Evaluation of adsorbent materials for the removal of textile dyes

Emanuele D. Guerra[a], Jhonatan R. da S. Cascimiro[a], Felipe P. C. Gomes[a], Marta M. M. B. Duarte[a], Luciano C. Almeida[a*]

[a] *Department of Chemical Engineering, Federal University of Pernambuco, 50.740-521 Recife, Pernambuco, Brazil*

Abstract

Despite the significant number of jobs and income generated for the country, the textile industry is responsible for a worrying environmental impact, such as the discharge of effluents with high polluting potential. Effluent Treatment Plants (ETPs) employ physical-chemical processes with some limitations, such as the excessive generation of sludge and inefficiency in removing certain pollutants. In this context, the aim of this study was to evaluate potential adsorbents for the removal of various textile dyes. BET and FT-IR spectroscopy were used to characterize and compare the adsorbents: commercial activated carbon 1012 (CA1012), peanut shell activated carbon (Ca), and titanium dioxide (TiO_2G5). The adsorption of single and two component textile dye solutions was evaluated in batches. Based on the characterization results, CA1012 had a larger surface area (As), a PCZ (point of zero charge) of 7.4 and functional groups similar to those of Ca. Despite having the lowest As among the adsorbents studied, TiO_2G5 exhibited PCZ and functional groups favoured the adsorption of dyes, especially anionic ones. The average adsorption capacities ($q_{average}$) of CA1012, TiO2G5, and Ca were 4.15, 3.87, and 3.25, respectively. The $q_{average}$ results showed that the CA1012 and TiO_2G5 adsorbents were the best for adsorbing textile dyes and their respective mixtures, especially anionic dyes.

Keywords: activated carbon; TiO2G5; textile dye; batch adsorption; Quartile-Pynthon

1. Main text

Textile and clothing industries drive the economy and generate direct and indirect jobs in Brazil. However, despite its economic importance, this sector consumes a large amount of water. The generated wastewater has a high pollution load, which is mainly due to the concentration of dyes added during the fabric dyeing stage [1]. In view of the problems caused by the disposal of textile effluents, it is necessary to treat them both to meet the standards established by law and to enable the treated effluent to be reused for irrigation purposes or in the industry's own processes [2]. Adsorption is a frequently used [3]. In view of the wide versatility of adsorbents, this study evaluated the adsorption capacities of three materials: two commercial activated carbons, peanut shell activated carbon, and TiO_2G5 anatase, for the removal of textile dyes.

2. Methods

2.1 Characterization of the adsorbents

Fourier Transform Infrared (FT-IR) analysis was carried out using a mid-infrared equipment with attenuated total reflectance (ATR) (tensor model 27 BRUKER), in the 4000-600 cm^{-1} range. To determine the surface area (As), N_2 adsorption/desorption was carried out at 77 ± 5 K using the Brunauer-Emmett-Teller (BET) method (BELSORP-MINI from Bel Japan Inc). The BJH method was used to determine the pore diameter (Dp) and pore volume (Vp).

2.2 Evaluation of adsorption capacity

The adsorption capacity of each material was evaluated by performing batch tests. This was carried out with each adsorbent, commercial activated carbon CA1012 (brand: Labsynth), peanut shell charcoal (Ca), and TiO_2G5, following the methodology of [4], in which 25 mL of dye solution at 25 ppm, at natural pH, and 0.1 g of adsorbent were added to a 125 mL erlenmeyer flask, and the solution was left to stir at 300 rpm on a shaking table (IKA KS130 control) for 2 h at room temperature (28±1°C). After this period, the dye solution with the adsorbent was filtered through blue filter paper (90±1mm) and then centrifuged (model Q222T216, QUIMIS) for 10 min at 10 rpm. Dye removal was assessed using absorbance in a UV/Vis spectrophotometer. It is possible to quantitatively define the removal using Equation 1.

$$q = \frac{(C_0 - C_f) * V}{m} \quad (1)$$

Where q is the adsorptive capacity ($mg \cdot g^{-1}$); C_0 and C_f are the initial and final dye concentrations ($mg \cdot L^{-1}$), respectively; V is the volume of the solution (L), and m is the mass of the adsorbent (g)[5].

