14º ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
23 a 25 de Novembro de 2022

Use of PET bottles as adsorbent support for Direct Red 83 adsorption: A kinetic and equilibrium study

Nívea B. S. Araújo[a], Evelle D. C. Oliveira[a], Ivana C. F. Araújo[a], Émerson F. M. Silva[a], Luciano C. Almeida[a*]

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

Abstract

The presence of PET bottles found in rivers, lakes, and on the ground, coupled with the increase in dye pollution in water bodies, is a major environmental concern. The application of adsorption to remove these dyes is a widely used technique, however, the search for minimizing costs and ensuring efficiency, developing methods that meet these requirements has become imperative. Therefore, this work evaluates the adsorption and removal capacity of direct red dye 83 using TiO_2 as an immobilized adsorbent on a PET substrate. The adsorbent was characterized using adsorption-desorption of N_2, kinetics and equilibrium tests were conducted at 10 °C and 20 °C. The technique of recovery and reuse of the photoreactor, was conducted and statistically evaluated. The kinetic behavior of the reaction was best described by the Elovich model (R^2 = 0.98). The equilibrium study was best fitted to the Freundlich model ($R^2 > 0.96$). The reuse tests indicated that the removal efficiency was maintained at 38.86%, with low mass loss, and high repeatability. The results exhibit the promising potential of TiO_2/PET surface for environmental application, it is a low cost, efficient and scalable technique.

Keywords: Red Direct 83; adsorption; titanium dioxide

1. Introduction

The continuous increase in surface and groundwater pollution has become a major source of environmental concern for both governmental and industrial institutions around the world [1]. Among the most polluting sectors is the textile sector, due to the use of azo dyes in the dyeing stages. This, because of the presence of aromatic groups, are toxic. Due to high water solubility and incomplete attachment to fibers, about 10% - 20% of the dye is discharged as effluent [2].

Given this scenario, it is important to remove such components before final disposal. The development of alternative treatment technologies has become increasingly imperative, adsorption and advanced oxidative processes (photo fenton and photocatalysis)[3], have gained prominence.

Therefore, the objective of the work was to study the adsorption process of the azo dye Red Direct 83 under a structured PET plate photoreactor coated with TiO_2, with recovery of the adsorbent in the presence of ultraviolet light.

2. Methodology

2.1 Characterization of the adsorbent

The texture characteristics of TiO2-G5 powder (TiO2-G5/P), were analyzed by adsorption-desorption of N_2 (Quantachrome Autosorb-iQ). Previously degassed at 60 °C for 8 h.

2.1 Adsorbent preparation

A 10% TiO_2-G5 suspension was prepared and kept at pH 4, favoring the zero charge point (PZC) of TiO_2-G5. The PET substrate was cleaned with a sponge and a 10% neutral detergent solution, and subjected to consecutive ultrasonic baths, the first in detergent solution and the second in a 10% ethanoic solution, both for 15 min.

2.2 Substrate coating

Using the washcoating technique, the PET plates were immersed in the suspension at a speed of 5 cm.min-1, then oven dried for 15 min at 50°C,

weighed, and subjected to the procedure repeatedly until 4 mg mass stability was achieved

2.3 Adsorption isotherm

The study was conducted at pH 4, under 10 °C and 20 °C, for 24 h in the absence of light. The monitoring of the concentration was done with the aid of UV-Vis spectrophotometer (Spectroquant® Prove 300). The removal percentage (%) was calculated according to Equation 1 and the adsorptive capacity, according to Equation 2.

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

$$qe = \frac{V(C_0 - C_e)}{M_{ads}} \quad (2)$$

C_0 and C_e (mg.L^{-1}) are initial and equilibrium concentrations, respectively, V is the solution volume and M_{ads} is the mass of the adsorbent. The Langmuir, Freundlich and Langmuir-Freundlich isotherms were applied, represented by equations 3, 4 and 5, respectively.

$$qe = \frac{q_{max} K_L C_e}{(1 + K_L C_e)} \quad (3)$$

$$qe = k_F Ce^{1/n} \quad (4)$$

$$qe = \frac{q_{max} K_s C_e^n}{(1 + (K_s C_e^n))} \quad (5)$$

Where, q_{max} (mg.g^{-1}) is the maximum amount of dye adsorbed per unit mass of the adsorbent and, K is the characteristic adsorption constant of the model, and n is the adsorption intensity.

