

Inovações e Soluções Sustentáveis em Engenharia Ambiental

Synthesis and characterization of a sustainable adsorbent from WTP sludge and orange peel: application for removal of reactive blue BF5G dye

Síntese e caracterização de adsorvente sustentável a partir de lodo de ETA e casca de laranja: aplicação para remoção de corante reativo azul BF5G

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ABSTRACT

This study produced and characterized a mixed adsorbent material from Water Treatment Plant (WTP) sludge and orange peel waste (*Citrus sinensis* (L.) Osbeck) for use in the removal of Reactive Blue BF 5G dye from aqueous solutions. The pellets were thermally treated at 950°C. The material produced, named MAT, was characterized for its chemical and surface properties using XRF, XRD, FTIR, SEM, BET, PZ, and pH-PCz. The results reveal that MAT showed promising chemical and mineralogical composition for adsorption, with a predominance of silica (>45%) and aluminum (>30%), a mesoporous and rough surface, negative charge under neutral conditions, and a buffering effect at pH 5.7. The dye removal efficiency of MAT was evaluated in terms of solution pH, temperature, contact time, and MAT mass. The results showed that MAT exhibited adsorption capacity and removal efficiency with the best performance at pH 3. The process was favorable at room temperature and rapid, using just one unit of the pellet. However, the adsorption capacity was lower than expected ($q < 0.26 \text{ mg g}^{-1}$), suggesting that sintering at lower temperatures might be more suitable to optimize its effectiveness.

Keywords: Treatment; Residues; Textile industry

RESUMO

Este trabalho produziu e caracterizou um material adsorvente misto a partir do lodo de Estação de Tratamento de Água (ETA) e resíduos de casca de laranja (*Citrus sinensis* (L.) Osbeck) visando sua aplicação na remoção do corante azul reativo BF 5G de soluções aquosas. As pastilhas foram tratadas termicamente a 950°C. O material produzido, denominado MAT, foi caracterizado quanto a propriedades

químicas e de superfície por FRX, DRX, FTIR, MEV, BET, PZ e pH-PCz. Os resultados revelam que a MAT apresentou composição química e mineralógica promissora para adsorção, com predominância de sílica (>45%) e alumínio (>30%), superfície mesoporosa e rugosa, com carga negativa em condição neutra e efeito tampão em pH 5,7. A eficiência de remoção do corante pela MAT foi avaliada quanto ao pH da solução, temperatura, tempo de contato e massa da MAT. Os resultados mostraram que a MAT apresentou a capacidade de adsorção e eficiência de remoção com melhor desempenho em pH 3. O processo mostrou-se favorável em temperatura ambiente e rápido, aplicando apenas uma unidade da pastilha. No entanto, a capacidade de adsorção foi inferior ao esperado ($q < 0,26 \text{ mg g}^{-1}$), sugerindo que a sinterização a temperaturas menores pode ser mais adequada para otimizar sua eficácia.

Palavras-chave: Tratamento; Resíduos; Indústria têxtil

1 INTRODUCTION

The textile industry is one of the largest and oldest sectors in the world, playing a significant role in job creation and economic growth (Kaushal and Mahajan, 2022). According to Rendón-Castrillón et al. (2023), the global fashion and apparel market was valued at US\$993.6 billion in 2021, with an expected annual growth rate of 4% until 2030. However, this industry consumes approximately 300 liters of water per kilogram of fabric produced and is responsible for 20% of global wastewater production (Can-Güven et al., 2024; Ma et al., 2024).

Textile wastewater contains organic dyes and various chemical stabilizers, along with washing, bleaching, and color-fixing agents (Uğan et al., 2024). It is estimated that 1.6 million tons of dyes and pigments are consumed annually (Elgarahy et al., 2023), with 10 to 15% of this volume being discharged into water bodies (Du et al., 2022), posing a significant threat to water security (Wong et al., 2020).

Dyes can originate from either natural or synthetic sources. Natural dyes are extracted from living organisms, such as plants and animals, which provide pigments like luteolin and betanin, derived from daisy flowers and beetroot, respectively (Kushwaha et al., 2024). Synthetic dyes, such as rosaniline and reactive blue, are produced through organic synthesis (Zanoni and Yamanaka, 2016). In the industry, synthetic dyes are more prevalent due to their superior color properties and lower

cost (Uğan et al., 2024). Beyond their origin, these compounds can be classified based on their chemical structure, color, application, and particle charge in aqueous media (Streit et al., 2024).

Among the major classes of dyes based on chemical structure, the azo group is particularly notable, accounting for 60% of annual dye production (Elgarahy *et al.*, 2023). In terms of application, azo dyes comprise 30% of the dyes used in the textile industry (Freire-Boina et al., 2024). Depending on their charge in solution, they can be either cationic or anionic, both of which are soluble in water and pose significant environmental risks (Haag and Ibsch, 2022).

Reactive blue BF 5G is an azo dye characterized by complex aromatic rings and stable functional groups containing N=N double bonds, which are highly toxic and carcinogenic (Elgarahy et al., 2023). Maeda et al. (2019) describes this dye as dark in color, non-flammable, with a solubility of 100 g L⁻¹ (at 25 °C), a molecular weight of 1.051 g mol⁻¹, and a molecular size of 24.16 Å. It exists in an anionic form due to its sulfonic acid group, with four negative sites balanced by Na⁺ cations (Colte et al., 2020).