The adsorption study was conducted with monocomponent and bicomponent solutions. Three different dyes were studied: the anionic dye direct blue 71 (AD71), remazol red 133 (VR133), and the cationic dye reactive yellow 186 (AR186). In order, to identify the concentration of the dye solutions, spectral scanning was carried out in the wavelength range (λ), 190-900 nm to identify the peaks associated with the chromophore group of each dye. The linear working range was 0.5 to 30 $mg \cdot L^{-1}$ for all solutions. The wavelength with the highest absorbance of 425 nm corresponds to the AR186 dye, with the method’s detection limit (DL) being 0.1 $mg \cdot L^{-1}$ and the quantification limit (QL) 0.7 $mg \cdot L^{-1}$. The wavelength of 587 nm corresponded to AD71 dye, where the LD was 0.07 $mg \cdot L^{-1}$ and the LQ was 0.4. It should be noted that these dyes also have the same chromophore peaks in a bicomponent solution. The highest absorbance length of 520 nm corresponds to VR133 dye, with an LD and LQ of 0.09 $mg \cdot L^{-1}$ and the LQ being 0.5 $mg \cdot L^{-1}$. In the bicomponent mixture of AD71 and VR133, the peaks changed, with the peak at 542 nm corresponding to the VR133 dye and the peak at 580 nm corresponding to the AD71 dye, in which case the LD was 0.09 $mg \cdot L^{-1}$ and the LQ was 0.5 $mg \cdot L^{-1}$.

2.3 Quantitative data analysis

Once the adsorptive capacities had been defined in the previous step, a statistical study was carried out in quartiles using the Python program to identify the adsorbent with the best average q. The library used for the statistical analysis was pandas, and the Python program was used from Google colab. The adsorption capacities were presented as a matrix to be used as a DataFrame in the statistical analyses performed in Python.

3. Discussions and results

3.1 Characterization of the adsorbents

The porosity data and surface characteristics of the materials, zero charge point (ZCP) are shown in Table 1.

Table 1. Characteristics of the adsorbents.

Adsorbent	As($m^2 \cdot g^{-1}$)	PCZ
TiO_2G5	280	6,8 [6]
CA1012	549	7,4
Ca	403	10,4 [5]

Source: Autor, 2024.

Table 1 shows that activated carbons CA1012 and Ca have greater surface areas than TiO_2G5. As coals undergo physical and/or chemical activation processes, their physical properties can be altered, increasing their surface area [7]. The zero-charge points of TiO_2G5, CA1012, and Ca were 6.8, 7.4, and 10.4, respectively. These values indicate that their surfaces are positively charged, which favours the adsorption of anionic dyes because they are negatively charged [5]. Spectrophotometric analysis in the Fourier transform infrared region was used to identify the functional groups in each adsorbent (Figure 1). Figure 1 shows that both materials have hydroxyl functional groups. In charcoal, these groups may be lignocellulosic compounds derived from alcohols and phenols [9].

The molecular structures of the coals are similar, and the bands between 1620 and 1680 cm1 correspond to the double bonds between carbons. This stretching is characteristic of alkenyl groups [5]. In both coals, it is also possible to observe a trace band referring to a simple C-O bond characteristic of carboxylic functional groups, alcohols, phenols, and esters, in the range between 1223 cm^{-1} and 1000 cm^{-1} [8]. In the spectrum of TiO_2G5, the band near the 826 cm^{-1} region is characteristic of Ti-O-Ti stretching vibrations. This material also has a hydroxyl band at 1630 and 3419 cm^{-1}. This band may be due to a stretching vibration, which may indicate the adsorption of H_2O molecules adsorbed by the material. Hydroxyl functional groups are important for the photocatalysis of TiO_2 [10].

