Vol. 20, No. 3(2021) IA2426 Revista Mexicana de Ingeniería Química

# Synthesis of adsorbents from wheat hulls, extracted cellulose and modified with Cetyl trimethyl ammonium chloride to remove Congo Red in aqueous solution

# Síntesis de adsorbentes a partir de cascarillas de trigo, celulosa extraída y modificada con Cloruro de cetil trimetril amonio para remover Congo Rojo en solución acuosa

A. Villabona-Ortíz<sup>1</sup>, C. Tejada-Tovar<sup>1</sup>, R. Ortega-Toro<sup>2\*</sup>, F. Aguilar-Bermúdez<sup>1</sup>, Y. Pájaro-Moreno<sup>1</sup>

<sup>1</sup>Universidad de Cartagena, Chemical Engineering Department, Avenida del Consulado Calle 30 No. 48 ?152, Cartagena de Indias D.T. y C., Colombia.

<sup>2</sup>Universidad de Cartagena, Food Engineering Department, Avenida del Consulado Calle 30 No. 48-152, Cartagena de Indias D.T. y C., Colombia.

Received: April 9, 2021; Accepted: June 23, 2021

#### Abstract

Adsorbents from the wheat husk (WH), wheat husk cellulose (WHC) and the cellulose modified with Cetyl trimethyl ammonium chloride (MWHC), in the removal of Congo Red were evaluated. Experiments were carried out in batch at different concentrations (40, 70 and 100 mg/L) and adsorbent doses (15, 25 and 35 mg), following a multifactorial 3<sup>3</sup> design of experiments. It was found the adsorption efficiency of Congo red increased with initial concentration and decrease in adsorbent dosage using all adsorbents. WHC and MWHC showed a rapid adsorption rate in the initial minutes of the process, reaching equilibrium at 480 and 120, respectively. The adsorption equilibrium on WHC and MWHC was described by the Freundlich model; showing this affinity: MWHC>WHC>WHC>WH. It was concluded wheat residues are a good precursor for the preparation of efficient adsorbents to remove Congo Red. CTAC functions as an adsorbent modifying agent for use in the removal of anionic contaminants. These results have a potential application in the treatment of wastewater from industries such as food and textiles. *Keywords*: adsorption, Congo red dye, isotherms, wheat hulls.

#### Resumen

Se evaluaron adsorbentes a partir de cascarillas de trigo (WH), celulosa de trigo (WHC) y la celulosa modificada con Cloruro de Cetil trimetil amonio al 25 % (MWHC), para la remoción de Rojo Congo. Se realizaron experimentos de adsorción por lotes para diferentes concentraciones (40, 70 y 100 mg/L) y dosis de adsorbentes (15, 25 y 35 mg), siguiendo un diseño de experimentos multifactorial 3<sup>3</sup>. Se encontró que el rendimiento de la adsorción del Rojo Congo aumentó con la concentración inicial y la disminución de la dosis de adsorbente al usar todos los adsorbentes. La WHC y MWHC mostraron una taza de adsorción rápida en los minutos iniciales del proceso, logrando el equilibrio a los 480 y 120 respectivamente. El equilibrio de adsorción sobre WHC y MWHC fue descrito por el modelo de Freundlich; mostrando la siguiente afinidad: MWHC>WHC>WHC>WH. Se concluye que los residuos de trigo son un buen precursor para la preparación de adsorbentes eficientes en la remoción de Rojo Congo. El CTAC funciona como agente modificante de adsorbentes para su uso en la remoción de contaminantes aniónicos. Estos resultados tienen una aplicación potencial en el tratamiento de aguas residuales de industrias como la de alimentos y textil. *Palabras clave*: adsorción, Colorante rojo congo, isotermas, cáscaras de trigo.

<sup>\*</sup> Corresponding author. E-mail: rortegap1@unicartagena.edu.co https://doi.org/10.24275/rmiq/IA2426 ISSN:1665-2738, issn-e: 2395-8472

# 1 Introduction

Dyes are essentially synthetic chemical compounds with a specific color that can be chemically bonded to the substrate (e.g., fiber, paper, leather) to provide beautiful color. (Litefti et al., 2019). They are widely applied in the textile, paper, printing, plastics and leather sectors; and daily life in food, beverages, medicines, cosmetics and personal care products. (Said et al., 2020). Dyes are classified as cationic, anionic and nonionic (insoluble in water) according to the chromophore group's charge dissolved in the aqueous solution. (Yagub et al., 2014). More than 100,000 dyes and colorants are applied in the printing and dyeing industry, where most industrial wastewater is discharged into surface water bodies. (Sanchez et al., 2018); and more than  $7 \times 10^5$  tons are produced annually worldwide. (Kelm et al., 2019).

The presence of dyes in effluents generates great concern due to the impacts it causes to living beings (Katheresan *et al.*, 2018). Wastewater contaminated with dyes presents a complex and variable composition characteristics, large discharge with a wide distribution of dissolved dye molecules that are difficult to degrade. If this wastewater is discharged without treatment, it will cause serious damage to the environment. (Hussain *et al.*, 2018). In particular, Congo red (CR) is a diazo-anionic dye mainly used to dye paper and textiles, including cotton, hemp and silk. (Zheng *et al.*, 2021).

In addition to affecting water transparency, Congo Red is considered highly toxic to living organisms because it causes carcinogenesis, mutagenesis, teratogenesis, respiratory damage, allergies and problems during pregnancy (Rani *et al.*, 2017). This dye is contained in industrial wastewater worldwide and can be quickly released into water bodies such as rivers, lakes, seas and even groundwater. (Zhang *et al.*, 2019). Decontamination techniques have been applied to remove dyes from wastewater, including solvent extraction, ion exchange, and ion exchange. (Li *et al.*, 2019), oxidative techniques and photodegradation (Chakraborty *et al.*, 2020), adsorption (Singh *et al.*, 2018), and reverse osmosis (Ding *et al.*, 2020).

