1. FTIR spectra of coconut shell bioadsorbents before and after Congo red removal.

CS, CC and MCC had similar structures; a pronounced breadth pinnacle was present near 3350 cm^{-1} of the product, tightening the vibration of the OH^- , COOH and NH_x groups matching to the vibration of the functional groups in cellulose and hemicellulose [31]. Between 3400 and 3500 cm^{-1} , the appearance of amines and small carbonyl overtones due to the elongation vibrations of the O-H bond were observed [17]. The presence of methoxy groups was also confirmed in the peak at 2904 cm^{-1} ; alkynes and carboxylic acids were found between 2000 and 2500 cm^{-1} . The vibration observed from 1733.37 cm^{-1} was due to the straightening of the C=O bonds in carboxylic acids; these peaks were lighter in CC and MCC. The peaks from 1490 to 829 cm^{-1} were due to the stretching and bending throbbing of $-\text{CH}_2$ as well as the $-\text{CH}$, $-\text{OH}$ and C-O bonds in cellulose [32]. The peaks in MCC were broader and with a higher intensity, which was attributed to the modification of the structure of the material with respect to CS and CC [33]. After the adsorption tests, there was evidence of a band shift and the disappearance of adsorption peaks, attributed to the capture of the dye in the active adsorption centers of the bioadsorbents such as stretching at $4000\text{--}2995\text{ cm}^{-1}$ and 2900 cm^{-1} as well as the band expanding between 2300 and 2500 cm^{-1} and bending between 1635 or 1638 cm^{-1} .

3.1.2. Point Zero Charge

Considering that the performance of the adsorbents was highly influenced by the pH, which impacted on the sorbent superficial charge, the degree of ionization and the species of sorbate, pH_{PZC} , was measured. Figure 2 shows the intersection lines, presenting the behavior $\text{CS} > \text{CC} > \text{MMC}$, when the raw material reported a higher PZC. CC had a pH_{PZC} value of 5.88, which was within the pH range for crude cellulose (5.0–7.0) [34]. When the pH was lower than pH_{PZC} , the active centers on the surface were proton-charged and vice versa when the pH was greater than pH_{PZC} . Taking into account the nature of anionic dyes, their elimination was also improved at $\text{pH} > \text{pH}_{\text{PZC}}$ for the rise of H^+ ions. Figure 2 shows that if the cellulose was chemically modified with CTAC, its pH_{PZC} decreased slightly to 5.73, which could be attributed to the formation of acidic functional groups on the carbon surface. It must be pointed out that the surface of the sorbent switched its polarization depending on the pH value of the solution and to the pH_{PZC} of the solid. It was expected that at a lower pH, the sorption of dyes would be enhanced. Thus, in this study, the adsorption test was carried out at pH 4.

Figure 2. pH_{PZC} of bioadsorbents from coconut coir.

3.1.3. Bromatological and Structural Analysis

Table 2 shows the compositional bromatological analysis of the coconut mesocarp, which presents a high content of lignin and cellulose typical of lignocellulosic materials. This suggested the presence of active centers that could be used in the capture of pollutants and for the entry of modifying agents. The presence of these compounds in the structure of biomaterials guarantees a large number of hydroxyl, amino and carboxylic groups [31].

Table 2. Coconut husk bromatological analysis.

Component	Composition %	Method
Lignin	48.94 ± 0.88	TAPPI T 203 os-74
Cellulose	35.99 ± 0.45	TAPPI T 222 om-83
Hemicellulose	10.51 ± 0.37	TAPPI T 222 om-83
Extractives	4.56 ± 0.2	TAPPI T 204 D-2

An SEM analysis of the coconut mesocarp (Figure 3a) exhibited the essential superficial characteristics of materials of a lignocellulosic origin where folds and roughness are present with an irregular exposed area and the presence of fibrous filaments with heterogeneous spirals. The fiber filaments are due to the existence of cellulose, hemicellulose and lignin in the structure of the coconut residue; this facilitates the adsorption capacities of the material for the appearance of carboxyl, amino and hydroxyl functional groups, which can retain cationic contaminants due to their net negative electrostatic charge [35].