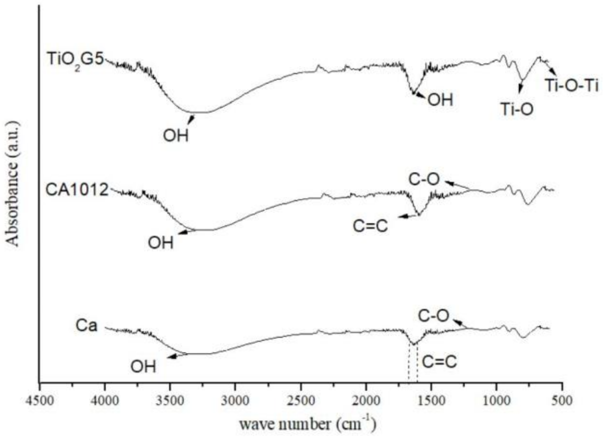

Fig. 1. FT-IR spectra of the materials: TiO_2G5, CA1012 and Ca. Source: Author, 2024.

3.2 Adsorption study

Batch adsorption tests were carried out for monocomponent and bicomponent dye solutions (Table 2).

Table 2 presents the adsorptive capacities as a function of the dye type and its mixture. The results showed that there was a relationship between the adsorption capacity and specific characteristics of the dye. For single-component solutions, Ca (Mono I) and TiO_2G5 (Mono III) are added. Although the AR186 dye is cationic and Ca has a PCZ of 10.4, it has oxygenated functional groups on its surface, as can be seen in Figure 1, and this characteristic contributes to the adsorption of cations [7]. On the other hand, TiO_2G5 stood out, regardless of the type of mixture, achieving adsorption capacities of over 4.2 $mg \cdot g^{-1}$. Furthermore, when it comes to anionic dye solutions, the adsorption capacity is low (2.17 and 2.22), so the average $q_{average}$ was 3.25.

Table 2. Adsorptive capacities

	Solution	TiO_2G5	CA 1012	Ca
q ($mg \cdot g^{-1}$)	**Mono I**	0,83	4,11	5,12
	Mono II	3,90	3,82	3,82
	Mono III	4,62	4,32	2,17
	Bi-I-425 nm	4,01	4,28	4,37
	Bi-I-587 nm	5,08	4,54	2,53
	Bi-II-542 nm	4,20	4,20	2,53
	Bi-II-580 nm	4,48	3,84	2,22

Monocomponent solutions: I, AR186; II, AD71; III, VR133. Bicomponent solutions: Bi-I- AR186 and AD71; Bi-II- AD71 and VR133.

Although TiO_2G5 is inorganic [6] and activated charcoal comes from organic material [5], they obtained close $q_{average}$ values. This result may have been due to As and the PCZ (Table 2), on the one hand, the charcoal having a larger surface area, on the other hand, TiO_2G5 favored by the PCZ being more suitable for adsorbing these dyes. Due to the complexity of the obtained adsorption capacity results, the data was analyzed using the quartile method. Figure 2 shows the q behavior of each adsorbent.

Figure 2 shows boxplots of the adsorption capacities of the adsorbents. The orange dashed line indicates the median, the line above the quadrant indicates the upper limit, and the line below the quadrant indicates the lower limit of the adsorption capacity of each adsorbent. Only TiO_2G5 exhibited a discrepancy of 0.83 $mg \cdot g^{-1}$. The median adsorption capacities of each adsorbent were 4.2, 4.2, and 2.5 $mg \cdot g^{-1}$ for

TiO_2G5, CA1012 and Ca, respectively. Note that TiO_2G5 and CA1012 obtained similar results; thus, the median data corroborated the mean data because the distribution of data for TiO_2G5 and CA1012 was very similar.

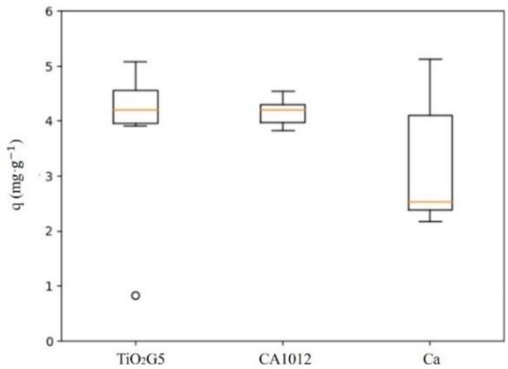

Fig. 2. Quartile analysis in boxplot. Source: Author, 2024.

