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Optimization and evaluation of the indigo blue vat dye removal process on rice husk through statistical design

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ABSTRACT

Agricultural wastes have shown to be efficient adsorbents for the treatment of dissolved pollutants. In this research, the adsorption of the indigo blue dye (IB) on rice husk (RH) was evaluated and RH bromatological and structural characterizations were carried out. A 2^3 full factorial design allowed to achieve a 90.0% IB removal at pH = 2.0, initial IB concentration of 30 mg/L, RH dosage of 8.0 g/L, contact time of 4 h and at 65°C. Further optimization of the process through a central composite surface design led to a minimal increase in efficiency, with a maximum removal of 92.0%. As for the adsorbent characterization, the infrared spectrum showed that the most important bands correspond to the associated hydroxyl group (3,300 cm^{-1}) and silicon oxide (750 and 1,020 cm^{-1}), whereas scanning electron microscopy indicates a uniform surface composed of concave cells. These results suggest that RH is an effective adsorbent for the removal of IB, whose treatment is recognized as difficult due to its poor solubility.

Keywords: Adsorption; Agricultural by-product; Vat dye; Design of experiments; Structural characterization

1. Introduction

The textile industry is considered one of the most important economic activities worldwide because of the income it generates; however, it has also been classified as one of the most polluting ones [1]. Several chemical substances used in the dyeing process, which includes degumming, scouring, bleaching and washing, lead to the discharge of effluents with a large amount of toxic organic compounds, such as synthetic dyes by textile dyeing and processing factories [2]. Vat dyes are widely used for cotton dyeing that is required in blue jeans production and other blue denim products, as they are known. These dyes possess an important market in the fashion world, where this style has found acceptance in all ages and has been characterized by its permanent creativity and innovation [3], including shades, faded, new models and trends [4,5].

Despite the organic structure of these dyes, their degradation is slow and difficult since microorganisms present in nature do not have adequate mechanisms to carry out their decomposition, for this reason they are accumulated in the ecosystem and become pollution sources [6]. In particular, mutagenic and carcinogenic effects have been attributed to the presence of such pollutants with severe sequels for aquatic biota [7,8]. In addition, the discharge of dye-bearing wastewater into rivers inhibits the photosynthesis process, leading to a significant reduction of the available oxygen, which at the same time, makes it difficult to achieve the self-equilibrium and purification of the ecosystem, causing a detriment of aquatic life [9].

Indigo color (2,2′-bis indigo), or vat indigo, is part of the vat dye family. Its chemical formula is $C_{16}H_{10}O_2N_2$, is a dark blue crystalline powder and is probably the most common vat dye used in cotton dyeing [10]. Indigo blue dye (IB) is characterized by being insoluble in water, but this behavior is reduced in the presence of a reducing agent such as sodium dithionite ($Na_2S_2O_4$), in a basic medium [11]. So, with this

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reagent it becomes a soluble anthrahydroquinone compound (leuco form), which has affinity for the cellulosic fibers, making the dyeing process possible, as shown in Fig. 1. It has been reported that during the dyeing process of cotton with IB, up to 20% of the dye is discharged in effluents due to lack of fixation [12]. For the above reasons, these colored effluents represent a serious environmental concern that claims a prompt solution.

Both conventional physico-chemical methods and biological methodologies have been reported for the treatment of this vat dye. Biological processes are novel and undoubtedly efficient; they include anaerobic systems and the use of bacterial and fungal species. They have been investigated at laboratory scale with satisfactory results; however, the required growing conditions and the long occurrence times are definitely difficult aspects to overcome for a subsequent scaling, limiting their use and application [13,14]. For instance, the use of three cyanobacteria for IB degradation is reported, one of which was efficient but generated isatin and anthranilic acid, the latter product is apparently non-toxic but requires further treatment for complete degradation [15]. Manu and Chaudhari [16] proposed semicontinuous reactors for IB decolorization, reporting a color removal higher than 90% but in long periods of time, between 58 and 65 days, by which this methodology is discarded from any point of view.