Cellulose extracted from the coconut mesocarp (CC) showed the presence of lamellar folds due to the removal of the lignin present in the biomass (Figure 3b) [36]. The filaments observed could be explained due to the removal of non-cellulosic components during the NaOH treatment [37]. The EDS spectrum showed that the elements with the highest presence in CC were carbon (55.43% wt.) and oxygen (43.01% wt.) with slight traces of sodium (0.65% wt.) and chlorine (0.92% wt.); the absence of magnesium, phosphorus, sulfur and potassium was due to the treatment with NaOH [36]. After the modification with CTAC, the pronouncement of the folds in the exposed structure of the bioadsorbent was evident [38]. In addition, there was a change in the exposed surface of the material after the modification, increasing the roughness of the material [39]. A similar behavior was found when modifying magnetic biochar with cetyl trimethyl ammonium bromide with an observation that this modification was not evident in the EDS spectrum [40]. Similarly, the modification of cellulose nanocrystals obtained from kenaf with cetyl trimethyl ammonium bromide was also not evident by a SEM-EDS analysis [33]. The mean particle size of CC and MCC was estimated from the SEM images using Image J software and was approxi-

mately 0.45 mm. Porosity was determined using the procedure proposed by Abdullah and Khairurrijal [41] in which, from the SEM images, the volume below the surface and the volume below a flat surface whose height is equal to the maximum height from any point on the sample surface are calculated using OriginPro[®] software; following this method, a porosity of around 0.58 was obtained.

Figure 3. SEM and EDS micrographs of (a) coconut shell (CS), (b) coconut cellulose (CC) and (c) modified coconut cellulose (MCC).

3.2. Congo Red Adsorption Tests

For a fixed pH of 4, the percentage of CR removal was examined by changing the initial dye concentration and CS, CC and MCC dosage. All three adsorbents evaluated showed a good performance, which could be explained by the reactive nature of the dye [4]. However, MCC showed removal efficiencies > 99.9% in most cases (Figure 4).

Figure 4. Congo red removal efficiency on coconut shell bioadsorbents at different initial concentrations and adsorbent dosage conditions.

Previously, it was reported that adsorption efficiency is enhanced with an increase in the adsorbent quantity due to the increase in the number of available adsorption centers [42]. A similar behavior was observed when removing CR with a membrane prepared from eggshells modified with HCl [30] and cellulose microcrystals of oil palm leaves immobilized on PVC [43]. Regarding the initial concentration, no significant effect on the adsorption process was observed; however, when using CC, a 12% decrease was found when raising the concentration from 40 mg L⁻¹ (99.65%) to 100 mg L⁻¹ (77.63%). Elsewhere, the adsorption capacity presented an increase from 4.8 mg g⁻¹ to 15.5 mg g⁻¹. This could be explained because a greater concentration produced a relevant driving force to exceed the resistances of the RC between the aqueous and solid phases as well as to increase the collisions between the dye ions and the adsorbent, thus improving the adsorption process [44]. Almost similar CR dye adsorption results were obtained when using banana peel [29] as well as biochar and biomass from *Cornulaca monacantha* [45]. However, the adsorption capacity (q_e) decreased with an increase in the adsorbent dosage and a decrease in the initial dye concentration; this was explained by the fact that there would be an excess of unused adsorption sites and a small amount of dye present to occupy them [46].

The results found in this study were higher than those reported when using cellulose treated with glycidyl trimethyl ammonium chloride [47] and cellulose from pine water functionalized by epichlorohydrin cross-linking and oxidation with periodate to cross-link cellulose dialdehyde [4] where removal efficiencies of 75% and 85% were obtained in a day, respectively. The good result of the modified coconut mesocarp cellulose was due to the fact that it is a porous material in which active sites are present. As the maximum removal capacity was achieved using 3 g L⁻¹ and 100 mg L⁻¹, in order to guarantee complete adsorption these conditions were chosen to estimate the effect of time over the process.

3.3. Statistical Analysis

The individual interaction of the variables and their quadratic effects were analyzed by ANOVA to determine their statistical influence on RC removal. From the results obtained, it was established that the initial concentration was the variable with the largest significant statistical effect on the removal efficiency [48]. The F-factor values are shown in Table 3 [49]. It can be said that only the initial dye concentration was statistically significant on CC. The F-ratio and *p*-value for CC had a value of zero, which suggested that both variables and their quadratic interactions positively influenced the removal efficiency as observed in Figure 2; as the adsorbent dose and the initial dye concentration increased, the adsorption efficiency increased.

Table 3. ANOVA for the removal efficiency of tartrazine on bioadsorbents prepared from coconut shells.

