Chapter 4 Evaluation of activated carbon from cactus residues in the colour removal process in synthetic water

Capítulo 4 Evaluación de carbón activado de residuos de nopal en el proceso de remoción de color en agua sintética

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Abstract

The removal efficiency of activated carbons prepared from *Opuntia* spp. cladodes in the adsorption of Crystal Violet from the synthetic wastewater was investigated in a 3^2 factorial design (two factors and three levels). *Opuntia* spp. powder was processed into activated carbon by carbonizing at 650 ºC and activated with acetic acid (60% v/v) for 1 h. Then, synthetic solutions of crystal violet were prepared and the adsorption process was carried out by varying initial crystal violet concentration and carbon activated dose, at room temperature. The results showed that 77.8% of adsorption of crystal violet from the syntethic water and an adsorption of 622.3 mg/g at room temperature and 10 min of contact.

Dyes, Remotion, Wastewater, Cristal-violet

Resumen

Se investigó la eficacia de eliminación de carbones activados preparados a partir de cladodios de *Opuntia* spp. en la adsorción de Violeta de Cristal de las aguas residuales sintéticas en un diseño factorial de 3^2 (dos factores y tres niveles). El polvo de *Opuntia* spp. se transformó en carbón activado mediante carbonización a 650 ºC y se activó con ácido acético (60% v/v) durante 1 h. A continuación, se prepararon soluciones sintéticas de violeta de cristal y se llevó a cabo el proceso de adsorción variando la concentración inicial de violeta de cristal y la dosis de carbón activado, a temperatura ambiente. Los resultados mostraron un 77,8% de adsorción de violeta de cristal del agua sintética y una adsorción de 622.3 mg/g a temperatura ambiente y 10 min de contacto.

Colorantes, Remoción, Aguas residuales, Cristal-violeta

4.1 Introduction

A significant impact of dyes is observed in the environment due to their important production of several goods, notably papers, textiles, plastics, leather, rubber, cosmetics, and food. For example, the textile industry can produce 7x metric tons of dye annually. The widespread of these dyes and immense utilization increasingly contribute to the wastewater, causing a detrimental effect on the environment. Along with it, the color effluents present in the dyes negatively impact the penetration capacity of the sunlight, which is harmful to the aquatic environment (Al-Shahrani, 2020).

Dyes can be described as colored substances chemically bonded to an applied substrate, conveying the desired color to that material. The dye's chemical bond (fastness) with the substrate can be improved using a mordant. Pigments are also dyeing agents. However, pigments do not chemically bond; rather, they adhere by physical adsorption, covalent bond formation, or mechanical retention. The organic dye molecules comprise delocalized electronic systems with conjugated double bonds that possess exclusive chemistry. It usually consists of a chromophore component, capable of absorbing a visible range of the light spectrum imparting toward color development for the dye molecules, and an auxochrome constituent that generally increases its affinity toward the substrate (Roy and Sahaa, 2021).

Dyes used in industry are classified into three categories of cationic dyes (all base dyes), anionic (direct, acidic, and reactive dyes), and non-ionic (disperse dyes). Cationic dyes, being more dangerous than other types, are widely used. It is reported that 12% of the annual production (about 700,000 tons) of cationic dyes is wasted through industrial water streams polluting the environment. Crystal violet (CV) dye is a cationic triphenylmethane dye with high intensity. It is used in various industries such as pharmaceuticals, paper, textiles, and printing inks (Foroutan *et al*., 2021). CV dye is more toxic than negative dye and, if present in water, can reduce the penetration of sunlight and disrupt the process of photosynthesis. In addition, CV dye in certain concentrations can cause various diseases and illnesses such as respiratory failure, eye irritation, increased heart rate, skin irritation, blindness, cyanosis, cancer, and mutagenesis (Essandoh *et al*., 2021, Mittal *et al*., 2021). Therefore, removing the CV dye from industrial wastewater streams is necessary before entering the environment.