2.4 Adsorption kinetics

The pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich (EL), and intra-particle diffusion(ID) models, expressed below in equations 6, 7, 8 and 9, were applied.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

$$h = k_2 . qe^2 \quad (7)$$

$$qt = \frac{1}{\beta} ln(1 + \alpha\beta t) \quad (8)$$

$$q_t = k_d t^{0,5} + C \quad (9)$$

k_1 and k_2 are the pseudo-first-order (min^{-1}) and pseudo-second-order adsorption rate constants respectively (g.mg^{-1}.min^{-1}), q_e is the adsorptive capacity at equilibrium (mg.g^{-1}), q_t is the adsorption capacity at time t (mg.g^{-1}), and h (mg.g^{-1}min^{-1}) is the initial adsorption velocity constant.

In Elovich's model, α is the initial adsorption rate (mg.g^{-1}.min^{-1}), β (g.mg^{-1}) is the desorption constant. In equation 8, C is a constant related to diffusion resistance, kd (mg.g^{-1} min$^{-0.5}$) is the velocity constant of intraparticle diffusion.

2.5 Reuse of the adsorbent

The plates were placed in adsorption for 3 h, at 20 °C and in the absence of light, after which they were exposed to a sunlight lamp (Osram®, 300W) for 180 min. At the end of exposure, the plates were immersed for 15 min in water at pH 10 and for 15 min in distilled water. Afterwards, they were dried in an oven at 50 °C for 90 min. The cycle was performed 5 times and the study was conducted in triplicate.

3. Results and discussion

3.1 Characterization of the adsorbent

The adsorption/desorption isotherm of N_2 (not shown here) of TiO_2-G5/P presents a type IV characteristic, a particularity of solids with possibly large pores, mesoporous type according to the classification of IUPAC (International Union of Pure and Applied Chemistry) [4]. Corroborating with the average pore size (3.8 nm) and total pore volume (0.31 cm^3.g^{-1}), calculated using the Barrett-Joyner-Halenda (BJH) method. As well as, the specific surface area (277 m^2.g^{-1}), calculated from the Brunauer-Emmet-Teller (BET) method.

3.2 Adsorption isotherm

Table 1 presents the equilibrium parameters obtained from the application of the models studied. The Freundlich isotherm fitted better in both conditions, indicating that the adsorption process occurs with multilayer formation with the interaction between the adsorbed molecules [5]. The value of n, between 1 and 10, suggests affinity between the dye molecules on the surface of the adsorbent [3]. Fig.1, shows the plot of the experimental data.

Table 1. Parameters of the adsorption equilibrium of RD 83 in TiO_2.

Model	**Parameters**	
	10 ºC	20 ºC
Langmuir	q_{max} = 731.54mg.g^{-1} R^2 = 0.94226 K_L= 0.048L.mg^{-1}	q_{max} =1895.55 mg.g^{-1} R^2 =0.96042 K_L=0.035 L.mg^{-1}
Freundlich	n=1.91109 R^2=0.9851 K_F=124.86 L.g^{-1}	n =1.3162 R^2= 0.96344 K_F= 84.84 L.g^{-1}
Langmuir-Freundlich	q_{max}= 904.24mg.g^{-1} R^2= 0.9392 n_S=0.683 K_S=0.048 L.mg^{-1}	q_{max}=258.88x10^{3}mg.g^{-1} R^2= 0.95887 n_S= 0.760 K_S=2.601x10^{-5}L.mg^{-1}

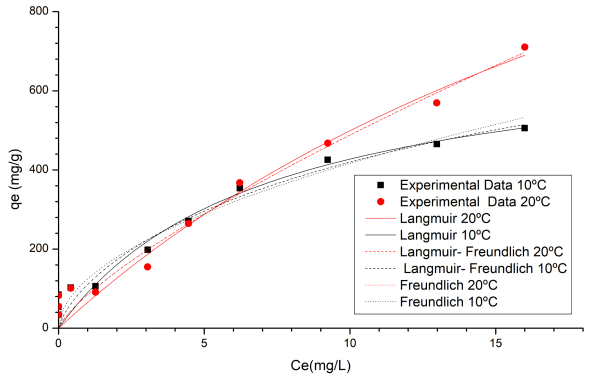


Fig. 1 Plot of C_e vs. q_e for adsorption of RD 83.