Due to the presence of these organic compounds in textile effluent, conventional wastewater treatment processes are ineffective, as the dyes possess resistant structures and low biodegradability (Can-Güven et al., 2024). In this context, adsorption emerges as an efficient alternative, offering operational simplicity and low cost (Zonato et al., 2022; Martins et al., 2022; Freire-Boina et al., 2024).

Among the adsorbent materials that have demonstrated good efficiency in dye removal are raw or chemically treated agricultural residues (Castro et al., 2021; Ramos et al., 2022; Khan et al., 2024). Orange peel is one of the most widely used agricultural residues in adsorption tests due to its chemical composition, which is rich in pectin, hemicellulose, cellulose, and lignin (Feltrin and Cechinel, 2024; Souza et al., 2019). These components contain polar functional groups, such as carboxylic and phenolic groups, that provide a porous surface for the adsorbent (Feltrin and Cechinel, 2024; Souza et al., 2019; Sousa et al., 2021).

Another residue that has recently been investigated for dye removal is sludge from Water Treatment Plants (WTP). WTP sludge is generated in large volumes during the coagulation, flocculation, decantation, and filtration stages of water treatment (Freire-Boina et al., 2024). According to Nayeri and Mousavi (2022), 'the average sludge production is estimated to be 3.8 kg per inhabitant', with a tendency to increase alongside population growth and rising demand for drinking water. WTP sludge can be used as an adsorbent in its raw form or after physical and/or chemical activation (Martins et al., 2022). Its chemical and mineralogical composition, combined with the absence of acquisition costs, has increased interest in its use (Siswoyo et al., 2022).

Table 1 – Main results obtained from the application of WTP sludge and orange peel in the adsorption of various dyes

Adsorbent	Dye	D g	C ₀ mg L ⁻¹	pH	T °C	ER %	q _e mg g ⁻¹	t _e min.	q _{max} mg g ⁻¹	Reference
Dried orange peel	Malachite green	2.5	25 - 200	8	25 - 45	62	NR	100	42.55	Maheshwari et al. (2023)
Orange peel (activated with phosphoric acid)	Methylene blue	0.01 - 0.8	50 - 200	2 - 10	25	98	NR	20	38	Ramutshatsha-Makhwedzha et al. (2022)
Orange peel (hydrochar)	Methyl orange	0.5	75	3	25	89.2	NR	60	113.3	Hamad et al. (2024)
Orange pomace (in natura)	Reactive blue BF 5G	0.3	100	2	40	84	15.1	240	32.65	Freitas et al. (2019)
Orange peel (activated biochar)	Cationic methylene blue	0.1 - 0.5	0 - 1.100	7 - 8	25	99	378.89	1.440	382.15	Bediako et al. (2019)
Electrocoagulated WTP sludge	Red 28	0.1 - 2	20 - 80	2 - 10	25 - 80	NR	NR	NR	NR	Aragaw (2020)
Thermally treated WTP sludge	Reactive blue BF 5G	0.45	1 - 30	3	25	60 - 90	1.65	2.880	0.765	Freire-Boina et al. (2024)
WTP sludge sintered with clay material	Rosaniline	6 - 6.5	15 - 50	NR	25	NR	0.19	NR	NR	Shalaby et al. (2017)

Source: Authorship (2024)

Note: D: dosage (g); C₀: initial dye concentration (mg L⁻¹); T: temperature (°C); ER: removal efficiency (%); t_e: equilibrium time (minutes); q_e: adsorption capacity at equilibrium time (mg g⁻¹); q_{max}: maximum adsorption capacity (mg g⁻¹); NR: Not reported

Table 1 provides a summary of the main results obtained in dye adsorption using two residues: orange peel and WTP sludge. The studies indicate that orange peel demonstrated favorable adsorption capacity ($30 < q_{\max} < 400 \text{ mg g}^{-1}$) at acidic to neutral pH, for dye concentrations ranging from 25 to 1.000 mg L^{-1} . This process is fast and influenced by temperature. In contrast, WTP sludge exhibits a slower adsorption process, which is dependent on the solution's pH and surface characteristics, such as porosity and functional groups.

Freire-Boina et al. (2024) suggest that WTP sludge, given its potential, should undergo chemical activation to introduce active sites, thereby increasing the reaction rate and adsorption capacity. Building on these findings, this study introduces a novel approach by developing and characterizing a mixed composition tablet (MAT) made from WTP sludge and orange peel, demonstrating its viability for the removal of textile dyes, particularly reactive blue BF 5G.

The study produced an easy-to-apply, non-powdered product designed to facilitate use in adsorption separation processes. Additionally, the product was developed to be both durable and sustainable. It is expected to provide an environmentally appropriate disposal option for both precursor residues, while offering a low-cost solution for treating wastewater from the textile industry.