In Mexico, arid and semi-arid lands constitute 49.20% of the national territory. Therefore, Mexico is also considered one of the main diversity centers of cacti. There are 586 species of cacti and the highest number of native species in Mexico (Ortega-Baes *et al*., 2010). The cacti of greatest economic importance globally are the *Opuntia spp*., commonly named "nopales". There is a big interest in valorizing nopales; for example, it has been used as reagent material in wastewater treatment (Vishali and Karthikeyan, 2015; Barbera and Gurnari, 2018). The production of nopales for consumption generates waste at agricultural and industrial levels. For example, in Mexico City, each year dethroning process of nopal generates around 40,000 tons of waste (Marin-Bustamante *et al*., 2017). This can become a focus of contamination (insects and microorganisms) (Colín-Chávez *et al*., 2021)

On the other hand, to improve the quality of water bodies, the recent modifications in Mexican regulations have included the removal of color in wastewater, which is why industries need to implement efficient, cheap, and sustainable treatments. That is why the objective of the present study was to evaluate the efficiency of crystal violet removal from aqueous solutions using high surface area activated carbon prepared from *Opuntia* spp. cladodes by chemical activation of acetic acid as a cheap and readily available adsorbent.

4.2 Metodology

4.2.1 Sample preparation

First, spines were removed from the *Opuntia* spp. cladodes (referred to now as nopal), then the cladodes were washed and cut into 1-2 cm squares and dried in an oven at 100° C for 24 h. Grinding was carried out in an industrial blender until a homogeneous powder was obtained. The powder was sieved to retain the particle sizes <1 mm.

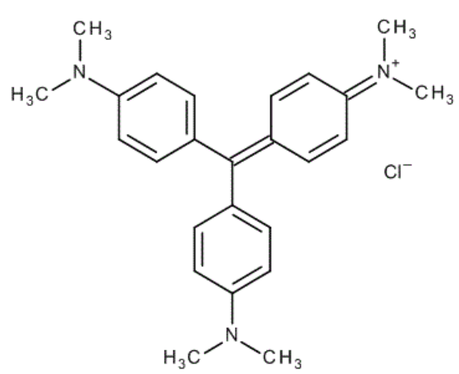
4.2.2 Activated carbon

Cactus powder with particle sizes less than 1 mm was taken. The impregnation was carried out with a 1:1.5 ratio of powder: acetic acid (60% v/v), and subsequently, the temperature was brought to 650 ºC and maintained for one h.

4.2.3 Crystal violet dye

Synthetic water was prepared with Crystal Violet Dye ($C_{25}H_{30}CIN_3$ CAS#548-62-9) and distilled water. A calibration curve was arranged for the Crystal Violet dye. Nine points were used: 0, 400, 800, 1200, 2000, 4000, 4800, 5600, and 6400 ng/ml; the absorbance was measured at a wavelength of 590 nm using a visible spectrophotometer (Thermo Fisher Scientific type Genesys 20 4001/4). The equation of the curve $y = 163.91x - 0.0716$ was obtained with a linear fit of $R^2 = 0.9907$.

Figure 4.1 Crystal violet



4.2.4 Experimental Design

A 3^2 factorial design (two factors and three levels) was used to optimize the removal of crystal violet dye (CV) in synthetic water. The initial dye concentration and the nopal activated carbon dose were selected as the main independent variables (factors), which varied at two levels (low and high) with central points.

Different combinations of conical tubes with 10 ml of synthetic water with CV and activated carbon of nopal were prepared according to the 3^2 factorial design proposals at room temperature. All the combinations used in the experiment are presented in Table 4.1. After termination of the adsorption experiments, the remaining concentration of CV in each sample dye was investigated as a dependent variable (response). It was measured by UV spectroscopy after 10 min of contact. Subsequently, it was centrifuged to separate the carbon solids from the liquid phase at 3000 rpm for 1 min. Statgraphics Centurion XVI software generated and evaluated the statistical experimental design. The percentage removal (%) was calculated using the following equation:

$$\%\,removal = \frac{(C_0 - C_e)}{(C_0)} \times 100 \quad (1)$$

The amount of adsorption at equilibrium q_e (mg/g) was calculated as follows:

$$q_e = \frac{(C_0 - C_e)}{(V/M)} \quad (2)$$

Where C_0 is the liquid-phase concentration of dye at initial (mg/L), and C_e is the liquid-phase concentration of dye at final (mg/L), V is the volume of the solution (L), and M is the mass of activated carbon used (g).

