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Performance of Monolithic Mesoporous TiO_2 Structures in the Adsorption of Anionic Dyes

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Abstract

The application of monolithic structures in fixed-bed columns for the removal of organic compounds has rarely been explored in the literature. This type of bed makes it possible to use versatile columns for the treatment of textile effluents, and it provides low cost, ease of operation, easy recuperation of the bed, and reduced pressure drop, thus allowing larger volumes to be treated. Brass monoliths with parallel channels were constructed and coated using the washcoating technique to study the pH. The effect of pH on dye adsorption showed satisfactory results under conditions of pH 4. At pH 4, the adsorption capacity and dye removal were approximately 50% higher than those at the other pHs studied. The Yoon-Nelson model provided a good fit to the experimental data over the three pH ranges, with a correlation coefficient of 0.967. The obtained results indicate the possibility of applying this system with a view to explore other operating conditions.

Keywords: Monolith; adsorption; dyes anionic; titanium dioxide; *Yoon-Nelson model*

1. Introduction

Anionic dyes, defined by solubilizing auxochromic acid groups such as NO2-, SO3-, -COOH, are known for their solubility in aqueous solutions and their affinity for positively charged substrates, including certain textile fibres [1]. This class can be subdivided into other groups of dyes, such as reactive and direct dyes [2], like reactive black 5 (RB5) and direct red 83 (DR83).

However, these textile dyes are resistant to conventional treatments because of their molecular complexity and low biodegradability [3]. These characteristics can result in various environmental problems, including water reoxygenation obstruction, ecosystem water activity, and interference with sunlight penetration [2, 4]. To promote sustainable production and minimize environmental impacts, complementary treatments must be explored. On a large scale, the use of fixed-bed adsorption columns is an efficient and adaptable solution for treating effluents [5].

Adsorption is a mass transfer process involving the physical sorption of molecules or ions onto a solid surface. The substances that accumulate on solids are called adsorbates, whereas the solid material that traps them is called an adsorbent [6].

Adsorbents are commonly applied in fixed-bed column systems as powders, pellets, and other materials packed as a bed [7]. This work aims to analyze the performance of structured beds coated with mesoporous TiO_2 supported on monolithic structures as fixed beds in an adsorption column for the removal of anionic textile dyes.

2. Methodology

2.1 Preparation of monoliths

Brass C-260 was used to fabricate the monoliths. The preparation involved three stages: cutting and washing the brass sheets, forming the channels, and assembling them, following the methodology described in [8]. The TiO_2-G5 suspension was then prepared using 10% solids and 12.5% PVA and maintained at pH 4. In the final stage, the monolith was coated on the TiO_2-G5 suspension by successive coating techniques. This process involves immersing monoliths at a constant speed, followed by emersion at the same speed. After each coating, the monoliths were centrifuged for 30 s and then kept in an oven at 50°C for 15 min, followed by a further 15 min at 120ºC. They were then weighed and subjected to further immersion until reaching the desired masses. Finally, the monoliths were calcined at 400°C for 2 h to remove the additives.

2.2 Characterization of the adsorbent

N_2 gas adsorption/desorption was used to determine the textural characteristics of the TiO_2-G5 suspension. The sample was degassed at 100°C for 6 h. Finally, the pH of the zero-charge point (pHPCZ) of the TiO_2-G5/PVA suspension was determined using a methodology adapted from [9].

2.3 Column adsorption study

Fixed-bed column adsorption experiments were carried out in a column with upflow. The column was

6.5 cm long and had a diameter of 2.32 cm. The monolith, measuring 4.5 cm in height and 2.3 cm in diameter, was positioned at a distance of 1 cm from the top and bottom of the tube. The column was then filled with Fecralloy mesh and glass spheres to distribute fluid in the system. HNO_3 and NaOH solutions were used to correct the pH of RB5 and DR83. Samples were collected at set times, and the concentration was monitored using a UV-Vis spectrophotometer (Spectroquant® Prove 300) at pH 4, 6, and 10. All calculations were based on the equations proposed by [10], and the model was adjusted using the CAVS adsorption software.

3. Results and Discussions

3.1 Characterization of the adsorbent

The N_2 adsorption–desorption isotherm at -196° C for the TiO_2G5 adsorbent was obtained to determine its surface area and porosity. The results are shown in Fig. 1, along with the pore-size distribution.