2 MATERIALS AND METHODS

2.1 Preparation of precursors and production of mixed adsorbent tablets

The WTP sludge used in this study was provided by a sanitation company responsible for the Water Treatment Plant (WTP) in a city located in the interior of São Paulo State, Brazil. The WTP operates using a conventional cycle, employing polyaluminum chloride (PAC) as a coagulant and a non-ionic polyelectrolyte as a coagulation aid. The sludge sample was drained on a geotextile blanket (105 g m^{-2}) placed in a conical-bottomed box, kept in the shade, and then dried in an oven at 90°C .

($\pm 5^{\circ}\text{C}$) to remove residual moisture. Afterward, the material was crushed in a mortar, ground in a plate mill, and sieved (42 Tyler), producing a fine powder referred to as Dry Dewatered Sludge (DDS).

The oranges used were pear-shaped (*Citrus sinensis* (L.) Osbeck), purchased locally. Before use, the fruits were cleaned under running water. The epicarp was then separated from the endocarp, which was rinsed with distilled water and cut into smaller pieces. The material was dried in a forced-air oven at 60°C ($\pm 5^{\circ}\text{C}$) for 24 hours. The dried orange peel was crushed in a knife mill, pulverized in a micronizer, and passed through a sieve ($<0.355\text{ mm}$). This product was referred to as Dried Orange Peel (DOL).

The Mixed Adsorbent Tablet (MAT) was produced using a mixture of 95% DDS and 5% DOL. The mixture was divided into 0.50 g portions, weighed on an analytical balance with an accuracy of $\pm 0.001\text{ g}$. These portions were molded into circular tablets with a diameter of 13 mm and a thickness between 1 and 2 mm, using a hydraulic press at 60 kN for 3 minutes. The resulting tablets were sintered in a muffle furnace in two stages: first, from room temperature to 450°C , and then from 450°C to 950°C , with a heating rate of $5^{\circ}\text{C min}^{-1}$ and a 2-hour dwell time at each stage. The final product was referred to as the Mixed Adsorbent Tablet (MAT).

2.2 Mineralogical, chemical and surface properties of DDS, DOL and MAT

In order to understand the elemental chemical composition, DDS, DOL and MAT were characterized by X-ray Fluorescence (XRF). The pulverized samples were placed in a polymeric material capsule, retained by a mylar. The primary radiation source used was a Rhodium (Rh) cathode incident on a 5mm diameter collimator, with scanning capacity from Sodium (Na) to Uranium (U), operating in a controlled atmosphere and room temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

To verify the presence of possible functional groups of MAT and its precursors, Fourier Transform Infrared Spectroscopy (FTIR) was used, with a wave number ranging from $4,000$ to 500 cm^{-1} .

To understand the surface structure, verify porosity characteristics and morphology, the materials were also characterized by Scanning Electron Microscopy (SEM). For this analysis, the samples were covered with a thin layer of gold and analyzed at 1,000x magnification.

The crystalline phases of DDS and MAT were identified using X-ray Diffractometry (XRD). The measurements were conducted with CuK α radiation ($\lambda = 1.5405 \text{ \AA}$), generated at 40 kV and a current of 30 mA. The angular scanning measurements were performed over a range of 2θ from 10° to 90° , with a scanning speed of 10° per minute and a sampling interval of 0.02° . The peaks observed were identified through a direct comparative method, comparing the obtained diffractograms with records from the crystallographic database JCPDS-ICDD (Joint Committee on Powder Diffraction Standards - International Center for Diffraction Data).

The specific surface area (S_{BET}), pore volume (V_p), and pore diameter (D_p) were determined from the nitrogen (N_2) adsorption and desorption isotherms, evaluated using a gas sorption analyzer and calculated with the Brunauer-Emmett-Teller (BET) equation. All tests were performed in duplicate, and the average values were reported.

Additional information on surface charges was obtained through Zeta potential measurements at neutral pH and the Zero Charge Point (pH-ZPC) using the 11-point method as outlined by Regalbuto and Robles (2004). The analyses were performed at room temperature ($25^\circ\text{C} \pm 2^\circ\text{C}$) and conducted in duplicate.

2.3 Preparation of synthetic effluent

The synthetic effluent was prepared using powdered reactive blue dye BF 5G, supplied by a laundry in the State of Paraná, Brazil. The solutions were prepared as needed by diluting a standard solution of 100 mgL^{-1} to the appropriate volume.

The synthetic effluent containing the dye was analyzed using ultraviolet-visible (UV-Vis) spectroscopy within the range of 325 to 800 nm, which identified an absorption peak at 620 nm. A calibration curve for the BF5G dye was established using solutions

with concentrations ranging from 1.0 to 30.0 mgL⁻¹, with the zero point adjusted using a blank test (distilled water). This calibration curve was utilized to determine the initial and final concentrations of the dye samples during the adsorption experiments.

2.4 Batch adsorption tests

Batch tests were conducted to evaluate the effectiveness of MAT in removing the reactive blue dye BF 5G. Solutions containing the dye at a concentration of 10 mgL⁻¹ were used, with variations in the following parameters: pH, temperature, mass or quantity of tablets, and contact time. All tests were performed in a temperature-controlled shaker oven with an accuracy of $\pm 2^{\circ}\text{C}$, using 50 mL of the effluent at a stirring speed of 120 rpm, and each test was performed twice (in duplicate).