Table 4.2 Experimental design

Run	Independent variables			
	Coded values		Uncoded values	
	X₁	*X₂*	*X₁*	*X₂*
1	0	-1	8000	300
2	1	-1	16000	300
3	0	1	8000	500
4	-1	0	4000	400
5	1	0	16000	400
6	0	0	8000	400
7	-1	-1	4000	300
8	1	1	16000	500
9	-1	1	4000	500
X_1: CV concentration (ng/ml), X_2: activated carbon dose (mg).				

Source: Own elaboration, 2022

4.3 Results and Discussions

4.3.1 Color remotion

According to the 3^2 factorial design, the color removal tests were prepared using the combinations indicated in Table 4.1. The general description of the experimental test and the observed responses are presented in Table 4.2. The results of the ANOVA showed that the initial concentration of crystal violet color ($p<0.05$) and the interaction of the initial concentration of crystal violet with the dose of activated carbon has a significant effect ($p<0.05$) on the final residual concentration of dye.

Table 4.2 Observed responses to experimental design

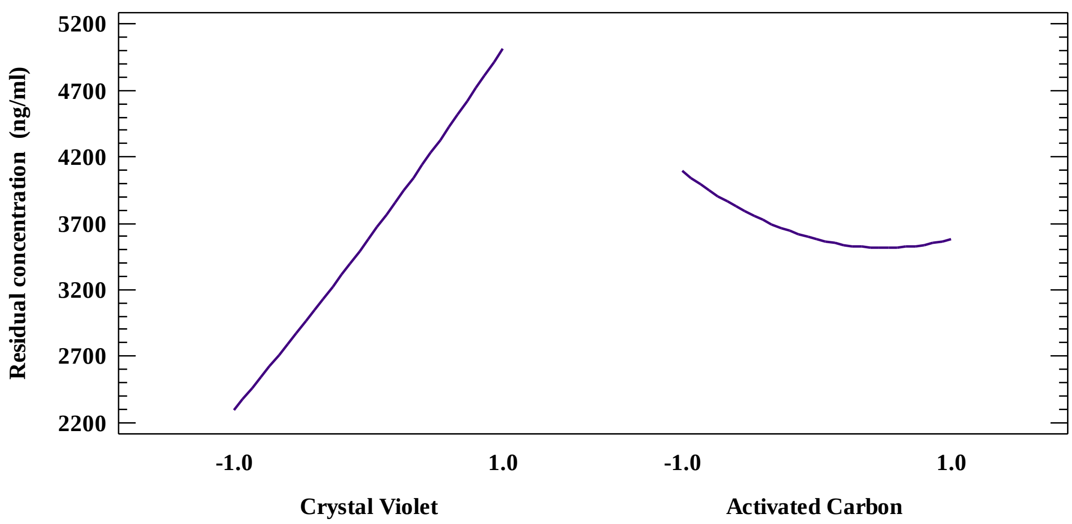
Run	Independent variables		Dependent variables		
	X_1	X_2	Y_1	Y_2	Y_3
1	0	-1	3841.1	52.0	124.8
2	1	-1	6525.5	59.2	284.2
3	0	1	4329.2	45.9	183.5
4	-1	0	2340.3	41.5	66.4
5	1	0	5470.1	65.8	421.2
6	0	0	3066.3	61.7	197.3
7	-1	-1	2047.5	48.8	58.6
8	1	1	3554.4	77.8	622.3
9	-1	1	2987.0	25.3	50.7
X_1: CV concentration (ng/ml), X_2: Activated Carbon dose (mg), Y_1: residual concentration of Crystal Violet dye (ng/ml), Y_2: color remotion (%), Y_3: amount of adsorption at equilibrium q_e (mg/g)					

Source: Own elaboration, 2022

Statgraphics Centurion XVI software provided an equation involving individual principal factors and interaction factors after fitting these data. The model equation relating the residual color concentration as a response became:

$$Y_1 = 3575.4 + 1362.54 \cdot X_1 - 257.255 \cdot X_2 + 75.2445 \cdot X_1\text{^}2 - 977.671 \cdot X_1 \cdot X_2 + 255.221 \cdot X_2\text{^}2 \qquad (3)$$