As for physico-chemical methods, flocculation has been used for the treatment of aqueous solutions with vat dyes. Nevertheless, the efficiency is affected due to the change in pH by the addition of salts [17]. For example, removal percentages of 71% for golden yellow and 35% for reactive black 5 are reported [18]. On the other hand, photocatalytic degradation methods have been poorly studied, probably due to the low solubility of IB, the difficulty of the irradiation of titania with visible light in solid state, the long period of occurrence time, and the high cost for the implementation of this technology [19]. It is also worth noting the study presented by Manu [20], who reports a 95% efficiency for the treatment of IB dye by combining flocculation and coagulation techniques with advanced oxidation processes. Apparently, it is an efficient process, however, very expensive, since it involves the use of several compounds, such as the Fenton reagent, alum, lime and different polyelectrolytes. Another disadvantage of this method is associated with the difficulty of desorbing this dye when the electrolyte is used. Furthermore, flocculation and coagulation processes generate a great amount of sludge of complex nature that hinders a subsequent deposition. For the previous reasons, it is clear that this methodology is inapplicable in emerging countries, where effective and low-cost solutions are required.

Regarding the treatment of IB through the adsorption process, the authors have found few works reported, probably due to the lack of solubility of this dye in aqueous solutions. Wambuguh and Chianelli [21] registered the use of palygorskite clay for the treatment of IB through adsorption, but it was really a conversion of this clay material into a hybrid pigment with applications in painting and coating activities, where the adsorption was only an intermediate step. To date, the authors have not come across any reports on the use of agricultural by-products for IB removal. It should be mentioned that the literature registered the use of rice husk (RH) ash for vat indigo carmine dye adsorption, but this dye includes two sulphonate groups in its structure, therefore, it does not exhibit solubility problems. They reported a satisfactory removal of this dye, although it was carried out under a univariate method [22,23].

RH is a widely available agricultural by-product and could be a great alternative of non-conventional adsorbents. In Colombia, the annual rice production rises to 2,543,161 metric tons (Tm) of paddy rice and 1,729,349 tons of white rice, with an estimated amount of RH at around 400,000 Tm, which is usually wasted [24]. The aim of this work was to evaluate the feasibility of using this agricultural by-product as an efficient adsorbent in the IB treatment. In order to establish the most appropriate conditions of this dye adsorption process, the study was carried out using statistical tools such as factorial design, where temperature was undoubtedly a key aspect to achieve a successful removal. In addition, the bromatological and structural characterization of this novel adsorbent was carried out in order to determine the functional groups and the morphological structures that are involved in the adsorption process.

2. Materials and methods

2.1. Adsorbent pre-treatment

The husk of native rice was obtained from the rice agro-industries located in the department of Cordoba – Colombia. Its treatment included three washes with distilled water, dried at a temperature of 80°C during 24 h in a digital oven HDF-64,

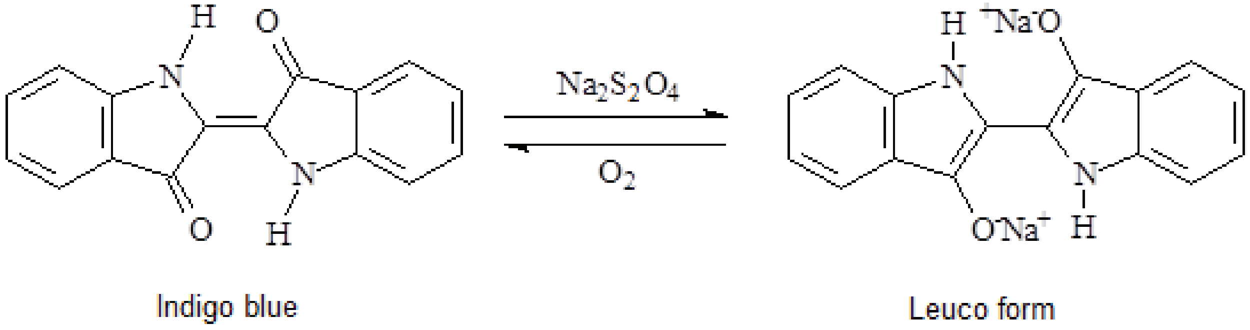

Fig. 1. Soluble and insoluble forms of IB (Source: Authors). Software: ACD/ChemSketch 2016.2.2, freeware versión was the program used to draw the chemical structures.

grinding and sieving to obtain particles with a homogeneous diameter in the specific range between 0.3 and 0.5 mm. Then, this adsorbent was stored in airtight glass boxes.