Initially, the effect of pH on the adsorption process was investigated. For this purpose, approximately 0.30 g of MAT was added to the synthetic effluent at three different pH levels: 3, 6, and 9. The temperature was maintained at 25°C, and the contact time was set at 24 hours. Adjustments to the pH of the synthetic effluent were made using 0.1 molL⁻¹ solutions of H₂SO₄ or NaOH. The results of this test will help determine the optimal pH for future investigations.

The influence of the mass or quantity of MAT on the removal of the reactive blue dye BF 5G was evaluated at 25°C for 24 hours at the ideal pH. The quantities of tablets tested were: 1 unit (~0.30 g), 2 units (~0.60 g), and 3 units (~0.90 g). Additionally, the effect of contact time was examined using 2, 12, and 24-hour intervals, maintaining the ideal pH and tablet quantity at 25°C. Lastly, the influence of temperature was investigated at 25°C, 35°C, and 45°C, using one unit of MAT (~0.30 g) for the treatment of the synthetic effluent at the ideal pH over a duration of 24 hours.

The adsorption capacity (q , in mg g⁻¹), also referred to as the adsorption rate, and the removal efficiency (ER, in %) of the process were calculated using the following equations:

$$q = \frac{(C_o - C_e)}{m} \cdot V \tag{1}$$

$$ER = \frac{(C_o - C_f)}{C_o} \cdot 100 \tag{2}$$

Where:

C_o is the initial concentration of the solute (mg L⁻¹);

C_e is the final concentration of the solute at equilibrium (mg L⁻¹);

C_f is the final concentration of the treated solution (mg L⁻¹);

V is the volume of the solution (L);

m is the mass of the dry MAT adsorbent (g).

3 RESULTS AND DISCUSSION

3.1 Chemical and mineralogical composition

The chemical composition (Table 2) of DDS and MAT revealed a predominance of silica (>45%) and aluminum (>30%). In DOL, potassium (>40%) and calcium (>30%) were the most significant components. Additionally, no harmful or dangerous chemical elements were detected.

Table 2 – Elemental chemical composition of DDS, DOL, and MAT sintered at 950 °C

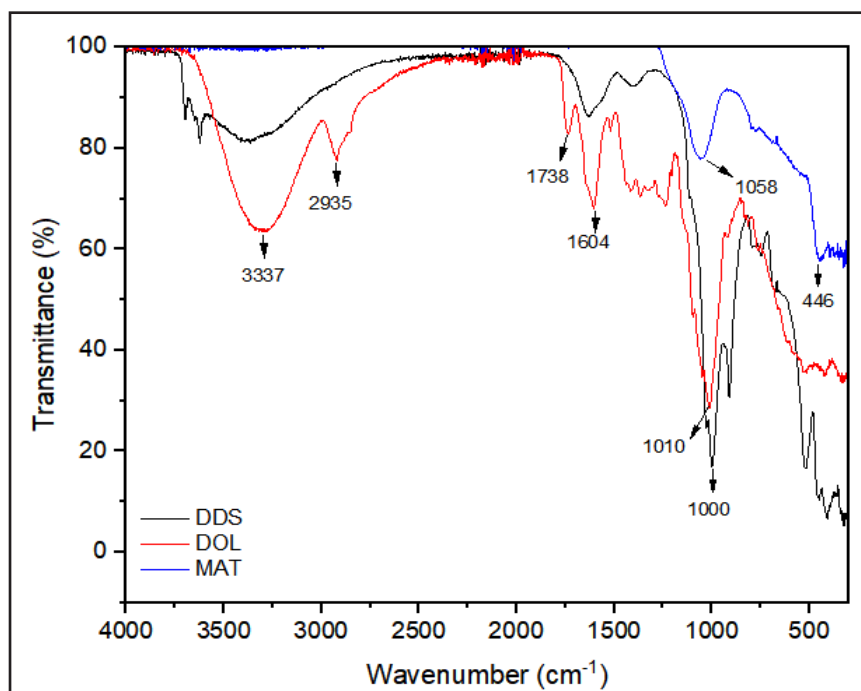
Element (%)	DDS	DOL	MAT
SiO ₂	50.09	8.20	50.44
Al ₂ O ₃	33.35	-	34.74
Fe ₂ O ₃	10.75	-	9.19
TiO ₂	2.09	-	-
K ₂ O	1.58	44.30	1.62
CaO	-	35.19	-
P ₂ O ₅	-	5.06	-
Outros	2.14	1.93	2.13

Source: Authorship (2024)

The MAT exhibited the composition of the predominant precursor, with a minor presence of potassium from the activating component. García et al. (2023) and Cruz et al. (2023) indicate that organic compounds tend to volatilize at high temperatures. The degradation of hemicellulose, cellulose, and lignin occurs between 400°C and 700°C (Agostinho et al., 2021). This suggests that the elements from the DOL may not have endured the temperatures used during tablet synthesis, leading to their release in the process. Such an effect could be advantageous, as it may enhance the tablets' porosity and surface area, making them more favorable for adsorption.

Regarding the functional groups (Figure 1), the peaks identified in DDS between 1,170 cm^{-1} and 1,000 cm^{-1} are attributed to the vibrational mode of the OH^- group in mineral compounds, with silicates also being absorbed in this region. Additionally, an asymmetric stretch of Si-O-Si and Si-O-Al occurs between 1,003 cm^{-1} and 1,030 cm^{-1} , while the vibration of the Al-O-Si bond is observed within the 400 cm^{-1} to 800 cm^{-1} bands (Kumar e Lingfa, 2020).