Several research studies have indicated that the adsorption process is considered one of the most promising technologies for treating wastewater containing dyes due to its simple and cost-effective operation. (Khurana *et al.*, 2017). Biomass-based bioadsorbents are relatively low cost because their precursors are generally derived from waste; they consist primarily of cellulose, hemicellulose, and lignin that bind as effective adsorbents for a wide range of contaminants containing hydroxyl, carboxyl, phenols, and methoxy functional groups. (Koay *et al.*, 2014). The development of environmentally friendly adsorbents such as cellulose for dye adsorption receives great attention due to their non-toxicity, renewability and high economic value. (Tan *et al.*, 2018).

However, in the removal of anionic dyes, the use of lignocellulosic material requires modification of the biomass in order to protonate its surface and promote electrostatic exchange between the active centers and the contaminated solution. (Widjanarko *et al.*, 2018). To remove Congo Red in aqueous solution, live and dead biomasses have been modified, such as: *Funalia trogii* with iminodiacetic acid and triethylenetetramine. (Bayramoglu & Arica, 2018), lignina aminada y salinizada (An *et al.*, 2020), microparticles of *Chrysanthemum indicum* (Chukki *et al.*, 2018) and *Trichoderma* (Argumedo-Delira *et al.*, 2021).

Thus, in this work the cationic surfactant methyl trimethyl ammonium chloride (CTAC) was used to modify the cellulose extracted from wheat husk for its evaluation in the removal of Congo red; obtaining a new adsorbent MHCR (modified wheat husk cellulose); also performing a comparative study with unmodified cellulose. CTAC is a quaternary ammonium salt commonly used in cosmetic products for its antimicrobial properties and preservatives. It has a hydrophobic character because of an alkyl group of 16 and quaternary nitrogen linked to chlorine in their structure. This surfactant was used as a modifying agent since it would react with the cellulose surface leaving it positively charged according to the reaction shown in Figure 1. The characterization analysis was performed before and after adsorption using Fourier transform infrared spectroscopy (FTIR). The effect of adsorbent dose, initial dye concentration and contact time on the removal efficiency was studied.

# 2 Materials and methods

### 2.1 Materials, equipment, and reagents

In the present investigation, a multilevel  $3^3$  factorial experimental design was used to evaluate the effect of the initial concentration (40, 70, 100 mg/L) and



Figure 1. Schematic reaction of cellulose modification with CTAC.

the adsorbent dose (15, 25, 35 mg) on the removal efficiency of the diazoanionic dye Congo Red, using bioadsorbents prepared from wheat husks.

Cetyl trimethyl ammonium chloride (CTAC) at 25 % was used as a cellulose modifying agent. Congo Red (3,3'-(4,4'-biphenylenebis (azo) bis (4amino) disodium naphthyl sulfonic acid salt) of analytical grade was used to prepare the synthetic solution. The pH was adjusted with 0.1 M HCl and NaOH solutions. Dye measurement was performed on a Shimadzu UV/Vis UV 1700 Hach DR 2700 UV/Vis Spectrophotometer. FTIR analysis was performed on a Perkin Elmer model 1600 series spectrophotometer. The remaining concentration of the dyes was carried out in an infrared spectrophotometer Biobase model BK-UV1900.

#### 2.2 Adsorbent preparation

The WH was washed with deionized water to remove soluble compounds and impurities, dried at 65 °C to constant mass, and reduced in size in a blade mill. The classification was carried out in a Shaker-type sieve shaker using a series of stainless steel sieves. (Han *et al.*, 2016).

WHC was obtained by double alkaline extraction; for this, 20 g of pretreated WH was immersed in 500 mL of a 4 % w NaOH solution at 200 rpm, 80 °C for 2 h. The resulting sample was washed, repeated extraction with NaOH, and washed again until clear. The resulting sample was washed, the extraction was repeated with NaOH and washed again until the wash water was clear. The resulting sediment was treated with 50 g of sodium chloride and 50 mL of glacial acetic acid mixed in 500 mL of distilled water; subsequently, the mixture was decanted. The sediment was washed to pH 7 and dried at 60 °C until constant mass. (Xu *et al.*, 2018).

The quaternization was carried out by treating the cellulose obtained with the etherifying agent CTAC. For this purpose, for each gram of cellulose, 10 mL of CTAC at 25% was added, the mixture was stirred for 24h at 300 rpm. (Xia *et al.*, 2019). Subsequently, the sample was decanted, washed with distilled water to neutral pH and dried at 50 °C.

The bioadsorbents were characterized before and after adsorption by Fourier transform infrared spectroscopy (FTIR) to determine the functional groups involved in the adsorption process. (Jiang & Hu, 2019).

#### 2.3 Adsorption test

For the adsorption tests, a stock solution was prepared at 1000 mg/L, from which it was diluted to lower concentrations. The experiments were carried out by placing the adsorbent at the different doses evaluated in the experimental design, in contact with 5 mL of solution in a Thermo Scientific model MAXQ 4450 orbital shaker agitation of 250 rpm, at 30 °C for 24 h. The remaining concentration of Congo Red was determined by UV spectrophotometry. The remaining concentration of Congo Red was determined by UV-Vis spectrophotometry at 427 nm. (Zubir & Zaini, 2020). Removal efficiency (%R) was determined with equation (1) (Koley *et al.*, 2016).

$$R[\%] = \frac{(C_0 - C_f)}{C_o} \times 100 \tag{1}$$

Where  $C_0$  (mg/L) is the initial concentration of dye in the solution and  $C_f$  (mg/L) is the final concentration of dye in the solution. Statistical analysis was performed using Statgraphics Centurion 1XVIII software. I. II. This analysis made it possible to determine the effect of each of the variables on the material's adsorption efficiency, based on the analysis of variance. (Roy & Mondal, 2019).

The effect of time on the removal efficiency was determined at the best experimental condition of initial concentration and adsorbent dose found at 250 rpm and room temperature. Aliquots were taken at different time intervals (5, 10, 20, 30, 30, 60, 60, 120, 240, 480, 720 and 1440 min), and the remaining concentration of Congo Red was determined. (Parvin *et al.*, 2019).