Studies with different adsorbents [6], showed that the Freundlich model obtained in fact the best fit, because it considers the adsorbate-adsorbate interactions of the system and it is an empirical equation.

3.3 Adsorption kinetics

Table 2, presents the parameters obtained from the application of the kinetic models. The adjustment of experimental data to the Elovich model proved to be quite satisfactory. This model is appropriate for gas-solid adsorption processes, however, studies conducted with dyes [7] point to the assertiveness of this model. The high α and low β values suggest that the process involves chemisorption steps [8]. Other studies [9], observed similar behavior when studying the adsorption of Acid Red 114 and Basic Blue 69 on cement powder.

Table 2. Kinetic parameters of the adsorption of RD 83 on TiO_2.

Model	Parameters	
PFO	q_{exp}= 273.39 mg.g^{-1} q_{calc}= 249.39 mg.g^{-1}	R^2 = 0.91569 K_1=0.0088min^{-1}
PSO	q_{exp}= 273.39mg.g^{-1} q_{calc}= 287.72mg.g^{-1} h = 3.3353	R^2 = 0.95194 K_1= 4.029x10^{-5} g.mg^{-1}.min^{-1}
EL	α= 7.1140 mg.g^{-1}min^{-1}	R^2= 0.98442 β=0.0166 g.min^{-1}
ID	K_d= 10.005 mg.g^{-1} min$^{-0,5}$	C = 31.1395mg.g^{-1} R^2 = 0.96964

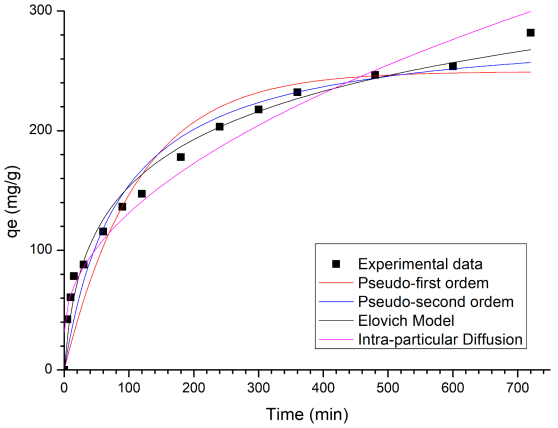


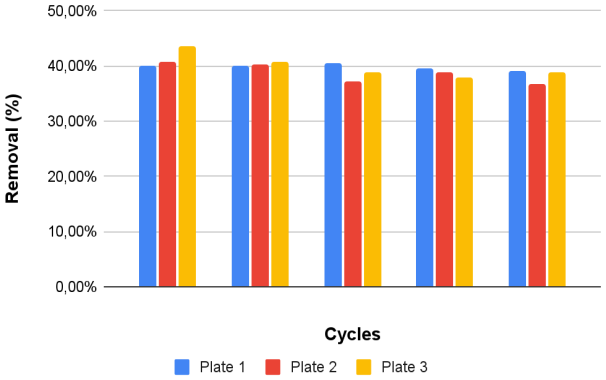
Fig.2 Plot of time vs. qe for adsorption kinetics of RD 83

3.4 Reuse of the adsorbent

In order to verify if there was detachment of TiO2, which could interfere in the adsorption of the dye, the study of the reuse of the adsorbent was performed in triplicate. In Fig. 3, it can be observed that there was no significant loss of removal efficiency after the 5 cycles, a difference of 3.23%. What corroborates with the minimum mass loss of the adsorbent equivalent to 0.0002 grams.

With a mean of 38.86% and standard deviation of 0.01%, the method is efficient, reproducible and stable. The variability of the UV incidence under the plates caused fluctuation of the % removal between plates.

Fig.3 Regeneration cycles applied for adsorbent reuse



The use of adsorbents such as modified activated carbon[10], and metallic organic structures[11] has been extensively studied and brings encouraging results. [12] Compared TiO_2 reuse by thermal, solvent elution and photocatalytic regeneration, it was concluded that photo-regeneration maintained high efficiency rate and removal stability over 5 cycles.