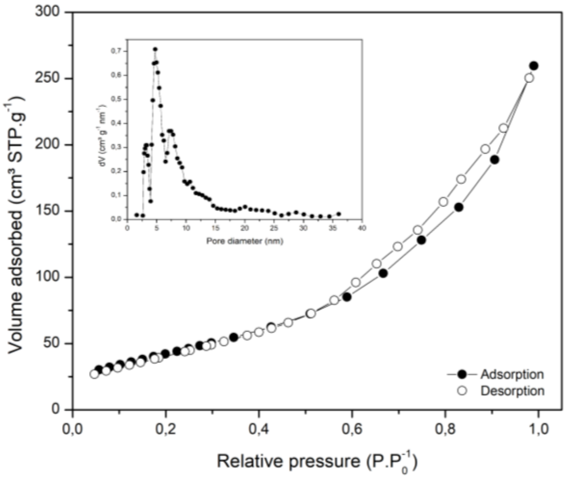

Fig. 1. Isotherm and pore distribution profile of calcined TiO_2G5/PVA suspension.

As can be seen in Fig. 1, the adsorption/desorption isotherm showed characteristics typical of mesoporous materials, classified as type IV(a) according to the IUPAC (International Union of Pure and Applied Chemistry) standard. This classification shows a hysteresis loop, indicating that capillarity is associated with the porous structure of the material. The average pore size and total pore volume, calculated using the density functional theory (DFT) method, were (4.752 nm) and (0.357 $cm^3 \cdot g^{-1}$), respectively. The specific surface area calculated using the Brunauer-Emmet-Teller (BET) method was 159 $m^2 \cdot g^{-1}$.

The surface charge is fundamental to dye adsorption and can facilitate or limit the process. In this case, the pH of the point-of-zero charge (pH_{PZC}) of TiO_2-G5 was evaluated. Fig. 2 shows the surface charges of TiO2-G5 at different pHs.

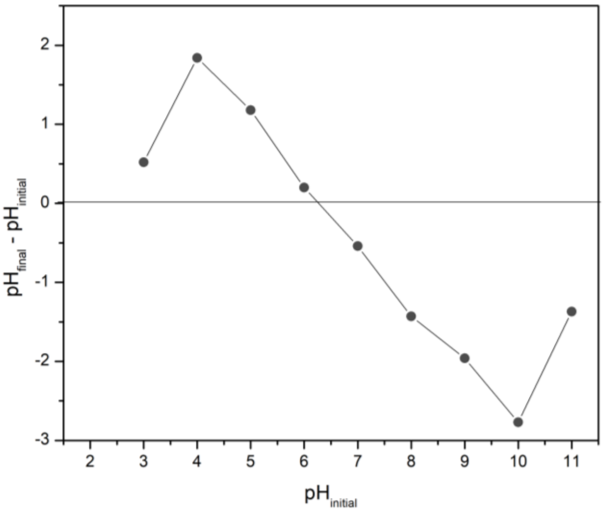

Fig. 2. The pH of the zero charge point of the calcined TiO_2-G5/PVA suspension.

The pH_{PZC} was measured by intersecting the curve with the initial pH axis, which was determined as 6.2 [11, 12] (Fig. 2. Thus, the surface charge of TiO2 is negatively charged at pH >6.2 and positively charged at pH < 6.2. This indicates that for anionic dyes, adsorption is favoured at pH values below the PCZ.

3.2 Fixed bed adsorption

Fig. 3 shows the breakthrough curves obtained for the effect of pH on the adsorption of anionic dyes on a fixed-bed column with a structured monolith.

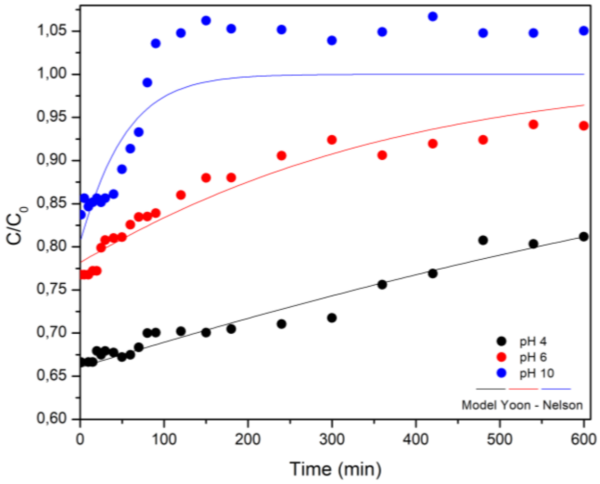

Fig. 3. Breakthrough curve of the effect of pH on the adsorption of the anionic dye mixture RB5 and DR83 at a concentration of 6.5 $mg \cdot L^{-1}$. Conditions: flow rate of 6 $mL \cdot min^{-1}$, monolith height of 4.5 cm and nominal load of 3 $mg \cdot cm^{-2}$.