### 2.4 Adsorption isotherm

Adsorption isotherms were determined by varying the initial concentration of tartrazine (25, 50, 75, 100, 125 and 150 ppm), at the best condition of adsorbent dosage and contact time experimentally found, at 250 rpm and 30 °C. (Salahuddin *et al.*, 2020). The experimental data were fitted to the Langmuir and Freundlich models to interpret the interactions between the contaminant and the adsorbent's active centers. (Bayramoglu & Arica, 2018).

# **3 Results and discussion**

### 3.1 Characterization of the bioadsorbent

Figure 2 shows the IR spectra for wheat husk (WH), wheat husk cellulose (WHC) and modified wheat husk cellulose (MWHC), before and after Congo Red adsorption.

It is observed that the biomaterials before adsorption presented a similar spectrum, being the structure of WHC and MWHC more diverse than WH, with the characteristic spectrum of lignocellulosic materials containing natural polymeric compounds, such as carboxylic acids, alcohols and phenol (Alhujaily *et al.*, 2018); a strong and broad peak was presented around 3350 cm<sup>-1</sup> which is characteristic for stretching the vibration of the hydroxyl, carboxyl and amine group corresponding to the vibration of the functional groups in cellulose and hemicellulose. (Fan & Zhang, 2018). Between 3400 and 3500 cm<sup>-1</sup> amines and carbonyls appear due to the stretching vibrations of the O-H bond. (Al-Lagtah *et al.*, 2016; Rinaldi *et al.*, 2018).



Figure 2. FTIR spectra of (a) WH, (b) WHC, (c) MWHC, (d) WH-Congo red, (e) WHC-Congo red and (f) MWHC-Congo red, before and after Congo Red adsorption.

The peak observed at 2904  $\text{cm}^{-1}$  is attributed to the C-H bonds present in the methyl groups. Between 2000 and 2500 cm<sup>-1</sup> signals from alkynes and carboxylic acids are observed. From 1733.37 cm<sup>-1</sup> there are bands resulting from the stretching of the c=o in the carboxylic acids. In the region between 1669 and 829 cm<sup>-1</sup> bands corresponding to the vibration of adsorbed water molecules in cellulose are observed; the absorption band at 1490 to 829  $\text{cm}^{-1}$  corresponds to the stretching and bending vibration of methyl, -OH and C-O bonds in cellulose. In addition, it is worth mentioning that the band around  $1418 \text{ cm}^{-1}$  is associated with the crystalline structure of cellulose, while around 900 cm<sup>-1</sup> is related to the amorphous region of cellulose. (Hospodarova et al., 2018). The presence of the aforementioned functional groups in the 400-4000  $\text{cm}^{-1}$  spectrum is attributed to the high content of lignin, cellulose and hemicellulose in the structure of the characterized biosorbents. (Johari et al., 2016). According to Kruer-Zerhusen, Cantero-Tubilla and Wilson (2018), the regions found contain the peaks of the individual chemical vibrational modes relevant to measuring cellulose crystallinity. After adsorption of Congo Red, the adsorbents showed some changes in characteristic bands related to physical and chemical changes; OH bound by hydrogen bonds evidenced stretching at 4000-2995 cm<sup>-1</sup>, OH lexion of adsorbed water at 1635 or 1638 cm<sup>-1</sup>, CH stretching at 2900 cm<sup>-1</sup>, as well as band broadening between 2300 and 2500  $\text{cm}^{-1}$ ; such variation in the spectrum is attributed to the presence of the dye in the bioadsorbent.

Bioadsorbent	$\mathbf{pH}_{pzc}$
Wheat husk	4.92
Wheat husk cellulose	4.69
CTAC-modified wheat husk cellulose	5.38

Table 1.  $pH_{pzc}$  of bioadsorbents from wheat hulls.

Similar behavior was observed when modifying sagú hampas with cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant similar to that used in the present study. It was evidencing the stretching of the methyl groups, stretching by CO vibration, as well as an increase in the presence of peaks between  $3000-2850 \text{ cm}^{-1}$ , which refer to the asymmetric and symmetric stretching vibrations of the -CH<sub>3</sub> and -CH<sub>2</sub> groups in CTAB (Mohamed Pauzan & Ahad, 2018).

### 3.2 Zero point of charge

The point at which the bioadsorbents exhibit zero net charge was determined using the pHPZc (Afshin *et al.*, 2019). Table 1 summarizes the results for the bioadsorbents under study.

It is observed that the three bioadsorbents prepared from wheat residues present an acidic  $pH_{PZC}$ . The crude biomass and cellulose presented a  $pH_{PZC}$  of 4.92 and 4.69, respectively, which is slightly lower than the pH range for crude celluloses (5.0-7.5) (Saha *et al.*, 2019), and when it is chemically modified with CTAC, its pH increases. From the pHPZC values, it was determined that the operating pH for the adsorption tests would be 4 for the three adsorbents; taking into account that their adsorptive capacity depends, to a great extent, on the electrostatic exchange with the pollutant; thus, the surface of the material would be positively charged and would attract the anions due to electrostatic forces (Hu *et al.*, 2016).

#### 3.3 Adsorption test

Figure 3 summarizes the adsorption results of Congo Red on the three bioadsorbents prepared from wheat husk, at the different conditions of adsorbent dosage and initial concentration evaluated. It was found that the adsorption performance of Congo Red on WH increased from 88.2 % to 91.6 % with initial concentration and decrease in adsorbent dose; when using WHC increased from 97.04 % to 79.03 % when the initial concentration of Congo Red increased from 40 mg/L to 70 mg/L; decrease in adsorbent dose and increase in initial concentration caused the



Figure 3. Removal efficiency of Congo red on adsorbents from wheat husks.

increase in removal efficiency by MWHC from 98.88 % to 99.8 %. The good performance of the biomaterials in dye removal is due to the reactive nature of the dye (Kumari *et al.*, 2016), since it binds easily to any type of fibrous material.