2.2. Bromatological analysis

In order to determine the main components of the adsorbent material, starch was analyzed by the polarimetry method, ash by direct incineration, nitrogen by the Kjeldahl method, while acid detergent fiber (ADF), neutral detergent fiber (NDF) and lignin by the Van Soest method. The results of the analysis of ADF, NDF and lignin allow establishing the content of cellulose and hemicellulose in RH. These analyses were performed in the Laboratory of Chemical and Bromatological Analysis at the Universidad Nacional de Colombia – Sede Medellín.

2.3. Infrared analysis

For determining the possible functional groups of greater participation in the adsorption process, spectra of the RH samples were taken before and after the removal of IB dye. The spectra comprised the range of 4,000–500 cm^{-1} with a resolution of 2.0 cm^{-1}. This analysis was measured in the Laboratory of Experimental Chemistry at the Universidad Nacional de Colombia – Sede Medellín, using a PerkinElmer (Universidad Nacional de Colombia, El Volador Campus) spectrometer with attenuated total reflectance Fourier transform-infrared (ATR FT-IR) spectroscopy, Spectrum Two.

2.4. Morphological analysis

The surface morphological analysis of the adsorbent material was carried out by scanning electron microscopy (SEM). Micrographs were taken before and after IB adsorption on the studied adsorbent with an acceleration voltage of 10–18 kV prior to metallization with gold, using a magnification of X300 and X600. The morphological analysis was performed in the Advanced Microscopy Laboratory at the Universidad Nacional de Colombia – Sede Medellín with a JSM 5910LV scanning electron microscope (JEOL, El Volador campus).

2.5. Preparation of the IB dye solution

The company Sumicolor S.A. (Medellin City, Colombia) delivered the commercial IB dye with 98% purity. Its color index corresponds to CI 73000. As this vat dye is insoluble in water; its solubilization was achieved by reduction, adding sodium dithionite, $Na_2S_2O_4$, according to the textile industry protocol [25]. Fig. 1 shows the reaction by which IB became into its leuco soluble form.

Standard solutions of IB dye of 100 mg/L were prepared in deionized water, from which dilutions to the respective calibration curve were made, the absorbance was measured at the maximum wavelength, $\lambda_{max} = 710$ nm [19].

2.6. IB removal

The adsorption studies were carried out under a batch system. Shaker equipment with incubation was used to maintain temperature and agitation of the process. All measurements were performed in triplicate for statistical support. IB dye content was estimated by UV–Vis spectrophotometry in a PerkinElmer double beam spectrophotometer. The adsorption percentage of the dye on RH was determined by Eq. (1):

$$\text{Removal \%} = \frac{C_o - C_e}{C_o} \times 100\% \tag{1}$$

where c_o and c_e correspond to the initial concentration and the concentration in the equilibrium of the dye, respectively.

Initially, a preliminary assessment of the pH value and particle size in the adsorption process of IB dye was made maintaining a constant agitation of 180 rpm and at 338 K, temperature at which the IB soluble in aqueous solution. For the pH effect analysis, the interval between 2.0 and 6.0 units was considered, based on the previously reported value for the zero point charge of this adsorbent equal to 5.4 [26].

2.7. Factorial design and response surface through a central composite design

A 2^3 full screening design was performed to evaluate the importance of the adsorbent dosage (DA), initial dye concentration (C_o) and contact time (TC) in IB dye removal. A subsequent central composite design was implemented with the purpose of optimizing the IB removal process, the characteristics of both designs are detailed in Table 1.

The parameters pH, particle size, temperature and stirring speed were kept constant and their most appropriate values were taken from previous assays. Thus, the experiments were carried out using 20 mL of the dye solution at pH = 2.0, the adsorbent had a particle size between 0.3 and 0.5 mm, the stirring speed was 180 rpm, and at 338 K. It is important to point out that this temperature condition allows IB to remain dissolved in the solution and in this way, the adsorption process could happen efficiently. A decrease in temperature of the order of 10 units leads to an ineffective removal process of this dye, as showed below.

