MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Novel desert rose fiber (*Adenium obesum*) as adsorbent for Rhodamine B removal

Davisson C. Galindo[a], Kaline C. Vasconcelos[a], José L.S. Duarte[b], Vanderson B. Bernardo[a,c], Leonardo M.T.M. Oliveira[a]

[a] *Laboratório de Materiais para Remediação Ambiental (LabMARE), Centro de Tecnologia, Universidade Federal de Alagoas, Maceió, AL, Brazil*
[b] *Departamento de Ingeniería Química y de Materiales, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain*
[c] *Laboratório de Pesquisa em Recursos Naturais (LPqRN), Centro de Ciências Agrárias, Universidade Federal de Alagoas, Maceió, AL, Brazil*

Abstract

The desert rose (*Adenium obesum*) is an attractive shrub that has been studied for potential purposes beyond ornamentation. The exponential development in floriculture production, which earns billions of dollars each year globally, has led to an increase in waste of this sort of material. Thus, this work aims to evaluate the desert rose fiber as an absorbent to remove Rhodamine B dye from the aqueous solution. The material was characterized by SEM and pH_{PZC}. The adsorptive performance was tested by pH variation, adsorbate concentration, kinetics, and isothermal equilibrium studies. Adsorption was favored by reducing pH and increasing temperature for most scenarios. The decay of the Rhodamine B concentration displays that equilibrium is attained in 400 min for 10 $mg \cdot L^{-1}$. The best-fitted kinetic model was pseudo-second order. Langmuir Isotherm model had the best adjustment, obtaining a maximum adsorption capacity of 19.12 $mg \cdot g^{-1}$.

Keywords: Natural adsorbent; effluent treatment; batch test adsorption;

1. Introduction

The global search for sustainable productive activities and the advancement of research focused on streamlining procedures and lessening environmental impacts has sharply increased considering the depletion of natural reserves, shortage of hydric resources, and the growing accumulation of solid, liquid, and gas residues produced daily through conventional production processes [1,2].

Drugs, pesticides, dyes, and other chemicals may be included among these contaminants. Rhodamine B (RhB) is a cationic dye extensively utilized as a tracer stain in scientific fields and the textile industry [3]. In addition to being used as a tracer for hydrological studies [4] and in pens, paints, leather, inks, and fireworks [5], RhB is also found in food coloring, despite most nations banning its usage for this purpose [6]. All these uses have the potential to contaminate water supplies [4].

Decades of research have shown the harmful effects of RhB on human and animal cells, which appear through both acute and chronical exposures [3]. The adverse impacts on human fibroblasts have been demonstrated in recent studies [7]. In several species, this dye can also result in mutagenesis and cancer [8,9].

These studies show how important it is to reduce the concentration of the dye in water bodies. Furthermore, several authors have already used biomasses to treat RhB, including modified orange peel (with removal of 3.58 $mg \cdot g^{-1}$) [10], kapok pods (39.29 $mg.g^{-1}$) [3], banana peel (16.66 $mg \cdot g^{-1}$) [11], as well as leaves and roots of *Eichhornia crassipes* (27.15 $mg \cdot g^{-1}$ and 44.60 $mg \cdot g^{-1}$, respectively) [12]. Thus, aiming to compare the potentiality of a novel biomass material with commonly used ones, RhB was used to investigate the adsorptive capacity of the desert rose fiber (DRF), a particular kind of floricultural waste.

Desert rose (*Adenium obesum*), family Apocynaceae, is primarily an ornamental plant, although traditional medicine uses all components of this plant to treat numerous illnesses [13]. When the bloom reaches maturity, DRFs are produced, and they are responsible for preserving and dispersing the seeds after the desert rose pod opening.

Therefore, this work aims to evaluate the potential application of DRFs, a part of the plant discarded after cultivation, to the removal of RhB using distilled water, to suggest the biosorption mechanism, making the raw DRFs a product able to act in environmental remediation process.

2. Experimental

Chemicals and raw materials

The DRF was obtained from a craft production located in Maceio city, Alagoas, Brazil. Rhodamine B, analytical grade (Êxodo Científica LTDA) was selected as the pollutant target. For the general testes, distilled water was used to create solutions of RhB at 2, 10, 50 and 100 mg·L^{-1}. Acid and base solutions were used to adjust pH as needed, using HCl, 0.1 M (37.0 % Dinâmica LTDA), and NaOH, 0.1 M (≥99.0 %, Dinâmica LTDA).