Fig. 3 revealed that the breakthrough curves do not have the "S" shape commonly found in the literature for conventional adsorption columns. This characteristic is directly related to the structured bed used in the column, which has high porosity (Ɛ = 0.957). In contrast, conventional beds have significantly lower porosity (Ɛ = 0.292) [15]. As a result, it can be seen that the C/C_0 values start at 0.65, unlike the packed beds, which are initially solute-free ($C/C_0 = 0.0$). Table 1 lists the parameters calculated from the effect of pH on anionic dye adsorption.

Table 1. Exhaustion time (te), breakthrough time (tr), saturation volume (Veff), total mass of adsorbed dye (qt), adsorptive capacity (q), and dye removal yield (%) at different pH values.

	pH		
	4	**6**	**10**
t_r *(min)*	80	60	40
t_e *(min)*	480	240	90
V_{eff} *(mL)*	2880	1440	540
q_t *(mg)*	4.69	1.06	0.04
q *(mg g^{-1})*	3.74	0.84	0.034
%	19.73	9.48	1.09

The results presented in Table 1 show that the adsorption capacity (q) and the dye removal rate (%) decreased with increasing the pH. The bed exhaustion times were 480, 240, and 90 min for pH 4.0, 6.0, and 10, respectively. This longer time for pH 4 is due to the electrostatic charge of the anionic dye molecules, which are attracted to the positive active sites of TiO2, resulting in a greater volume of treated effluent. At other pH values, repulsion forces predominate, which reduce the contact between the adsorbate and the adsorbent, resulting in shorter breakthrough times [14].

When designing a column adsorption process, breakthrough curve data should be used. Several mathematical models have been developed to analyze the behaviour of laboratory-scale columns for industrial applications. The Yoon-Nelson adsorption model (Equation 3) assumes that the rate of decrease in the adsorption probability on the adsorbate molecule is proportional to the breakthrough on the adsorbent [16].

$$\frac{Ct}{Ci} = \frac{1}{1+e^{-kYN(t-\tau)}} \qquad (3)$$

Sendo, k_{YN} (min^{-1}) é a constante do modelo de Yoon-Nelson; t (min) é o tempo de amostragem e τ (min) é o tempo necessário para 50% de penetração do adsorvato.

Table 2. Dados obtidos da aplicação do modelo de Yoon – Nelson para as curvas de ruptura do efeito do pH.

	pH		
	4	**6**	**10**
τ_{cal} (min)	501	379	64
k_{YN} (min^{-1})	0.0013	0.0033	0.022
R^2	0.967	0.965	0.939

According to the results shown in Table 2, the Yoon-Nelson model corroborated the importance of pH control to maximize the efficiency of the system. As the pH increased, there was an increase in the value of k_{YN}, which suggested a decrease in the adsorption efficiency at alkaline pH. The calculated time (τ_{cal}) was greater for pH 4, indicating that the time needed to reach 50% adsorption capacity was longer due to the greater interaction between the adsorbent and adsorbate. On the other hand, for pH 6 and 10, these values decreased, indicating low adsorption capacity. The R^2 values were satisfactory at all pH values, especially at pH 4 and 6, indicating that the Yoon-Nelson model could describe the experimental data with some precision.

Conclusions

This study investigated the performance of a fixed-bed column structured with a TiO_2 monolith for the treatment of textile effluents with anionic dyes, with a special focus on the influence of the pH of the medium. The analysis showed that pH 4 provided superior adsorption of the dyes on the TiO_2, suggesting that acidic conditions favor the interaction between the adsorbent and the anionic dyes. Furthermore, the application of the Yoon-Nelson model proved to be highly effective in predicting the breakthrough curves in an adsorption column using a structured bed, thus, validating its applicability for a detailed comprehension of the behavior of this type of system under different pH conditions. These study results highlight the importance of pH adjustment in the adsorption process and confirm the feasibility of using structured monoliths in practical wastewater treatment applications. Therefore, this study contributes significantly to the optimization of adsorption systems, offering a promising approach to environmental management and the efficient treatment of industrial waste.