Source	Bioadsorbent								
	BS			CC			MCC		
	Sum of Squares	F-Ratio	<i>p</i> -Value	Sum of Squares	F-Ratio	<i>p</i> -Value	Sum of Squares	F-Ratio	<i>p</i> -Value
A: adsorbent dosage	9.64	1.40	0.32	33.17	6.63	0.082	0.0	0	0
B: initial concentration	23.39	3.40	0.16	326.07	65.14	0.004	6.58×10^{-5}	0	0
AA	19.73	2.87	0.19	2.29	0.46	0.55	0.0	0	0
AB	0.73	0.11	0.77	34.3434	6.86	0.08	0.0	0	0
BB	58.78	8.54	0.06	10.19	2.04	0.25	3.96×10^{-6}	0	0
Total error	20.65			15.02			0.0		
Total (corr.)	132.91			421.09			6.98×10^{-4}		

3.4. Effect of the Contact Time

The effect of the contact time on the elimination of the CR dye was evaluated during a kinetic study to establish the saturation time and its interaction with the adsorbent [50]. As shown in Figure 5, CS showed a lower performance compared with CC and MCC, achieving a removal efficiency of 89% at 24 h without reaching an equilibrium and without any desorption phenomena during the contact time. Likewise, CS showed slow kinetics in the initial min, requiring a long contact time to remove and retain the biomaterial. On the other hand, CC and MCC had prompt adsorption kinetics in the beginning min of the process, reaching 78% and 99.98% removal at 120 min; an equilibrium was reached at 480 and 20 min, respectively. The fast equilibrium reached by MCC could be explained by the high disposition of active centers in the material before the experiments and the availability of RC in the water, achieving 97% removal in the first 5 min of the process [51].

Figure 5. Effect of time on adsorption efficiency of CR.

Slow CR adsorption kinetics have been reported when using cellulose–chitosan cross-linked foam, reporting a rapid increase in removal in the first 8 h that continued progressively for 120 h [52]. When using magnetic cellulose, the equilibrium adsorption time of CR was found to be 3 h, 6 h and 10 h as the initial concentration increased from 10 to 70 mg L^{−1}, respectively [53]. The kinetics of the adsorption of CR on silica-rich zeolite functionalized with ZnO [42] was rapid in the beginning phase of removal, as in the present study.

Adsorption can occur due to different mechanisms that establish the way in which the contaminant moves from the solution to the adsorbent and is retained there. Thus, the kinetics establish the intervening steps (intraparticle diffusion, interstitial diffusion, complexation, physisorption and chemisorption, among others) for the elimination of the solute [7]. The adjustment of the experimental kinetic data to the mentioned models in Table 1 is shown in Figure 6.

Figure 6. Non-linear fitting of RC adsorption kinetics on adsorbents from coconut mesocarp for (a) CS, (b) CC and (c) MCC.

In the adsorption kinetics of CR on CS, at around 600 min a decrease in the amount of adsorbed dye was observed due to the saturation of the removal centers in the biomass [54]. This suggested that during the contaminant removal process, desorption occurred over periods of time, especially when time was prolonged. This provided valuable information

regarding the lifetime of the adsorbents for their potential implementation as packing in adsorption columns. It was observed that when using CS as an adsorbent, the kinetics were adjusted to the models of pseudo-first order and intraparticle diffusion; therefore, it could be said that the removal of RC on CS was controlled by chemical adsorption through the exchange of ions between the contaminant and the active centers of the bioadsorbent as well as the presence of diffusion from the center of the liquid phase to the solid and through the pores of the bioadsorbent [55]. The fit of the kinetic data to the pseudo-first order model suggested that the rate-limiting step of CR removal was mass transfer [56].

When using CC and MCC, it was found that the intraparticle diffusion model did not present a good fit to the data whereas the pseudo-first order, pseudo-second order and Elovich models fitted the data with a value of $R^2 > 0.93$ with CC and $R^2 > 0.99$ with MCC in all cases. Fitting to these models suggested that the adsorption was controlled by chemisorption. The fit to the Elovich model assumed that the adsorption surface was heterogeneous. The high value of α indicated that the adsorption occurred rapidly in the initial min (Figure 6c). On the contrary, the high value recorded for β indicated that desorption could be easily achieved in this system, which facilitated the recovery of the contaminant and the reuse of the biomaterial, especially using MCC [13]. The adsorption rate constants of the pseudo-first and pseudo-second order models expressed that the adsorption process occurred faster in CC; however, the q_e behavior was $MCC > CC > CS$ (Table 4).

Table 4. Adjustment parameters of Congo red adsorption on bioadsorbents from coconut mesocarp.