The cellulose modified from wheat milling residues had good removal percentages as the adsorbent dose increased; however, they did not differ much from the other biomaterials. The results obtained in the present study were superior to those obtained when cellulose nanofibers modified with glidicyltrimethylammonium chloride were used (Pei *et al.*, 2013) and pine cellulose functionalized with epichlorohydrin and dialdehyde (Kumari *et al.*, 2016), who presented removal percentages of 75% and 85% respectively in 24 hours. When evaluating different initial concentrations of contaminant (300, 500, and 700 mg / L), it was found that increasing the adsorbent mass from 0.2 to 1.0 g results in a decrease in the

	Bioadsorbent												
Fuente	WH					WHC				МѠНС			
	Sum squares	of	GL	F-Ratio	P-value	Sum of squares	GL	F-Ratio	P-value	Sum of squares	GL	F-Ratio	P-value
A:Adsorbent dosage	168.37	7	1	9.3	0.0554	361.106	1	11.61	0.0422	0.0424557	1	2.62	0.2042
B:Initial concentration	98.195	5	1	5.43	0.1022	46.2195	1	1.49	0.3099	0.375093	1	23.11	0.0171
AA	144.50	4	1	7.98	0.0664	77.582	1	2.49	0.2124	0.159184	1	9.81	0.052
AB	217.18	7	1	12	0.0405	50.3298	1	1.62	0.293	0.0207377	1	1.28	0.3405
BB	5.1694	2	1	0.29	0.6301	21.6706	1	0.7	0.4651	0.0144408	1	0.89	0.4151
Total error	54.301	3	3			93.2971	3			0.0486868	3		
Total (corr.)	687.73	4	8			650.205	8			0.660599	8		

Table 2. ANOVA for Congo Red removal efficiency on bioadsorbents prepared from rice husks.

adsorption capacity of the dye from 691.4 mg / g to 295.9 mg / g (Magdy and Altaher, 2018). The previous was explained because, at high adsorbent doses, the accumulation of adsorbent particles can occur, which decreases the specific surface area and the number of active sites available, lengthening the length of the diffusion path from the adsorbent surface to the pores (Kirbiyik et al., 2017). The increase in the adsorbent amount causes an increase in the adsorption sites available for the adsorbate molecules, resulting in lower saturation and lower adsorption capacity (Chukwuemeka-Okorie et al., 2021). Therefore, it is evident that at lower doses of adsorbent, there is a more efficient use of its available active adsorption sites with a higher dye load in them (Ezekoye et al., 2020).

From the present study results, the values of the F factor for the analysis of variance are shown in Table 2 for the percentage removals of Congo Red. A confidence level for the P-Value of 95% was established therefore that variables with a P-Value of less than 0.05 are significant (Reck *et al.*, 2018).

From the results obtained, it is established that the interaction between the increase of the initial concentration and the decrease of the adsorbent dose has a positive effect on the removal efficiency of Rojo Congo on WH; this is due to the fact that the initial concentration works as a driving force in the process, increasing the mass transfer and diffusive phenomena from the solution to the adsorbent. (Ramya Sankar et al., 2018). Regarding the WHC, it was determined that the decrease of the initial concentration favors the removal efficiency of the material: this could be because the WHC does not have many active adsorption sites of Congo Red available, due to its anionic nature due to the presence of hydroxyl, carboxyl, carbonyl and amino groups, detected in the FTIR (Figure 2) (Wekoye et al., 2020). On the other hand, the decrease of the adsorbent dose



Figure 4. Effect of contact time on the adsorption of Congo red.

and the increase of the initial concentration caused the increase of the removal efficiency by MWHC; this, due to the increase of the amount of pollutant available and the high availability of active centers in the modified adsorbent (Mondal & Kar, 2018).

### 3.4 Effect of contact time

The effect of contact time at pH 4, initial concentration of 100 mg/L and 15 mg adsorbent dose was evaluated, showing the times at which, the highest removal occurs by means of a graph of adsorption efficiency (%) vs time (min) (Figure 4).

It was observed that the removal of Congo red occurs rapidly in the initial minutes, with higher performance by MWHC, showing the success of the modification process with CTAC. It was found that the equilibrium time is reached at about 120 min with MWHC and at 480 min with WHC; the higher adsorption rate presented when using WMC could be due to the higher availability of active centers in the unsaturated material, as well as the availability of anions (Litefti *et al.*, 2019).

Model	Parameters	WH	WHC	MWHC	
	$q_{\rm max}~({\rm mg/g})$	53.4806	131.6312	137.1381	
	b (L/mg)	0.0031	0.7184	0.8345	
Langmuir	$R^2$	0.9006	0.8237	0.8691	
	SS	0.1547	2.3	2.4033	
	$k_f$	0.185	3.0135	5.3612	
	n	1.078	2.4568	2.2592	
Freundlich	$R^2$	0.8903	0.9617	0.9838	
	SS	0.3359	1.5107	0.9798	

Table 3. Adsorption isotherm parameters.

These results are similar to those found when removing Congo red on zeolites rich in silica functionalized with ZnO (Madan *et al.*, 2019). The kinetics were fast in the initial stages of elimination as in the present study. However, they differ from those reported when using cross-linked cellulose-chitosan foam, where adsorption was found to increase rapidly at 8 hours and then gradually continue for 120 hours (Kim *et al.*, 2019).

From the adsorption behavior of Congo red with WH, the presence of adsorption-desorption phenomena is evident during the process, attributed to the low affinity between this bioadsorbent and the contaminant. It has been reported for the removal of Congo red with cross-linked cellulose-chitosan foam, that adsorption increased rapidly in the initial 8 h of the process, and then continued gradually during 120 h. (Kim *et al.*, 2019). Using cabbage waste, they found equilibrium at around 200 min, with a removal efficiency of 97 % (Wekoye *et al.*, 2020).