Material preparation

The fiber was separated from seed and pod and used *in natura* in all experiments.

Characterization

The SEM analyzes were performed using a Scanning Electron Microscope (SEM), SSX-550 Superscan, Shimadzu). The samples were submitted to a previous process of metallization via platinum bath for 5 min and gold bath for 5 min at a current of 10 mA, using a Sanyu Electron metallizer model Quick Coater SC-701. After that, the material was analyzed via detection of secondary electrons with magnification of 500-1000x and voltage of 12 kV. The Point of Zero Charge pH (pH_{PZC}) was determined by the methodology used by Haddad et al. (2014) [14].

Adsorption studies

A shaking incubator (Shel Lab) was used to agitate the samples at 150 rpm, and a spectrophotometer (UV-Vis Shimadzu, model UV-1800) was used to determine the adsorbate concentration in solution, at 554 nm. All experiments were conducted in duplicate.

The effect of pH was carried out at four pH values. RhB solution (25 mL, 50 mg·L^{-1}) was prepared at 303 K and the pH was adjusted, using NaOH and HCl solutions, to 3, 5.65 (natural), 7, and 11. The adsorption capacity at any time (q_t, mg·g^{-1}) and the RhB removal percentage (%) were calculated by Eqs. (1) and (2), respectively.

$$q_t = \frac{(C_0 - C_t)}{m} * V \qquad (1)$$

$$\% \, removal = \frac{(C_0 - C_t)}{C_0} * 100 \qquad (2)$$

where C_0 is the initial concentration of the adsorbate in the liquid phase (mg·L^{-1}), C_t is the equilibrium concentration of the adsorbate in the liquid phase (mg·L^{-1}), V is the volume of solution (L), and m is the mass of adsorbent (g).

The kinetic studies were conducted varying the initial concentrations from 10 and 50 mg·L^{-1} at natural pH. RhB solution (25 mL) and 0.05 g of DRF were shaken at 303 K, and the absorbance was measured at time intervals of 0, 5, 15, 30, 60, 240, 420, and 1440 min. The data obtained were evaluated through mathematical models to describe the behavior of adsorption kinetics and fitted by the kinetic mathematical models: pseudo-first order and pseudo-second order, also Vasconcelos *et al.* [3].

Equilibrium study

Equilibrium data was fitted to the Langmuir and Freundlich models, as used by Xiao *et al.* [15].

3. Results and discussions

Characterization

The material surface morphology highlights the tubular shape of the fiber, with a diameter of roughly 40 µm, which may explain its ultralightweight. A rough surface can be also observed, and this may facilitate the adsorption of materials on it. The topography is mostly constant along the fiber.

The Point of Zero Charge pH shows that the region of neutrality of the fiber occurs at pH around 4.7, it means that when the pH of the solution is higher than this value, the surface of the material becomes negatively charged, otherwise, the surface is protonated. So, as the RhB is a cationic dye, it is expected that the adsorptive mechanism would be favored at alkaline pH.

Adsorption study

The effect of pH exerted a significant influence on RhB adsorption. The removal efficiencies found were 36.81 %, 36.11 %, 24.21 %, and 21.09 % for pHs 3, 5.65 (natural), 7 and 11, respectively, after 24 h contact. The adsorptive process was enhanced at pH 3, while the lowest removal rate was seen at pH 11. Even though the dye is cationic, the adsorption process was more efficient in the solution at pH 3 and less so at pH 11. It shows a complex relationship between RhB and DRF, in which there may be some form of interaction between the various functional groups present on the surface of the adsorbent at different pH values, as pointed out by Vasconcelos *et al.* [3].

According to the experimental curves for solutions at 10 and 50 mg·L^{-1}, it is evident that after around 400 minutes of interaction, the equilibrium at 10 mg·L^{-1} was reached. However, for the 50 mg·L^{-1} solution, the curve reached equilibrium after 24 hours. For the 10 mg·L^{-1} solution, approximately 87 % of the maximum adsorptive capacity (1.21 mg·g^{-1}) was reached in 240 min, and 66 % (0.92 mg·g^{-1}) in 120 min. More research on the removal of RhB had similar results [3]. The rapid initial decay in the first 120 minutes for both concentrations probably happens due to rugosity on the fiber surface. The long period taken for the solution of 50 mg·L^{-1} to reach the equilibrium may be due to the tubular shape of the fiber, it might take time for the solution to overcome the capillary force and fill the inside of the fiber, where the dye would also be absorbed.