Model	Parameter	CS	CC	MCC
Pseudo-first order	q_e (mg/g)	5.892	17.291	33.313
	k_1 (min^{-1})	0.004	15.187	1.087
	R^2	0.807	0.936	0.999
	X^2	0.939	1.843	0.003
Pseudo-second order	q_e (mg/g)	6.595	17.291	33.324
	k_2 ($\text{g/mg} \times \text{min}$)	9.21×10^{-4}	2.136	1.674
	R^2	0.8674	0.936	0.999
	X^2	0.646	1.843	0.003
Elovich	α ($\text{mg/g} \times \text{min}$)	0.948	1.576	3.206
	β (g/mg)	0.177	4.929	8.049×10^{43}
	R^2	0.885	0.987	0.997
	X^2	0.561	0.380	0.321
Intraparticle diffusion	k_3 ($\text{mg/g} \times \text{s}^{1/2}$)	0.194	0.797	1.452
	R^2	0.923	30.543	15.452
	X^2	0.373	101.964	449.515

The adjustment of the kinetics to the pseudo-second order could describe the breakup curve in a packed-bed column; this could be done by a general adsorbate material equilibrium to acquire easy mathematical equations for the breakthrough curve in a packed-bed. The obtained equations could then be used to scale-up, design and simulate fixed-bed adsorption columns for the removal of contaminants from effluents considering that practical adsorption systems generally operate in a continuous mode in order to treat large volumes of contaminated water [57].

3.5. Adsorption Equilibrium Isotherm

According to the parameters summarized in Table 5, it could be said that the models evaluated did not satisfactorily adjust the adsorption isotherm of RC on CS; this was due to the presence of desorptive phenomena during the process due to the decrease in the concentration of dye in the solution, the increase in the amount of anions on the surface of the adsorbent and the low affinity of CC due to its anionic nature [29]. On the other hand, the adsorption equilibrium of CR on CC and MCC showed a slight fit to the Langmuir model. This suggested that the limiting factor of the process was the physical interactions

between the adsorbent and the adsorbate, presenting the coating of the biomaterial surface in a monolayer. The active centers had a similar activation energy [58]. From the Langmuir parameter b , it could be intuited that the affinity of the adsorbents for the dye presented the sense $MCC > CC > CS$; the values of b oscillated between 0 and 1, which indicated a favorability of the process as well as a higher adsorption capacity according to the q_{max} [59]. Similarly, the parameter n of the Freundlich model suggested a high affinity of CC and MCC for CS as in both cases it was >1 whereas that of CS was <1 [58].

Table 5. Adsorption isotherm parameters.

Model	Parameters	Congo Red		
		CS	CC	MCC
Langmuir	q_{max} (mg/g)	17.758	121.618	256.115
	b (L/mg)	5.722	0.168	1.539
	R^2	0.6363	0.814	0.009
	χ^2	58.392	6.821	90.282
	k_f (mg/g)	0.019	5.402	15.189
Freundlich	n	0.588	2.983	4.572
	R^2	0.932	0.752	0.629
	χ^2	2.505	9.137	84.519

Table 6 shows the Langmuir parameter q_{max} data reported for removing CR with adsorbents of a different nature. The results obtained in the present study were in the average range for bioadsorbents of a lignocellulosic origin.

Table 6. q_{max} of CR according to the Langmuir model using various adsorbents.

Contaminant	Adsorbent	q_{max} (mg/g)	Reference
Congo Red	Cellulose nanocrystals modified with cetyl trimethyl ammonium bromide	448.43	[20]
	NaOH-modified water hyacinth cellulose nanocrystals	181.8	[31]
	Hydrogel from pineapple peel extracted by bleaching	138.89	[60]
	MCC	256.115	This study
	CC	121.618	
	CS	17.758	
	Coconut residues	128.94	[28]
	Hydrogel from water-extracted pineapple peel	114.19	[60]
	<i>Cornulaca</i> -activated carbon	78.19	[45]
	Hydrogel made from pineapple peel extracted with NaOH	77.52	[60]
	Hydrogel from pineapple peel extracted with bleached NaOH	75.19	[60]
	Date palm seeds	61.72	[27]
	<i>Cornulaca</i> biomass	43.42	[45]

4. Conclusions

From the results found, it was observed that: (1) the adsorbents synthesized had a heterogeneous structure with the presence of functional groups such as OH, carboxyl, amino and methyl; after the adsorption treatment, band deformation between 3400 and 3800 cm^{-1} was evidenced, which was accredited to the capture of RC in the bioadsorbent. (2) Increasing the initial concentration and adsorbent dosage positively affected the removal efficiency, achieving a 99.9% removal with MCC. (3) CS showed slow kinetics in the initial stages whereas CC and MCC achieved a 78% and 99.98% removal at 120 min, respectively; an equilibrium was reached at 480 and 20 min, respectively. (4) The adsorption isotherm did not present a significant fit to the models evaluated due to the possible presence of desorptive phenomena during the process. (5) Coconut cellulose modified with CTAC was a good adsorbent of Congo red in an aqueous solution.

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