### 3.5 Adsorption isotherms

From the data in Table 3, the adsorption of Congo Red on WHC and MWHC was fitted by the Freundlich model. This indicates that the process occurs by chemical adsorption with multilayer formation, due to the heterogeneity of the two adsorbents' active centres. (Jia *et al.*, 2020). Thus, it is established that the limiting step is the formation of multilayers, with nonuniform heat distribution and adsorption affinities on the heterogeneous surface (Rani *et al.*, 2017). Strong bonds first occupy the active adsorption sites, and this strength decreases as they are occupied by anions (Litefti *et al.*, 2019). The parameter  $k_f$  exhibited MWHC>WHC>WH behavior, thus intuiting that the active centers of MWHC are more dye-affine than those of WH and WHC. This, due to the protonation of the MWHC surface after modification (Ranjbar et al., 2020). The values of the Freundlich constant n are in the range 1-10, therefore the chemical bonds formed between the anions and the active centers are strong, decreasing the possibility of desorption (Mondal & Kar, 2018); this could be due to the importance in the formation of multilayers during adsorption [66]. On the other hand, Congo red's adsorption on WH was adjusted by the Langmuir model, therefore it is assumed that the process occurs in a monolayer with a prevalence of physical forces between the active centers and the contaminant (Sharma et al., 2019). The equilibrium of CR removal on the adsorbents shows high adsorption even at low concentrations, with an Htype isotherm in the Giles classification; this indicates the predominance of strong ionic interactions between the adsorbate-adsorbent (Elmoubarki et al., 2015).

Previously, Langmuir's  $q_{max}$  parameter values for Congo Red removal have been obtained for different adsorbents, such as: Fe<sub>x</sub>Co<sub>3</sub>-xO<sub>4</sub>-modified nanoparticles, Fe<sub>x</sub>Co<sub>3</sub>-xO<sub>4</sub>-modified nanoparticles, Fe<sub>x</sub>Co<sub>3</sub>-xO<sub>4</sub> (128.6 mg/g) (Liu *et al.*, 2019), Calcium alginate beads impregnated with nanogoethite (181.1 ng/g) (Munagapati & Kim, 2017), sol-gel-derived hydroxyapatite nanoparticle (487.8 mg/g) (Chahkandi, 2017), Hydroxyl-functionalized magnesium ferrite nanoparticles (71.4 mg/g) (Aoopngan *et al.*, 2019), and surfactant functionalized zeolite particles (200 mg/g). Concerning the results reported by other authors, those obtained in the present study for WHC and MWHC are in the range of 71 to 488 mg/g.

# Conclusions

The results concluded that: (1) The prepared adsorbents have diverse structures, with functional groups such as OH, carboxyl, amino, and hydrocarbon compounds, evidencing the displacement of the bands after the adsorption process. (2) The interaction between increasing the initial concentration and decreasing the adsorbent dose has a positive effect on the removal efficiency of Rojo Congo on WH; when using WHC, decreasing the initial concentration favors the removal efficiency of the material, decreasing the adsorbent dose and increasing the initial concentration caused the increase of the removal efficiency by MWHC. (3) WHC and MWHC showed a fast adsorption rate in the initial minutes of the process, achieving equilibrium at 480 and 120, respectively. (4) The adsorption equilibrium on WHC and MWHC was described by the Freundlich model; the affinity between active centers and contaminant showed the following pattern: MWHC>WHC>WH. (5) CTACmodified rice husk cellulose is a promising adsorbent of Congo Red in an aqueous solution. The importance of this work lies in the successful use of agroindustrial wheat residues, modified with a novel cationic surfactant such as CTAC in the removal of present anionic dyes. These results have a potential application in the wastewater treatment of the textile industry.

### Acknowledgements

The authors would like to acknowledge the Universidad de Cartagena to provide the materials, equipment, and laboratory facilities required to successfully conclude this research project.

# Nomenclature

- $q_t$  adsorption capacity in a time t
- $q_e$  adsorption capacity at equilibrium
- $k_1$  Lagergren constant
- $\alpha$  initial adsorption rate
- $\beta$  constant related to surface coverage and chemisorption energy
- $q_{\text{max}}$  maximum pollutant adsorption, corresponding to the active centres
- $k_2$  pseudo-second order constant
- *b* relationship between adsorption/desorption rates

$k_f$	Freundlich constant						
n	intensity of adsorption						
$C_e$	residual metal concentration in						
	solution						
rpm	revolutions per minute						
WH	wheat husk						
WHC	wheat husk cellulose						
MWHC	modified wheat husk cellulose						
CTAC	cetyl trimethyl ammonium chloride						

# References

- Afshin, S., Rashtbari, Y., Shirmardi, M., Vosoughi, M., & Hamzehzadeh, A. (2019). Adsorption of basic violet 16 dye from aqueous solution onto mucilaginous seeds of Salvia sclarea: Kinetics and isotherms studies. *Desalination and Water Treatment 161*, 365-375. https://doi.org/ 10.5004/dwt.2019.24265
- Al-Lagtah, N. M. A., Al-Muhtaseb, A. H., Ahmad, M. N. M., & Salameh, Y. (2016). Chemical and physical characteristics of optimal synthesised activated carbons from grass-derived sulfonated lignin versus commercial activated carbons. *Microporous and Mesoporous Materials* 225, 504-514. https://doi.org/10.1016/j. micromeso.2016.01.043
- Alhujaily, A., Yu, H., Zhang, X., & Ma, F. (2018). Highly efficient and sustainable spent mushroom waste adsorbent based on surfactant modification for the removal of toxic dyes. *International Journal of Environmental Research and Public Health* 2018, 15, 1421. https://doi.org/10.3390/ IJERPH15071421
- An, L., Si, C., Bae, J. H., Jeong, H., & Kim, Y. S. (2020). One-step silanization and amination of lignin and its adsorption of Congo red and Cu(II) ions in aqueous solution. *International Journal of Biological Macromolecules 159*, 222-230. https://doi. org/10.1016/j.ijbiomac.2020.05.072
- Aoopngan, C., Nonkumwong, J., Phumying, S., Promjantuek, W., Maensiri, S., Noisa, P., Pinitsoontorn, S., Ananta, S., & Srisombat, L. (2019). Amine-functionalized and hydroxylfunctionalized magnesium ferrite nanoparticles for Congo Red adsorption. ACS Applied Nano