3. Results and discussion

3.1. Bromatological characterization

RH composition and the particular analysis methods used for such determination are shown in Table 2. A percentage of 55.1% was found for cellulose, 14.4% for hemicellulose, 17.4% for silica and 8.3% for lignin. Generally, these values

Table 1
Factors and levels of the 2^3 full factorial design and the central composite response surface design for IB removal

Factors	2^3 factorial design		Surface design	
	Levels		Levels	
	(–1)	(+1)	(–1)	(+1)
Adsorbent dosage (g/L)	4	8	10	10
Concentration of IB (mg/L)	30	50	10	20
Contact time (h)	4	8	1	2

are similar to those reported in previous works for this agricultural by-product [27]. It is noteworthy that its high lignocellulosic content points it as a suitable adsorbent material and that the remarkable percentage of silicon oxide is verified in the spectrum of ATR FT-IR with one of the most prominent bands.

3.2. Characterization of the adsorbent material through IR analysis

ATR FT-IR spectroscopy analysis was performed to identify the functional groups present in RH, as well as to determine possible changes in its structure after IB dye adsorption.

The main peaks found in RH spectrum are located at 750; 950; 1,020; 1,407; 1,513; 1,657; 2,900 and 3,300 cm^{-1} (Fig. 2(a)), all of which are characteristic of the lignocellulosic nature of this agricultural by-product [28]. The peak at 750 cm^{-1} is associated with the Si–O bending motion. The prominent peak at 1,020 cm^{-1} is attributed to the asymmetric stretching movement of O–Si–O. The peak around 950 cm^{-1} can be assigned to the vibration of Si–OH bonds (silanols) [29,30]. The peak at 1,407 cm^{-1} corresponds to the methoxy groups (–OCH$_3$) present in the lignin and hemicellulose. The peak at 1,513 cm^{-1} is associated to the vibration of the C=C olefin bond of the aromatic rings and the band at 1,657 cm^{-1} is attributed to the absorption of carbonyl groups (C=O). The bands at 2,900 and 3,300 cm^{-1} are due to the vibrations of the CH and OH bonds, respectively; these are particularly prominent in the spectrum of Fig. 2(a), but lose intensity after the adsorption process, Fig. 2(b), indicating a possible interaction between IB dye and these bonds in the adsorbent.

In the ATR FT-IR spectrum after dye removal, Fig. 2(b), a single prominent band at 1,020 cm^{-1} corresponding to the Si–O bond is shown, associated with the asymmetric stretching movement O–Si–O, but unlike Fig. 2(a), this band appears widened, indicating its active participation in the IB removal process. This same situation is observed for the bands of the associated OH group previously described.

Table 2
Percentage composition of RH

Analysis	Composition (%)
Silica	17.4
ADF	63.4
NDF	77.8
Lignin	8.3
Nitrogen	0.3
Cellulose[a]	55.1
Hemicellulose[b]	14.4

[a] Cellulose (%) = ADF (%) – lignin (%).
[b] Hemicellulose (%) = NDF (%) – cellulose (%) – lignin (%)

3.3. Morphological analysis

As for the morphological analysis, Fig. 3 shows SEM micrographs of RH before and after IB adsorption. The natural RH (Figs. 3(a) and (b)) displays two particular features; a relatively uniform surface composed of concave cells with average diameter of 32 μm, corresponding to the endocarp (inner surface, Fig. 3(a)), and a rough-looking surface made up of convex cells, distanced by symmetrical grooves on which the presence of macro hairs corresponds to the exocarp (outer surface, Fig. 3(b)).

Micrograph in Fig. 3(c) corresponds to RH after IB dye adsorption. It shows the presence of small particles of spherical shape deposited on exocarp grooves, attributed to the precipitation of IB dye, since it is a vat dye its solubility is limited by time, because in contact with the oxygen it oxidizes quickly. It should be noted that the external structure in terms of convex grooves and cells is conserved. A similar description of this agricultural waste morphology has been reported in previous research [31,32].