Beyond that, considering the low cost, possibility of complete regeneration under solar radiation and high adsorptive capacity, the TiO_2 nanocomposite is a promising alternative in the removal of dyes.

Conclusions

The present work observed the reuse of an environmental liability as a substrate in the construction of an adsorbent for contaminant removal. The results obtained indicated that the adsorption process conforms to the Freundlich isotherm and follows the Elovich kinetics. The reuse methodology pointed to the maintenance of the removal efficiency and the good stability of the impregnation of the adsorbent on the substrate.

Acknowledgements

The authors thank the National Council for Scientific and Technological Development (CNPq) and the Dean of Research and Innovation (Propesqi/UFPE) for the financial support provided.

References

[1]Sivakumar, B. Statistical modeling steadiness and dynamics of direct red 83 establishment aqueous solution by *Balsamodedron caudatum* wood waste activated nanoporous carbon. Rasāyanj. Chem, India, v. 15, n. 3, p. 1744-1749, July 2022.

[2]Kunz, Airton et al. Novas tendências no tratamento de efluentes têxteis. Química Nova [online]. 2002, v. 25, n. 1 [Acessado 17 Setembro 2022] , pp. 78-82.

[3]NASCIMENTO, Ronaldo Ferreira do (org.) et al. Processos oxidativos avançados: fundamentos e aplicações em matrizes ambientais. E-book. Fortaleza: Imprensa Universitária da UFC, 2017. 282 p. (Coleção de Estudos da Pós-graduação).

[4]Melo, Diego & do Nascimento, Ronaldo & Raulino, Giselle & Vidal, Carla & Clecius, Ari. (2020). Adsorção: Aspectos Teóricos e Aplicações Ambientais (2ed).

[5]BARROW, N. J.. THE DESCRIPTION OF PHOSPHATE ADSORPTION CURVES. **Journal Of Soil Science**, [S.L.], v. 29, n. 4, p. 447-462, dez. 1978. Wiley.

[6] PELLICER, José. et al. Adsorption Properties of β- and Hydroxypropyl-β-Cyclodextrins Cross-Linked with Epichlorohydrin in Aqueous Solution. A Sustainable Recycling Strategy in Textile Dyeing Process. Polymers, [S.L.], v. 11, n. 2, p. 252, 2 fev. 2019.

[7]TSENG, Ru-Ling; WU, Feng-Chin; JUANG, Ruey-Shin. Liquid-phase adsorption of dyes and phenols using pinewood-based activated carbons. Carbon, [S.L.], v. 41, n. 3, p. 487-495, 2003. Elsevier BV.

[8] SILVA, José E. da. et al. Study of Kinetics and Adsorption Equilibrium Employing Chemically Modified Coconut Shell for the Removal of Pb(II) from Synthetic Bath. **Revista Virtual de Química**, [S.L.], v. 10, n. 5, p. 1248-1262, 2018. Sociedade Brasileira de Química (SBQ).

[9] MAGDY, Y.H. et al.. Kinetic analysis of the adsorption of dyes from high strength wastewater on cement kiln dust. **Journal Of Environmental Chemical Engineering**, [S.L.], v. 6, n. 1, p. 834-841, fev. 2018. Elsevier BV.

[10]GOHR, Mariam Sh. et al. Adsorption of cationic dyes onto chemically modified activated carbon: kinetics and thermodynamic study. Journal Of Molecular Liquids, [S.L.], v. 346, p. 1-12, jan. 2022. Elsevier BV.

[11]WU, Ruixue; et al. Two novel Zn (II)-based metal–organic frameworks for rapidly selective adsorption and efficient photocatalytic degradation of hazardous aromatic dyes in aqueous phase. Advanced Powder Technology, [S.L.], v. 33, n. 8, p. 1-14, ago. 2022. Elsevier BV.

[12]SONG, Chuanfu. et al. Sequential combined adsorption and solid-phase photocatalysis to remove aqueous organic pollutants by H3PO4-modified TiO2 nanoparticles anchored on biochar. Journal Of Water Process Engineering, [S.L.], v. 45, p. 102467, fev. 2022. Elsevier BV.