Figure 1 – FTIR spectrum for DDS, DOL and MAT

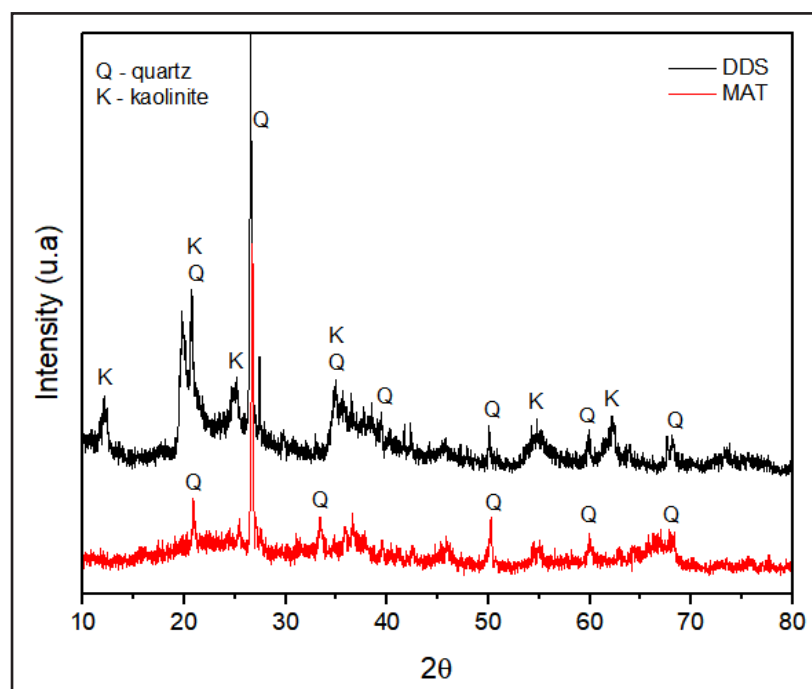


Source: Authorship (2024)

In DOL, there is a noticeable shift in the intensity of the transmittance peaks. The peaks between $3,337\text{ cm}^{-1}$ and $1,000\text{ cm}^{-1}$ are associated with the vibrations of O–H, –CH, –OH, –C–O, –COO, and –C=O, indicating the presence of carboxylic acids, alcohols, phenols, esters, and aromatic groups (Ramutshatsha-Makhwedzha et al., 2022). These functional groups are found in pectin, cellulose, and lignin derived from orange peel (Gnanasambandam e Proctor, 2000; Filho et al., 2020). In contrast, MAT contains the mineral functional groups characteristic of DDS.

The mineralogical composition (Figure 2) in the DDS and MAT samples showed crystalline phases of quartz (SiO_2) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). This composition is interesting for the use of MAT as an adsorbent. Trach et al. (2022) used kaolinite as an adsorbent, obtaining good nickel removal results at pH3. Shalaby et al. (2017) and Guerra et al. (2008) present quartz and kaolinite as interesting materials in adsorption processes and El-Tawil et al. (2019) removed 96% of mercury using quartz as an adsorbent.

Figure 2 – X-ray diffractogram of DDS and MAT

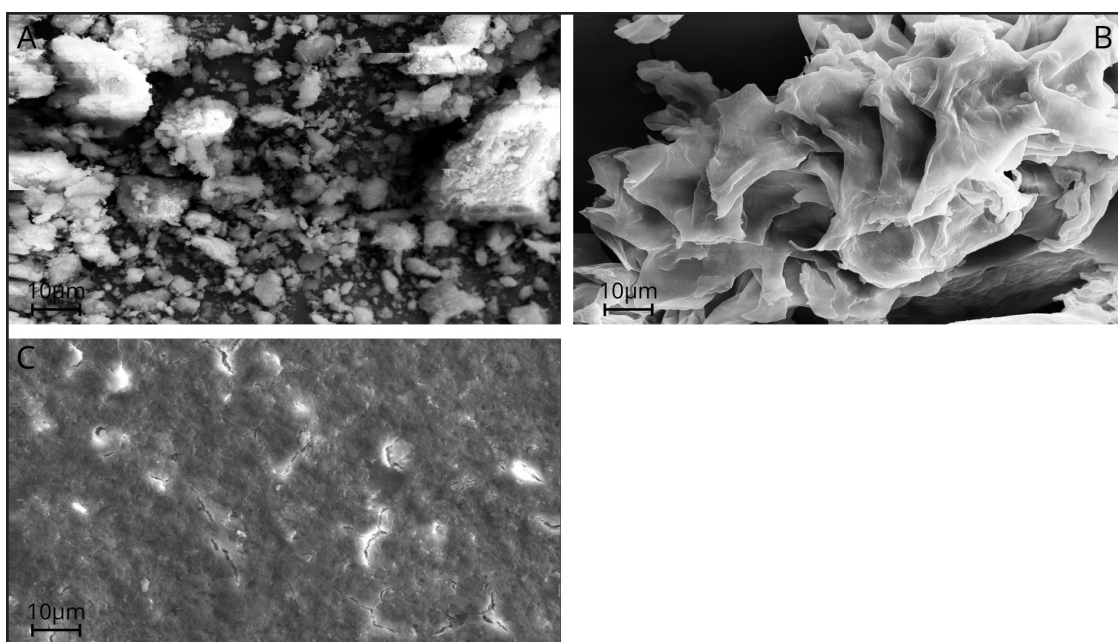


Source: Authorship (2024)