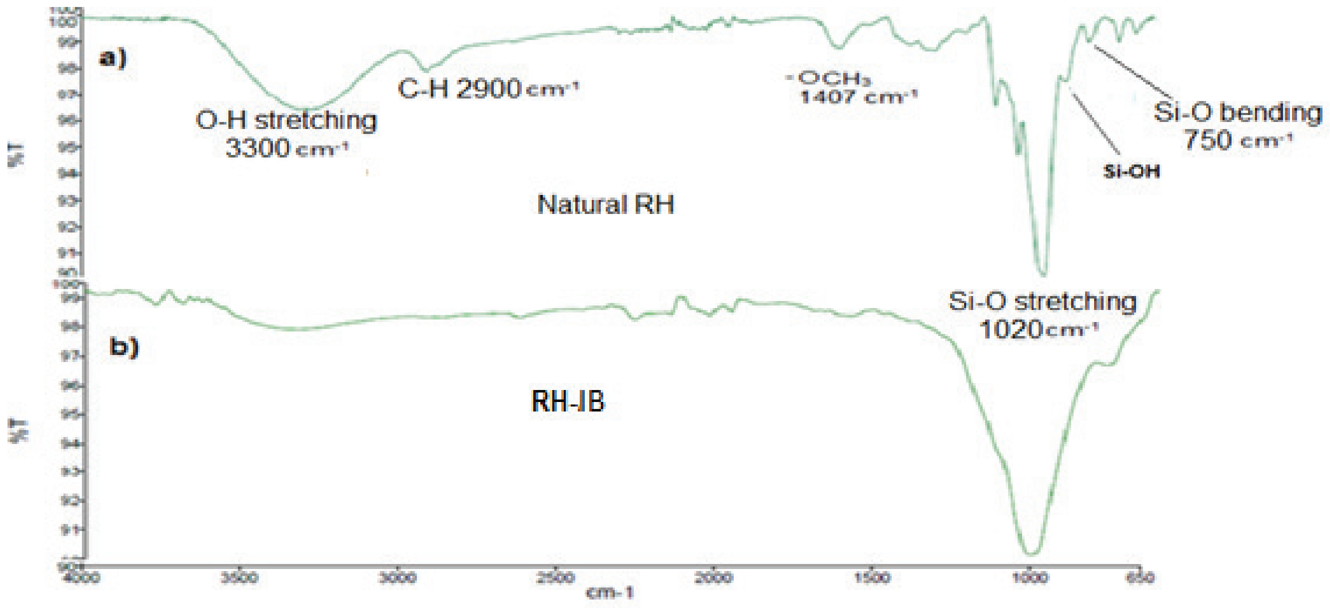

Fig. 2. (a) Infrared spectrum of RH and (b) RH after IB adsorption.