4. Conclusion

The study observed the influence of different types of adsorbents (TiO_2 and charcoal) on the adsorption of dyes and their mixtures. Despite having different characteristics, TiO_2G5 and CA1012 exhibited very similar adsorption capacity values. Therefore, among the adsorbents studied, TiO_2G5, CA1012, and Ca, TiO_2G5, and CA1012 were the most efficient at removing textile dyes in monocomponent and bicomponent solutions.

Acknowledgements

- Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).
- Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE).

References

[1]Zulqurnain; Sultana, S.; Sultana, T.; Mahboo, S. Fatty acid profile variations after exposure to textile industAR effluents in Indian Major Carps. Brazilian Journal of Biology, v.84, p.254252, 2024.

[2]López-rodríguez, D.; Micó-vicent, B.; Jordán-núñez, J.; Montava-seguí, I.; Bou-belda, E. Complete Desorption of Hybrid Nanoclays Composed of Hydrotalcite and Disperse Dye. International Journal of Molecular Sciences, v.24, p.10950, 2023.

[3]Baskar, A. V.; Bolan, N.; Hoang, S. A.; Sooriyakumar, P.; Kumar, M.; Singh, L.; Jasemizad, T.; Padhye, L. P.; Singh, G.; Vinu, A.; Sarkar, B.; Kirkham, M. B.; Rinklebe, J.; Wang, S.; Wang, H.; Balasubramanian, R.; Siddique, K. H. M. RecoveAR, regeneration and sustainable management of spent adsorbents from wastewater treatment streams: A review. Science of the Total Environment, v. 822, p. 153555, 2022.

[4]Campos, N. F., Barbosa, C. M. B. M., Rodríguez-Díaz, J. M., Duarte, M. M. M. B. Removal of naphthenic acids using activated charcoal: Kinetic and equilibrium studies. Adsorption Science and Technology, v. 36, n. 7–8, p. 1405–1421, 2018.

[5]Silva, T., Barbosa, C., Gama, B., Nascimento, G., & Duarte, M. Agregação de valor à resíduo agroindustrial: Remoção de fenol utilizando adsorvente preparado a partir de casca de amendoim. Revista Materia, v.1, n.23, 2018.

[6]Santos, R., Silva, É. F. M., Dantas, E. J. M., Oliveira, E. D. C., Simões, T. B., Araújo, Í. R. S., Ribeiro, A. T. S., Oliveira, L. P. S., Garcia, R. R. P., & Almeida, L. C. Potential Reuse of PET Waste Bottles as a Green Substrate/Adsorbent for Reactive Black 5 Dye Removal. Water, Air, and Soil Pollution, v. 231, n.11, 2020.

[7]Pessôa, N. T., Sales, D. C. S., Do Nascimento, G. E., dos Santos, J. H. L., Silva, M. N. dos S., Napoleão, D. C., Rodríguez-Díaz, J. M., & Duarte, M. M. M. B. Effective adsorption of cadmium and nickel ions in mono and bicomponent systems using eco-friendly adsorbents prepared from peanut shells. Environmental Research, *247*, 2024.

[8]Yagmur, E., Ozmak, M., & Aktas, Z. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. v.87, p.3278–3285, 2008.

[9]Zhong, Z., Yang, Q., Li, X., Luo, K., Liu, Y., & Zeng, G. Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption. Industrial Crops & Products, v.37, n.1, p.178–185, 2012.

[10]Wu, X., Ren, S., Hao, W., Yuan, K., Guo, H., & Li, Y. Modulating charge separation of Ce – TiO 2 aerogel supported on chitosan derived ordered porous carbonaceous frameworks for promoting CO2 photoreduction activity. Ceramics International, v.50, n.17, p. 31519-31531, 2024.