Materials 2(8), 5329-5341. https://doi. org/10.1021/acsanm.9b01305

- Argumedo-Delira, R., Gómez-Martínez, M. J., & Uribe-Kaffure, R. (2021). Trichoderma biomass as an alternative for removal of Congo Red and malachite green industrial dyes. *Applied Sciences 11(1)*, 448. https://doi.org/10. 3390/app11010448
- Bayramoglu, G., & Arica, M. Y. (2018). Adsorption of Congo Red dye by native amine and carboxyl modified biomass of Funalia trogii: Isotherms, kinetics and thermodynamics mechanisms. *Korean Journal of Chemical Engineering 35(6)*, 1303-1311. https://doi.org/10.1007/ s11814-018-0033-9
- Chahkandi, M. (2017). Mechanism of Congo red adsorption on new sol-gel-derived hydroxyapatite nano-particle. *Materials Chemistry and Physics 202*, 340-351. https: //doi.org/10.1016/j.matchemphys. 2017.09.047
- Chakraborty, S., Farida, J. J., Simon, R., Kasthuri, S., & Mary, N. L. (2020). Averrhoe carrambola fruit extract assisted green synthesis of ZnO nanoparticles for the photodegradation of Congo red dye. Surfaces and Interfaces 19, 100488. https://doi.org/10.1016/j. surfin.2020.100488
- Chukki, J., Abinandan, S., & Shanthakumar, S. (2018). Chrysanthemum indicum microparticles on removal of hazardous Congo red dye using response surface methodology. *International Journal of Industrial Chemistry* 9(4), 305?316. https://doi.org/10.1007/ s40090-018-0160-5
- Chukwuemeka-Okorie, H. O., Ekuma, F. K., Akpomie, K. G., Nnaji, J. C., & Okereafor, A. G. (2021). Adsorption of tartrazine and sunset yellow anionic dyes onto activated carbon derived from cassava sievate biomass. *Applied Water Science 11*(2), 27. https://doi.org/ 10.1007/s13201-021-01357-w
- Ding, C., Yi, M., Liu, B., Han, C., Yu, X., & Wang, Y. (2020). Forward osmosis-extraction hybrid process for resource recovery from dye wastewater. *Journal of Membrane Science* 612, 118376. https://doi.org/10.1016/j. memsci.2020.118376

- Elmoubarki, R., Mahjoubi, F. Z., Tounsadi, H., Moustadraf, J., Abdennouri, M., Zouhri, A., El Albani, A., & Barka, N. (2015). Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics. *Water Resources and Industry* 9, 16-29. https://doi.org/10.1016/j. wri.2014.11.001
- Ezekoye, O. M., Akpomie, K. G., Eze, S. I., Chukwujindu, C. N., Ani, J. U., & Ujam, O. T. (2020). Biosorptive interaction of alkaline modified Dialium guineense seed powders with ciprofloxacin in contaminated solution: central composite, kinetics, isotherm, thermodynamics, and desorption. *International Journal of Phytoremediation* 22(10), 1028-1037. https: //doi.org/10.1080/15226514.2020. 1725869
- Fan, C., & Zhang, Y. (2018). Adsorption isotherms, kinetics and thermodynamics of nitrate and phosphate in binary systems on a novel adsorbent derived from corn stalks. *Journal of Geochemical Exploration 188*, 95-100. https: //doi.org/10.1016/j.gexplo.2018.01. 020
- Han, Y., Cao, X., Ouyang, X., Sohi, S. P., & Chen, J. (2016). Adsorption kinetics of magnetic biochar derived from peanut hull on removal of Cr (VI) from aqueous solution: Effects of production conditions and particle size. *Chemosphere* 145, 336-341. https://doi.org/10.1016/ j.chemosphere.2015.11.050
- Hospodarova, V., Singovszka, E., & Stevulova, N. (2018). Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials. *American Journal of Analytical Chemistry* 9(6), 303-310. https://doi.org/10.4236/ajac.2018. 96023
- Hu, Q., Chen, N., Feng, C., Hu, W., & Liu, H. (2016). Kinetic and isotherm studies of nitrate adsorption on granular Fe-Zr-chitosan complex and electrochemical reduction of nitrate from the spent regenerant solution. *RSC Advances 6*, 61944-61954. https://doi. org/10.1039/c6ra04556a
- Hussain, I., Li, Y., Qi, J., Li, J., & Wang, L. (2018). Nitrogen-enriched carbon sheet for Methyl

blue dye adsorption. Journal of Environmental Management 215, 123-131. https://doi. org/10.1016/j.jenvman.2018.03.051

- Jia, Y., Ding, L., Ren, P., Zhong, M., Ma, J., & Fan, X. (2020). Performances and mechanism of methyl orange and Congo red adsorbed on the magnetic ion-exchange resin. *Journal of Chemical and Engineering Data* 65(2), 725-736. https:// doi.org/10.1021/acs.jced.9b00951
- Jiang, Z., & Hu, D. (2019). Molecular mechanism of anionic dyes adsorption on cationized rice husk cellulose from agricultural wastes. *Journal* of Molecular Liquids 276, 105-114. https:// doi.org/10.1016/j.molliq.2018.11.153
- Johari, K., Saman, N., Song, S. T., Chin, C. S., Kong, H., & Mat, H. (2016). Adsorption enhancement of elemental mercury by various surface modified coconut husk as eco-friendly lowcost adsorbents. *International Biodeterioration* and Biodegradation 109, 45-52. https://doi. org/10.1016/j.ibiod.2016.01.004
- Katheresan, V., Kansedo, J., & Lau, S. Y. (2018). Efficiency of various recent wastewater dye removal methods: A review. Journal of Environmental Chemical Engineering 6(4), 4676-4697. https://doi.org/10.1016/j. jece.2018.06.060
- Kelm, M. A. P., da Silva Júnior, M. J., de Barros Holanda, S. H., de Araujo, C. M. B., de Assis Filho, R. B., Freitas, E. J., dos Santos, D. R., & da Motta Sobrinho, M. A. (2019). Removal of azo dye from water via adsorption on biochar produced by the gasification of wood wastes. *Environmental Science and Pollution Research* 26(28), 28558-28573. https://doi.org/10. 1007/s11356-018-3833-x
- Khurana, I., Saxena, A., Bharti, Khurana, J. M., & Rai, P. K. (2017). Removal of dyes using graphene-based composites: a Review. Water, Air, and Soil Pollution 228(5). https://doi. org/10.1007/s11270-017-3361-1
- Kim, U. J., Kimura, S., & Wada, M. (2019). Highly enhanced adsorption of Congo red onto dialdehyde cellulose-crosslinked cellulosechitosan foam. *Carbohydrate Polymers 214*, 294?302. https://doi.org/10.1016/j. carbpol.2019.03.058