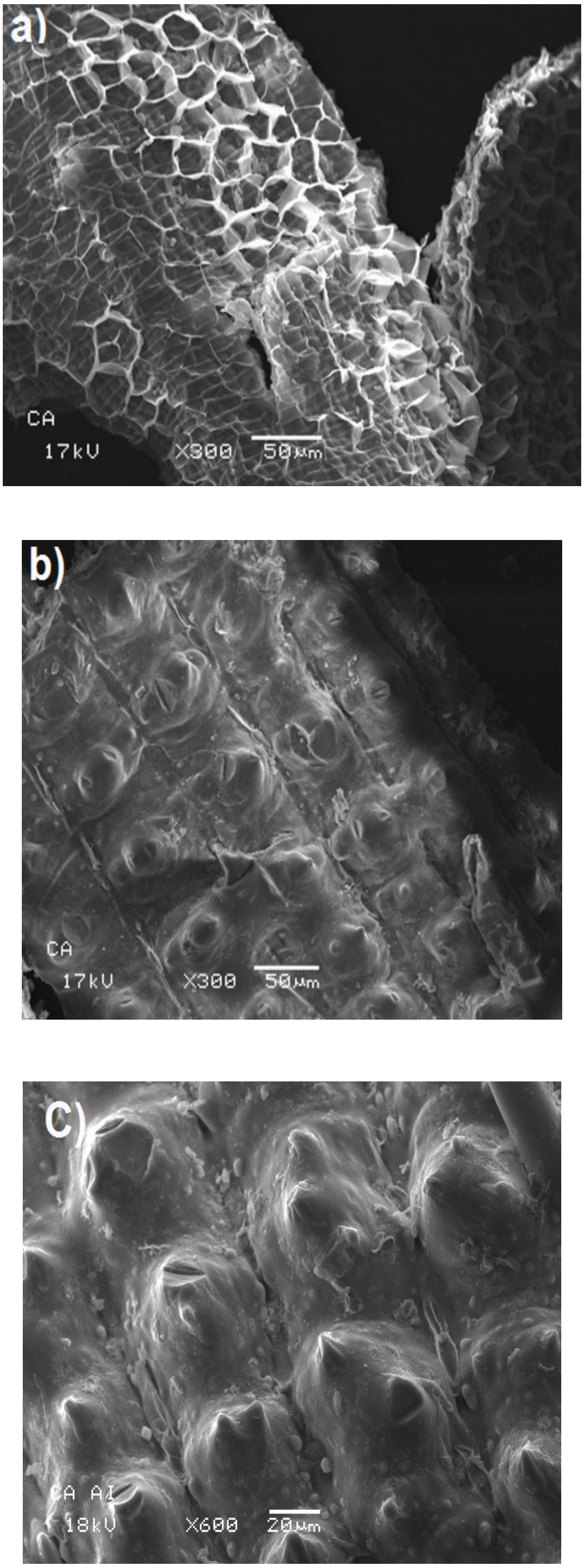

Fig. 3. (a) and (b) SEM micrographs of natural RH and (c) RH after adsorption of IB dye.

3.4. Statistical design of experiments

The 2^3 full factorial design performed under the factors described in Table 1 allowed a maximum IB removal of 90.0% under a RH dosage of 8.0 g/L, a dye concentration of 30.0 mg/L and a contact time of 4 h.

Analysis of variance (ANOVA; Table 3), where the significance of the regression coefficients was determined by applying Student's t-test, shows that the factors concentration (C_o), DA, TC and dosage–contact time binary interaction (DA–CT) meet the confidence level of 95% ($p < 0.05$). Therefore, these factors were taken into account to estimate the removal percentage.

The mathematical model for the 2^3 full factorial design is described in Eq. (2). As it can be observed, the predicted values for this dye removal are similar to those found experimentally, with a mean standard deviation of 2.15, indicating that the obtained model presents an adequate adjustment to the process.

$$\text{Removal \%} = 84.01 - 0.0945C_o + 1.52\text{DA} + 0.96\text{TC} - 0.184\,(\text{DA–TC}) \tag{2}$$

The main effects of the factors and their interactions in the IB dye removal onto RH through a 2^3 full factorial design are presented in the Pareto chart (Fig. 4). As shown in Fig. 4(a), the factors that exceed the reference line correspond to concentration (C_o) and TC with a negative effect, and the DA factor with a positive effect. This suggests that the removal process efficiency can be improved with a decrease in IB initial concentration and TC, as well as with an increase in the DA (Figs. 4(c) and (e)). Regarding interactions, only one of them was significant, adsorbent dosage–contact time (DA–TC), with a negative effect. The remaining two interactions do not exceed the reference line, indicating the absence of statistical significance, reason why they are not considered in the analysis [33].

The IB removal reached with RH under the most appropriate conditions determined with the factorial design, around 90%, was satisfactory; nevertheless it was decided to carry out a central composite surface design in order to optimize the process. Table 1 details the factors and their respective levels. Thus, in agreement with the results presented in the Pareto chart of the previous factorial design, a decrease in concentration levels and TC factors were included, while the DA was increased and fixed in a value of 10.0 g/L.

Before proceeding to the description of the central composite surface design, it is worth mentioning that the 90% efficiency obtained in the 2^3 full factorial design was reached at 65°C. The temperature is relevant variable for the efficiency of IB dye removal process, due to its insolubility in water at temperatures below 60°C requires that the removal process is carried out at a temperature of 65°C or higher. In this way, it is guaranteed that the dye is dissolved in the aqueous solution and its removal can take place. A decrease of 10°C led to a drastic reduction in IB adsorption efficiency, recording a percentage of 52% at 55°C, with an initial dye concentration of 10 mg/L, a DA of 4 g/L and 8 h of TC (data not shown).

3.5. Central composite response surface design

Under the conditions of the central composite surface design described in Table 1, an IB maximum removal of 92.0%

Table 3
ANOVA for the IB removal percentages

Factors	2^3 Factorial design		Response surface	
	Sum of squares	*p*-value	Sum of squares	*p*-value
C_o: Concentration	60.98	0.0001	35.25	0.0003
DA: Adsorbent dosage	11.63	0.0284	–	–
TC: Contact time	23.82	0.0034	17.60	0.0055
C_o – DA	0.03	0.9009	–	–
C_o – TC	0.79	0.5371	1.562	0.3692
DA–TC	13.01	0.0216	–	–