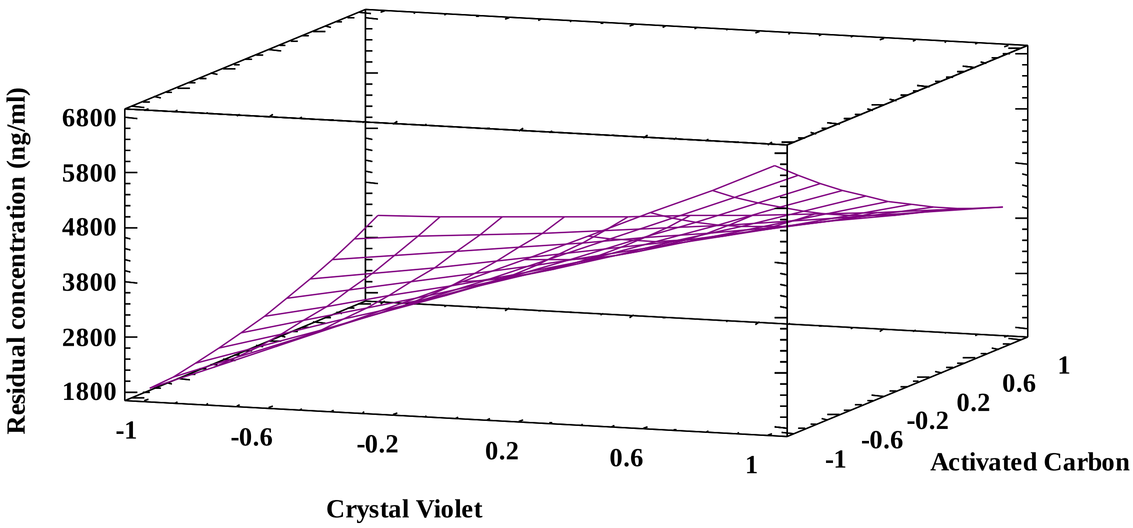
Graphic 4.1 Main effects plot for CV residual concentration



Source: Own elaboration, 2022

Graphic 4.1 shows the main effects of the residual concentration of CV. It is observed that a lower final concentration is obtained with a lower initial concentration of CV; this can be explained by the adsorption capacity of the material and the saturation of its pores. For Prías *et al*., (2015), activated carbon is a compound that contains carbon chains with structures and properties like graphite; its morphological formation is crystalline, carbon is determined by its high porosity, and because it can form extensive surface areas approximately between 500-1500 m^2 per gram of carbon, this is directly proportional to the chemical activation process that is carried out. Foroutan *et al*., (2021) mention that the initial concentration of the CV can have a significant effect on the efficiency and adsorption capacity of the process because it provides the necessary driving force for the mass transfer between the aqueous phase (aqueous solution containing dye) and the solid phase (adsorbent) (Sulyman, Namieśnik,& Gierak *et al*., 2016). On the other hand, a maximum q_e of 622.3 mg/g was obtained at high levels (1) of initial CV and carbon dose, while the minimum of 58.6 mg/g was found at low levels (-1). For various materials and dyes, for example, a q_{max} of 203.34 mg/g is reported for activated carbon from Waste tea activated carbon with Acid Blue 25 dye (Auta & Hameed, 2011) and one of 340.0 mg/g for activated carbon from date stones with Methylene Blue (Jassem *et al*., 2011). This represents a potential material for higher initial concentrations and controlling constant agitation.

Graphic 4.2 Main effects plot of CV residual concentration



Source: Own elaboration, 2022

Table 4.3 Optimization values obtained by the mathematical model

Factor	Low	High	Optimium
CV concentration (ng/ml)	-1.0	1.0	-1.0
Activated Carbon dose (mg)	-1.0	1.0	-1.0

Source: Own elaboration, 2022

4.4 Conclusions

It was confirmed that the activated carbon obtained from nopal bagasse and activated with acetic acid removes the crystal violet dye at 16,000 ng/ml and below it in synthetic waters. The analysis of the results obtained allows us to establish that the activated carbon reached an efficiency of 77.8% in the conditions handled during the tests. Therefore, it was identified that other levels of activated carbon dose should be experimented with to determine the maximum capacity of adsorption of the active sites and to evaluate the influence of agitation on the adsorbent-adsorbate contact. On the other hand, the material shows a good adsorption potential at room temperature compared to other materials.

4.5 Funding

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