- Kirbiyik, Ç., Pütün, A. E., & Pütün, E. (2017). Equilibrium, kinetic, and thermodynamic studies of the adsorption of Fe(III) metal ions and 2,4-dichlorophenoxyacetic acid onto biomass-based activated carbon by ZnCl 2 activation. Surfaces and Interfaces 8, 182-192. https://doi.org/10.1016/j.surfin. 2017.03.011
- Koay, Y. S., Ahamad, I. S., Nourouzi, M. M., Abdullah, L. C., & Choong, T. S. Y. (2014). Development of novel low-cost quaternized adsorbent from palm oil agriculture waste for reactive dye removal. *BioResources 9(1)*, 66-85. https://doi.org/10.15376/biores.9.1. 66-85
- Koley, P., Sakurai, M., Takei, T., & Aono, M. (2016). Facile fabrication of silk protein sericinmediated hierarchical hydroxyapatite-based bio-hybrid architectures: Excellent adsorption of toxic heavy metals and hazardous dye from wastewater. *RSC Advances*. https://doi. org/10.1039/c6ra12818a
- Kruer-Zerhusen, N., Cantero-Tubilla, B., & Wilson, D. B. (2018). Characterization of cellulose crystallinity after enzymatic treatment using Fourier transform infrared spectroscopy (FTIR). *Cellulose 25(1)*, 37-48. https://doi.org/10.1007/s10570-017-1542-0
- Kumari, S., Mankotia, D., & Chauhan, G. S. (2016). Crosslinked cellulose dialdehyde for Congo red removal from its aqueous solutions. *Journal* of Environmental Chemical Engineering 4(1), 1126-1136. https://doi.org/10.1016/j. jece.2016.01.008
- Li, Q., Wang, M., Yuan, X., Li, D., Xu, H., Sun, L., Pan, F., & Xia, D. (2019). Study on the adsorption and desorption performance of magnetic resin for Congo red. *Environmental Technology (United Kingdom)*. https://doi. org/10.1080/09593330.2019.1673830
- Litefti, K., Freire, M. S., Stitou, M., & González-Álvarez, J. (2019). Adsorption of an anionic dye (Congo red) from aqueous solutions by pine bark. *Scientific Reports 9(1)*, 1-11. https:// doi.org/10.1038/s41598-019-53046-z
- Liu, J., Wang, N., Zhang, H., & Baeyens, J. (2019). Adsorption of Congo red dye on FexCo3xO4 nanoparticles. *Journal of Environmental*

Management 238, 473-483. https://doi. org/10.1016/j.jenvman.2019.03.009

- Madan, S., Shaw, R., Tiwari, S., & Tiwari, S. K. (2019). Adsorption dynamics of Congo red dye removal using ZnO functionalized high silica zeolitic particles. *Applied Surface Science* 487(May), 907-917. https://doi.org/10. 1016/j.apsusc.2019.04.273
- Magdy, Y. H., & Altaher, H. (2018). Kinetic analysis of the adsorption of dyes from high strength wastewater on cement kiln dust. *Journal of Environmental Chemical Engineering* 6, 834-841. https://doi.org/10.1016/j.jece. 2018.01.009
- Mohamed Pauzan, A. S., & Ahad, N. (2018). Biomass modification using cationic surfactant cetyltrimethylammonium bromide (CTAB) to remove palm-based cooking oil. *Journal* of Chemistry 2018. https://doi.org/10. 1155/2018/5059791
- Mondal, N. K., & Kar, S. (2018). Potentiality of banana peel for removal of Congo red dye from aqueous solution: isotherm, kinetics and thermodynamics studies. *Applied Water Science* 8(6). https://doi.org/10.1007/ s13201-018-0811-x
- Munagapati, V. S., & Kim, D. S. (2017). Equilibrium isotherms, kinetics, and thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano-goethite. *Ecotoxicology and Environmental Safety 141*, 226-234. https://doi.org/10.1016/j. ecoenv.2017.03.036
- Parvin, S., Biswas, B. K., Rahman, M. A., Rahman, M. H., Anik, M. S., & Uddin, M. R. (2019). Study on adsorption of Congo red onto chemically modified egg shell membrane. *Chemosphere* 236, 124326. https://doi. org/10.1016/j.chemosphere.2019.07. 057
- Pei, A., Butchosa, N., Berglund, L. A., & Zhou, Q. (2013). Surface quaternized cellulose nanofibrils with high water absorbency and adsorption capacity for anionic dyes. Soft Matter 9(6), 2047-2055. https://doi.org/ 10.1039/c2sm27344f