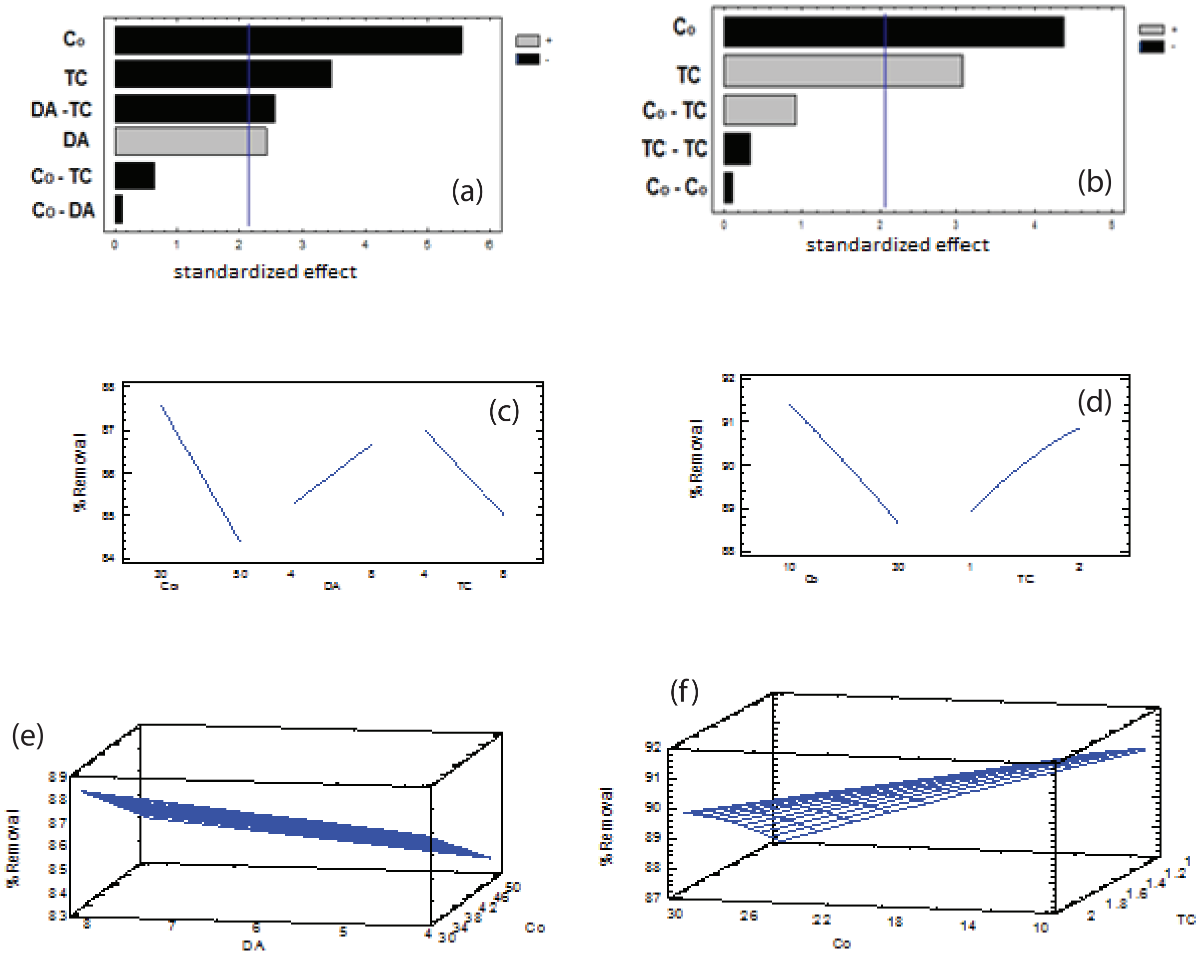

Fig. 4. Standardized Pareto chart of the IB removal onto RH. (a) 2^3 full factorial design, (b) response surface design, (c) main effects in the 2^3 full factorial design, (d) main effects in the response surface design, (e) 3D surface mapping plot for adsorbent dosage and concentration with fixed contact time of 4 h and (f) 3D surface mapping plot for concentration and contact time.

was achieved for an initial dye concentration of 10 mg/L and a DA of 10 g/L at a TC of 2 h (Table 4).