3.2 Morphology, porosity and surface charge

Figure 3 illustrates the texture characteristics of the surfaces of DDS (A), orange peel (B), and MAT (C) at a magnification of 1000x. The images highlight the roughness of the DDS and DOL surfaces, as well as the widely distributed cracks present on the MAT surface.

Figure 3 – Scanned electron microscopy images of DDS (A), DOL (B), and MAT (C) at 1,000x



Source: Authorship (2024)

According to Mouratib et al. (2020), sintering effects are minimal at temperatures below 950°C, resulting in poorly consolidated sludge particles and relatively large intergrain pores. In contrast, temperatures above 950°C promote significant sintering, enhancing particle cohesion and creating a more homogeneous tablet with fewer cracks and an appropriate porous structure. These characteristics of MAT are crucial for facilitating pollutant diffusion within the tablet, potentially enhancing the adsorption process by increasing the area of interaction between the adsorbent and adsorbate.

The surface area (S_{BET}) of MAT (Table 3) was lower than values reported in the literature. For instance, Siwoyo *et al.* (2014) found a surface area of $50 \text{ m}^2\text{g}^{-1}$ using only pulverized WTP sludge as an adsorbent, while Abo-El-Enein *et al.* (2017) reported $61.92 \text{ m}^2\text{g}^{-1}$ for sludge treated at 500°C . Kang *et al.* (2019) measured a surface area of $38.9 \text{ m}^2\text{g}^{-1}$ for pelletized WTP sludge. Caution is warranted when evaluating the surface area of WTP sludge as an adsorbent. Muisa *et al.* (2020) conducted a review on pulverized WTP sludge and reported an average surface area of $134.1 \pm 131.5 \text{ m}^2\text{g}^{-1}$. This high average suggests a favorable potential for use, but the large standard deviation indicates significant variability in the results.

Table 3 –Surface properties of the Mixed Adsorbent Tablet (MAT) sintered at 950°C , include surface area (S_{BET}), pore volume (V_p), pore diameter (D_p), pH of the point of zero charge (pH-ZPC), and zeta potential (PZ)

$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$V_p (\text{cm}^3 \text{g}^{-1})$	$D_p (\text{nm})$	pH-pCz	PZ
17.55 ± 10.84	0.074 ± 0.03	16.83 ± 3.63	5.7 ± 3	-42.00 ± 0.36

Source: Authorship (2024)

The pore volume (V_p) and diameter (D_p) indicate that MAT has a mesoporous material structure, which enhances its adsorptive capacity for larger molecules (Minho, 2023), making it suitable for various applications.

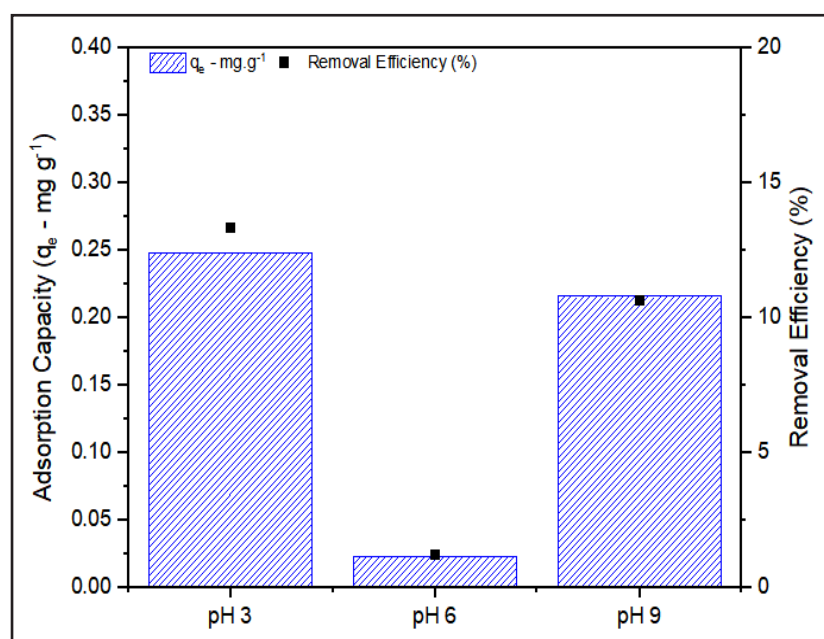
Additionally, the MAT surface exhibited a negative zeta potential (-42.00 ± 0.36) at pH 7, indicating anionic stability. However, it functions as a buffer at the point of zero charge (pH-PCZ) of 5.7. Under these conditions, the adsorbent will acquire a positive surface charge at pH values below the pH-PCZ (i.e., pH 5.7), which is advantageous for retaining anions, such as the reactive blue dye BF 5G (Ribeiro *et al.*, 2015). It is important to note that further research should be conducted to understand the behavior of the solute in the solution under pH conditions favorable for adsorption on MAT. This is crucial to avoid concurrent processes, as many cations may precipitate at pH values above 6.