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References

[1] Tripathi N. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review by. Journal of Applied Chemistry. Vol. 5, Nº 3, p. 91-108, 2013.

[2] Zanoni, M.V.B.; Yamanaka, H. Dyes: Toxicological chemical characterization, detection and treatment methods. 1ª ed. São Paulo: Cultura acadêmica, 2016.

[3] RAWAT, D.; SHARMA, R. S.; KARMAKAR, S.; ARORA, L. S.; MISHRA, V. Ecotoxic potential of a presumably non-toxic azo dye. Ecotoxicology and Environmental Safety, Vol. 148, p. 528–537, 2018.

[4] Adane, T.; Adugna, A. T.; Alemayehu, E. Textile Industry Effluent Treatment Techniques. Journal of Chemistry, vol. 2021, p. 14, 2021.

[5] Dichiara, A.; Weinstein, S.; Rogers, R. On the Choice of Batch or Fixed Bed Adsorption Processes for Wastewater Treatment. Industrial & Engineering Chemistry Research. Vol 54, 2015.

[6] Ujile, AA. Chemical engineering unit operations, synthesis and basic design calculations. 1. ed. Bomn Publishers, Ibadan Nigeria, 2014.

[7] Hu, A.; Ren, G.; Che, J.; Guo, Y.; Ye, J.; Zhou, S. Phosphate recovery with granular acid-activated neutralized red mud: Fixed-bed column performance and breakthrough curve modelling. Journal of Environmental Sciences. Vol. 90, p. 78-86, 2020.

[8] Silva, É. F.M.; Ximenes, É. R.B.; Sales, Letícia B.V.; Dantas, E. J. M.; Oliveira, E. D. C. Simões, T. B.; Ribeiro, A. T. S.; Sanz, O.; Machado G.; Almeida, L. C. Photocatalytic degradation of RB5 textile dye using immobilized TiO2 in brass structured systems. Catalysis Today, Vol. 383, p. 173-182, 2022.

[9] Prahas, D.; Kartika, Y.; Indraswati, N.; Ismadji, S. Activated carbon from jackfruit peel waste by H3PO4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal, v. 140, n. 1-3, p. 32–42, jul. 2008.

[10] Bhangi, B. K.; Ray, S. K. Nano silver chloride and alginate incorporated composite copolymer adsorbent for adsorption of a synthetic dye from water in a fixed bed column and its photocatalytic reduction. International Journal of Biological Macromolecules, V. 144, P. 801-812, ISSN 0141-8130, 2020.

[11] Verhovšek, D.; Štangar, U. L.; Kete, M.; Žagar, K.; ČEH, M. The Synthesis of Anatase Nanoparticles and the Preparation of Photocatalytically Active Coatings Based on Wet Chemical Methods for Self-Cleaning Applications. International Journal of Photoenergy, v. 2012, p. 1–10, 2012.

[12] Fessi, N.; Nsib, M. F.; Chevalier, Y.; Guillard, C.; Dappozze, F.; Houas, A.; Palmisano, L. Parrino, F. Photocatalytic Degradation Enhancement in Pickering Emulsions Stabilized by Solid Particles of Bare TiO2. Langmuir, v. 35, n. 6, p. 2129–2136, 18 jan. 2019.

[14] Strebel, A.; Behringer, M.; Hilbig, H.; Machner, A.; Helmreich, B. Anionic azo dyes and their removal from textile wastewater through adsorption by various adsorbents: a critical review. Frontiers in Environmental Engineering, Vol. 3, p. 2813-5067, 2024.

[15] NASCIMENTO, R. F.; LIMA, A. C. A.; VIDAL, C. B.; MELO, D. Q.; RAULINO G. S. C. Adsorção: Aspecto teórico e aplicações ambientais. Fortaleza: Imprensa Universitária, p. 256, 2014.

[16] Benjelloun, M.; Miyah, Y.; Evrendilek, G. A.; Zerrouq, F.; Lairini, S. Recent Advances in Adsorption Kinetic Models: Their Application to Dye Types. Arabian Journal of Chemistry, v. 14, n. 4, p. 103031, 2021.