Compared to other adsorbents, the desert rose fiber performed equivalent to other papers found in the literature. Although it might take some time to achieve equilibrium, the fact that the material is natural significantly decreases the cost of the procedure while still providing outstanding removal results, particularly for solutions with less than 50 ppm of RhB.

Table 1 shows the adjustment parameters to the adsorption models, where the pseudo-second order model presents the best fit, with R^2 and adjusted R^2 higher than 0.98. The data in Table 1 cannot be used to confirm what adsorption process is occurring in the system; nevertheless, the presence of chemisorption may be deduced from the best fit of the PSO model.

Table 1. Kinetic parameters of pseudo-first order (PFO) and pseudo-second order (PSO).

Model	10 mg·L^{-1}	50 mg·L^{-1}
PFO		
q_e (mg·g^{-1})	4.2030	0.9251
k_1 (min^{-1})	-1.6*10^{-6}	-3.1*10^{-6}
R^2	0.9760	0.7785
Adj. R^2	0.9720	0.7416
PSO		
q_e (mg·g^{-1})	1.5092	8.5034
k_2 (g^{-1}·mg·min^{-1})	2.29*10^{-2}	2.17*10^{-3}
R^2	0.9973	0.9892
Adj. R^2	0.9969	0.9874

Equilibrium isotherms

Equilibrium adsorption isotherms are commonly used to explain the interaction of a solute and an adsorbent in solution.

The behavior of Rhodamine B adsorption on the DRF surface was analyzed at different concentrations, and the system temperature increased from 303 K to 333 K, whose adsorption data was studied by Langmuir and Freundlich isotherm models. Table 2 summarizes all the parameters from these two isotherms.

Table 2. Isotherm models parameters for adsorption of RhB on DRF.

Langmuir Isotherm				
Temp (K)	q_{max} (mg/g)	K_L (L/mg)	R^2	Adj. R^2
303	10.8555	0.0871	0.9657	0.9486
318	41.1415	0.0076	0.9920	0.9879
333	55.6457	0.0079	0.9998	0.9997
Freundlich Isotherm				
Temp (K)	K_F (mg/g)·(mg/L)$^{1/n}$	n	R^2	Adj. R^2
303	1.6908	2.5035	0.8534	0.7801
318	0.6387	1.3692	0.9983	0.9975
333	0.7103	1.2705	0.9988	0.9983

For all temperatures, Langmuir model presents the best adjustment, reaching the highest values of coefficient of determination (R^2 > 0.96), and adjusted coefficient of determination (Adj. R^2 > 0.94). The Langmuir model also showed adsorption capacities compatible with the experimental values, increasing from 10.86 $mg \cdot g^{-1}$ to 55.65 $mg \cdot g^{-1}$, with the rise of temperature from 303 K to 333 K. This result suggests that the adsorption was characterized by being monolayer on a homogenous surface.

Conclusions

The primary goal of this study was to show the potential of desert rose fiber as a low-cost adsorbent to be employed in the treatment of liquid effluents polluted with RhB, and it provides promising results. Favorable results of adsorption capacity were obtained under natural pH conditions, ideal if it is intended to use the adsorbent in effluent treatment. Pseudo-second order model and Langmuir isotherm model were the best adjustments for this study scenarios.

Acknowledgements

The authors are grateful for the support of LabMARE (Laboratório de Materiais para Remediação Ambiental), LEAp (Laboratório de Eletroquímica Aplicada), and GON (Grupo de Ótica e Nanoscopia). All these labs are located at UFAL (Universidade Federal de Alagoas), A.C. Simões Campus.

References

[1] L.M.T.M. Oliveira, L.F.A.M. Oliveira, A.F. Sonsin, J.L.S. Duarte, J.L. Soletti, E.J.S. Fonseca, L.M.O. Ribeiro, L. Meili. Ultrafast diesel oil spill removal by fibers from silk-cotton tree: characterization and sorption potential evaluation, J. Clean. Prod. 263 (2020), 121448.