3.3 Batch adsorption experiments

The treatment of the 10 mg L⁻¹ reactive blue dye BF 5G solution resulted in adsorption capacity values six times lower than those reported in the literature (Table 1), with removal efficiency percentages below 15%. In light of these findings, we aim to identify factors that may help elucidate this phenomenon, as well as the properties of the produced adsorbent.

Analyzing the effect of pH variation (Figure 4) on a MAT (0.30 g), at 25°C and in 24 hours of contact time, a positive effect was observed at pH3 in relation to the other pH conditions. At pH6, the removal efficiency was less than 5%, making the success of the treatment unfeasible.

Figure 4 – Adsorption capacity and removal efficiency of the reactive blue dye BF 5G in MAT as a function of pH



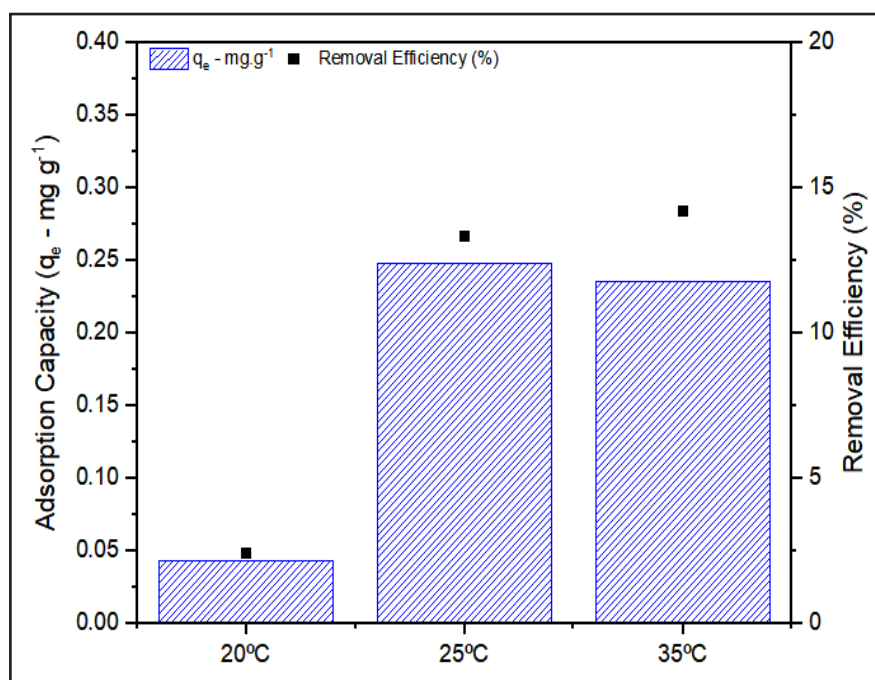
Source: Authorship (2024)

Regarding the adsorption capacity (q -mg g⁻¹), a value of 0.26 mg g⁻¹ was observed at pH 3, while at pH 9, “q” was 0.24 mg g⁻¹, indicating relatively close values. According to a bibliographic survey conducted by Freire-Boina et al. (2024), the reactive

blue dye BF 5G exhibits better performance under acidic pH conditions across various adsorbent matrices. Therefore, pH 3 was selected for subsequent tests.

Increasing or decreasing the treatment temperature did not provide a relevant increase in the adsorption rate of the reactive blue dye BF5G (pH3) on the MAT (~0.30 g) in the contact time of 24 hours (Figure 5). Therefore, the treatment of the reactive blue dye BF 5G can be carried out at ambient conditions ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$), without the need for cooling or heating.

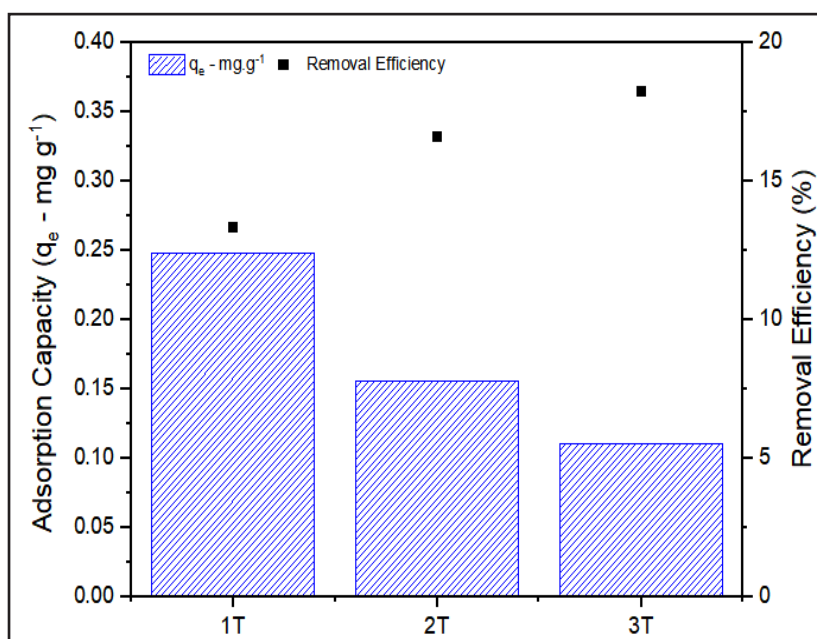
Figure 5 – Adsorption capacity and removal efficiency of the reactive blue dye BF 5G in the MAT, as influenced by temperature ($^{\circ}\text{C}$)