The ANOVA for the central composite surface design is displayed in Table 3. It is observed that the factors that exceed the reference line correspond to initial dye concentration (C_o) and TC. The mathematical model for this design is presented in Eq. (3). Predicted values for IB removal onto RH are shown in Table 3. As it can be seen, there is a great coincidence between the values obtained and those predicted, with a mean standard deviation of 1.47, indicating that this model presents an adequate adjustment to the process.

$$\text{Removal } \% = 80.27 - 0.223C_o + 2.61\text{TC} \tag{3}$$

Table 4
Experimental and predicted removal percentages for the 2^3 full factorial and central composite surface designs for the IB–RH system

2^3 Factorial design					Surface response design			
C_o (mg/L)	DA (g/L)	TC (h)	Experimental (%)	Predicted (%)	C_o (mg/L)	TC (h)	Experimental (%)	Predicted (%)
50	4	4	84.47	84.16	30	2	89.67	89.80
50	4	8	82.98	83.28	10	1	90.60	90.62
30	8	8	86.45	86.75	10	2	92.38	91.87
30	4	8	87.06	86.76	20	1	89.60	88.92
30	8	4	90.16	89.85	30	1	86.45	87.10
50	8	8	83.43	83.13	20	2	90.53	90.90
50	8	4	86.65	86.96	20	1.5	89.72	89.35
30	4	4	86.61	86.92	30	1.5	90.39	90.75

The main effects and interactions for the 2^3 full factorial design (Figs. 4(a), (c) and (e)) and for the central composite surface design are shown in the Pareto charts and in the response surface graphs for IB removal onto RH, Figs. 4(b), (d) and (f). The C_o factor shows a negative effect, while the TC has a positive effect (Fig. 4(b)). Therefore, an increase in IB initial concentration causes a decrease in the removal efficiency. In contrast, the pollutant removal increases while increasing the TC (Figs. 4(d) and (f)). The other effects and interactions do not go beyond the baseline, indicating their lack of statistical significance, reason why they are not considered in the analysis [33].

By comparing the results obtained through the central composite surface design with those of the 2^3 full factorial design, a minimal increase in the percentage of IB removal was observed, only 2.0% with respect to that achieved in the factorial design (90.0%). Furthermore, the central composite surface design conditions include a lower amount of the evaluated dye (10 mg/L) and requires a higher DA (10 g/L) compared with the conditions of the factorial design. Thus, these findings suggest that the optimization of the IB dye removal process onto RH is not recommended. The best alternative for IB removal on this agricultural by-product is using the conditions found in the 2^3 full factorial design, corresponding to an initial concentration of 30 mg/L of dye, DA of 8.0 g/L and TC of 4 h.

The 90.0% efficiency achieved in this work for IB removal through the factorial design is a valuable contribution for the treatment of industrial effluents polluted with vat dyes. Taking into account its low solubility, most research have focused into biological treatments that are not feasible for scaling due to the long duration of the processes, or alternatively to the evaluation of expensive physicochemical methodologies including a combination of reagents and electrolytes. On the other hand, the wide availability and minimum cost of this agricultural by-product plus the advantages of the adsorption process, allow suggesting that this methodology represents a viable and effective alternative for the treatment of this kind of colored effluents. Thus, the satisfactory results obtained encourage to continue studying components of equilibrium, kinetics and thermodynamics of this adsorption process in order to design a sustainable, efficient and economic strategy that could be of interest for the industries.

4. Conclusions

This investigation allowed to conclude that the RH residue represents a promising adsorbent material for the pollutant removal in this particular case IB dye. Structural and bromatological characterization, allows to determine that the RH exhibited a great adsorptive capacity of this vat dye under favorable conditions. A preliminary evaluation of the variables implied in the IB removal onto RH allowed to define those of greater influence for later assessment through a 2^3 full factorial design. Thus, it was possible to achieve a maximum IB adsorption of 90.16% under the most appropriate conditions, which were an initial dye concentration of 30 mg/L, a DA of 8.0 g/L and a TC of 4 h. This percentage is satisfactory, taking into account that IB vat dye has a low solubility in aqueous media, making it difficult to remove. The subsequent optimization of the process with a response surface design allowed the increase of the removal by 2% in the efficiency, reaching a removal of 92.38%, % under the most appropriate conditions, which were an initial dye concentration of 10 mg/L and a TC of 2 h.

Temperature is a variable of great importance for the IB removal process efficiency, due to its insolubility at temperatures lower than 60°C, condition that cause the precipitation of this dye. Therefore, it is absolutely essential that the adsorption process is performed at a temperature of 65°C or greater to ensure the dye is dissolved in the medium and thus its removal could be efficient.

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