[2] D.H.S. Santos, J.C.P.L. Paulino, G.F.S. Alves, L.M.T.M. Oliveira, P.C. Nagliate, J.L.S. Duarte, L. Meili, J. Tonholo, C.L.P.E.S. Zanta. Effluent treatment using activated carbon adsorbents: a bibliometric analysis of recent literature, Environ. Sci. Pollut. Res. 28 (2021) 32224-32235.

[3] K.C. Vasconcelos, S.G. Alencar, A.B. Ferro, L.F.A.M. Oliveira, E.J.S. Fonseca, V.B. Bernardo, C.L.P.S. Zanta, J.L.S. Duarte, L.M.T.M. Oliveira. Novel kapok pods (Ceiba pentandra (L) Gaerth) absorbent and its reusability by transformation on hydrochar with an outstanding adsorptive capacity for Rhodamine B removal. Separation and Purification Technology 326 (2023) 124787.

[4] A.A. Al-Gheethi, Q.M. Azhar, P.S. Kumar, A.A. Yusuf, A.K. Al-Buriahi, R.M.S.R. Mohamed, M.M. Al-Shaibani. Sustainable approaches for removing Rhodamine B dye using agricultural waste adsorbents: a review, Chemosphere 287 (2022), 132080.

[5] L.M. Skjolding, K.S. Dyhr, C.J. Koppl, U.S. McKnight, P. Bauer-Gottwein, P. Mayer, P.L Bjerg, A. Baun. Assessing the aquatic toxicity and environmental safety of tracer compunds Rhodamine B and Rhodamine WT, Water Res. 197 (2021), 117109.

[6] Q. Lu, W. Gao, J. Du, L. Zhou, Y. Lian. Discovery of Environmental Rhodamine B Contamination in Paprika during the Vegetation Process, J. Agric. Food Chem. 60 (2012) 4773-4778.

[7] T. Kaji, T. Kawashima, M. Sakamoto, Y. Kurashige, F. Koizumi. Inhibitory effect of rhodamine B on the proliferation of human lip fibroblasts in culture, Toxicology 68 (1) (1991) 11-20.

[8] V.M. Vucorovic, R.N. Razmovski, U.D. Miljic, V.S. Puskas. Removal of cationic and anionic azo dyes from aqueous solutions by adsorption on maize stem tissue, J. Taiwan Inst. Chem. Eng. 45 (2014) 1700-1708.

[9] J. Goscianska, M. Ptaszkowska, R. Pietrzak. Equilibrium and kinetic studies of chromotrope 2R adsoption onto ordered mesoporous carbons modified with lanthanum, Chem. Eng. J. 270 (2015) 140-149.

[10] A.A. Oyekanmi, A. Ahmad, K. Hossain, M. Rafatullah. Statistical optimization for adsorption of Rhodamine B dye from aqueous solutions, J. Molecular Liquids 281 (2019), 48-58.

[11] F. Shen, D. Shen, F. Shen, C. Wu, S. Gu. Kinetics, equilibrium and thermodynamics studies on biosorption of Rhodamine B from aqueous solution by earthworm manure derived biochar, International Biodeterioration & Biodegradation 120 (2017) 104-114.

[12] H. Saufi, M. El Alouani, J. Aride, M. Taibi. Rhodamine B biosorption from aqueous solution using Eichhornia crassipes powders: Isotherm, kinetic and thermodynamic studies, Journal of Cleaner Production 198 (2018) 1302-1310.

[13] M.A. Farah, M.A. Ali, S.M. Chen, F.M. Al-Hemaid, F.M. Abou-Tarboush, K.M. Al-Anazi, J. Lee. Silver nanoparticles synthesized from *Adenium obesum* leaf extract induced DNA damage, apoptosis and autophagy via generation of reactive oxygen species, Colloids and Surfaces B: Biointerfaces 141 (2016), p. 158-169.

[14] M. El Haddad, A. Regti, M.R. Laamari, R. Slimani, R. Mamouni, S. El Antri, S. Lazar, Calcined mussel shells as a new and eco-friendly biosorbent to remove textile dyes from aqueous solutions, J. Taiwan Institute of Chemical Engineering, 45 (2014), p. 533-540.

[15] W. Xiao, Z.N. Garba, S. Sun, I. Lawan, L. Wang, M. Lin, Z. Yuan, Preparation and evaluation of an effective activated carbon from white sugar for the adsorption of rhodamine B dye, Journal of Cleaner Production 253 (2020) 119989.