- Ramya Sankar, M. S., Sivasubramanian, V., Vidya Vijay, E. V., Jerold, M., Kanimozhi, J., Sinu, P., & Shankar, N. (2018). Kinetic, isothermal and thermodynamic investigation on electrocoagulation of congo red dye removal from synthetic wastewater using aluminium electrodes. *Desalination and Water Treatment* 122, 399-350. https://doi.org/10.5004/ dwt.2018.23082
- Rani, K. C., Naik, A., Chaurasiya, R. S., & Raghavarao, K. S. M. S. (2017). Removal of toxic Congo red dye from water employing lowcost coconut residual fiber. Water Science and Technology, 75(9), 2225?2236. https://doi. org/10.2166/wst.2017.109
- Ranjbar, D., Raeiszadeh, M., Lewis, L., MacLachlan, M. J., & Hatzikiriakos, S. G. (2020). Adsorptive removal of Congo red by surfactant modified cellulose nanocrystals: a kinetic, equilibrium, and mechanistic investigation. Cellulose, 27(6), 3211?3232. https://doi.org/10.1007/ s10570-020-03021-z
- Reck, I. M., Paixão, R. M., Bergamasco, R., Vieira, M. F., & Vieira, A. M. S. (2018). Removal of tartrazine from aqueous solutions using adsorbents based on activated carbon and Moringa oleifera seeds. *Journal of Cleaner Production 171*, 85-97. https://doi.org/ 10.1016/j.jclepro.2017.09.237
- Rinaldi, R., Yasdi, Y., & Hutagalung, W. L. C. (2018). Removal of Ni (II) and Cu (II) ions from aqueous solution using rambutan fruit peels (*Nephelium lappaceum* L.) as adsorbent. *AIP Conference Proceedings 2026*(Ii). https: //doi.org/10.1063/1.5065058
- Roy, T. K., & Mondal, N. K. (2019). Potentiality of Eichhornia shoots ash towards removal of Congo red from aqueous solution: Isotherms, kinetics, thermodynamics and optimization studies. *Groundwater for Sustainable Development 9*, 100269. https: //doi.org/10.1016/j.gsd.2019.100269
- Saha, N., Saba, A., & Reza, M. T. (2019). Effect of hydrothermal carbonization temperature on pH, dissociation constants, and acidic functional groups on hydrochar from cellulose and wood. *Journal of Analytical and Applied Pyrolysis* 137, 138-145. https://doi.org/10.1016/ j.jaap.2018.11.018

- Said, A. E. A. A., Aly, A. A. M., Goda, M. N., Abd El-Aal, M., & Abdelazim, M. (2020). Adsorptive remediation of Congo Red dye in aqueous solutions using acid pretreated sugarcane bagasse. *Journal of Polymers and the Environment* 28(4), 1129-1137. https://doi. org/10.1007/s10924-020-01665-3
- Salahuddin, N., Abdelwahab, M. A., Akelah, A., & Elnagar, M. (2020). Adsorption of Congo red and crystal violet dyes onto cellulose extracted from Egyptian water hyacinth. *Natural Hazards*, 1-20. https://doi.org/ 10.1007/s11069-020-04358-1
- Sanchez, L. M., Ollier, R. P., Gonzalez, J. S., & Alvarez, V. A. (2018). Nanocomposite materials for dyes removal. In *Handbook* of Nanomaterials for Industrial Applications (pp. 922-951). Elsevier. https://doi.org/ 10.1016/B978-0-12-813351-4.00053-5
- Sharma, A., Siddiqui, Z. M., Dhar, S., Mehta, P., & Pathania, D. (2019). Adsorptive removal of congo red dye (CR) from aqueous solution by Cornulaca monacantha stem and biomassbased activated carbon: isotherm, kinetics and thermodynamics. *Separation Science and Technology (Philadelphia)* 54(6), 916-929. https://doi.org/10.1080/01496395. 2018.1524908
- Singh, N. B., Nagpal, G., Agrawal, S., & Rachna. (2018). Water purification by using adsorbents: A review. Environmental Technology and Innovation 11, 187-240. https://doi.org/ 10.1016/j.eti.2018.05.006
- Tan, C. H. C., Sabar, S., & Hussin, M. H. (2018). Development of immobilized microcrystalline cellulose as an effective adsorbent for methylene blue dye removal. *South African Journal* of Chemical Engineering 26(July), 11-24. https://doi.org/10.1016/j.sajce.2018.08.001
- Wekoye, J. N., Wanyonyi, W. C., Wangila, P. T., & Tonui, M. K. (2020). Kinetic and equilibrium studies of Congo red dye adsorption on cabbage waste powder. *Environmental Chemistry and Ecotoxicology* 2, 24-31. https://doi.org/ 10.1016/j.enceco.2020.01.004

- Widjanarko, P. I., Widiantoro, W., Soetaredjo, L. F. E., & Ismadji, S. (2018). Kinetika adsorpsi zat warna Congo Red dan Rhodamine B dengan menggunakan serabut kelapa dan ampas tebu. *Jurnal Teknik Kimia Indonesia*. https://doi. org/10.5614/jtki.2006.5.3.1
- Xia, F., Yang, H., Li, L., Ren, Y., Shi, D., Chai, H., Ai, H., He, Q., & Gu, L. (2019). Enhanced nitrate adsorption by using cetyltrimethylammonium chloride pre-loaded activated carbon. *Environmental Technology* (United Kingdom), 1-11. https://doi.org/ 10.1080/09593330.2019.1615133
- Xu, J., Krietemeyer, E. F., Boddu, V. M., Liu, S. X., & Liu, W. C. (2018). Production and characterization of cellulose nanofibril (CNF) from agricultural waste corn stover. *Carbohydrate Polymers 192*, 202-207. https://doi.org/10.1016/j.carbpol.2018.03.017
- Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science* 209, 172-184. https://doi.org/10.1016/ j.cis.2014.04.002
- Zhang, H., Zhou, J., Muhammad, Y., Tang, R., Liu, K., Zhu, Y., & Tong, Z. (2019). Citric acid modified bentonite for Congo red adsorption. *Frontiers in Materials* 6(5), 5. https://doi. org/10.3389/fmats.2019.00005
- Zheng, Y., Cheng, B., Fan, J., Yu, J., & Ho, W. (2021). Review on nickel-based adsorption materials for Congo red. *Journal of Hazardous Materials* 403, 123559. https://doi.org/ 10.1016/j.jhazmat.2020.123559
- Zubir, M. H. M., & Zaini, M. A. A. (2020). Twigsderived activated carbons via H<sub>3</sub>PO<sub>4</sub>/ZnCl<sub>2</sub> composite activation for methylene blue and congo red dyes removal. *Scientific Reports 10(1)*, 14050. https://doi.org/10.1038/ s41598-020-71034-6