Source: Authorship (2024)

The increase in the number of MAT tablets (T), and consequently the mass of the adsorbent, demonstrated a positive effect on the removal of the dye at a concentration of 10 mg L^{-1} (Figure 6). When comparing the use of one MAT tablet (~0.30 g), the removal efficiency increased by 18% with two tablets (~0.60 g) and by 25% with three tablets (~0.90 g).

Figure 6 – Adsorption capacity and removal efficiency of reactive blue dye BF 5G in MAT as a function of the number of tablets (P) used



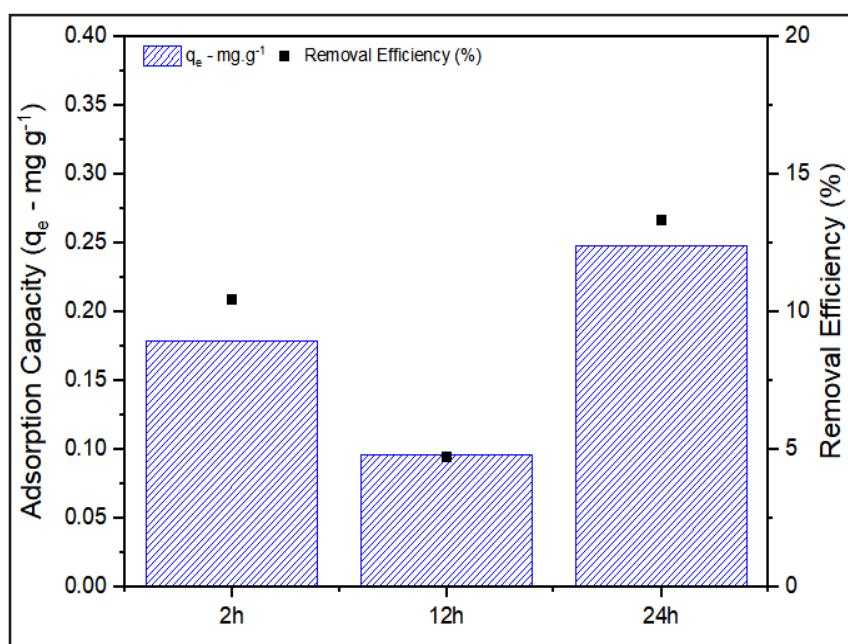
Source: Authorship (2024)

Conversely, increasing the adsorbent mass led to a reduction in the adsorption capacity (q - mg g^{-1}). According to Martins et al. (2022), a smaller amount of adsorbent allows better access to all active sites, leading to saturation of the adsorbent surface. However, when a larger fraction of low-energy sites become occupied, the availability of higher-energy sites diminishes, resulting in a lower “ q ” value. Additionally, the reduction in adsorption capacity can be attributed to unsaturated active sites remaining during the adsorption process, as well as the extended diffusion path caused by the overlap of adsorption sites due to increased adsorbent dosage (Ezeh et al., 2017).

Regarding the contact time (Figure 7), a duration of 24 hours resulted in an increase in the average removal efficiency of approximately 10% compared to the 2-hour contact time (13.85% vs. 12.49%). In terms of adsorption capacity, this increase was around 25%. It is important to note that access to the adsorbent’s active sites occurs rapidly during the initial moments of treatment. Over time, the diffusion process

enhances access to the active sites located in the deeper layers of the tablet, leading to improved adsorption performance.

Figure 7 – Adsorption capacity and removal efficiency of reactive blue dye BF 5G in MAT as a function of contact time (hours)



Source: Authorship (2024)

4 CONCLUSION

The preparation and synthesis of the mixed adsorbent tablet (MAT), derived from water treatment plant sludge and orange peel, were straightforward and not labor-intensive. Despite the favorable physical properties, chemical composition, and surface charge of MAT for the adsorption of reactive blue dye BF 5G in aqueous solutions, its surface area was significantly lower than that of its precursors and other engineered adsorbents.

The adsorption of the dye onto the MAT surface was influenced by the acidic pH of the solution. The process proved to be efficient at room temperature and occurred rapidly, requiring only a single MAT unit. However, the treatment resulted in lower removal efficiency and adsorption capacity than anticipated.

The factors contributing to this situation may be linked to the characteristics of the produced adsorbent. It is recommended that the tablet be sintered at a lower temperature to preserve the essential components of the activating precursors while still ensuring resistance and durability during use. Under these conditions, further research should focus on varying the proportions of the residues used in the MAT production, with an emphasis on understanding the underlying adsorption mechanisms.

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REFERENCES

- Abo-El-Enein, S. A., Shebl, A., & Abo El-Dahab, S. A. (2017) Drinking water treatment sludge as an efficient adsorbent for heavy metals removal. *Applied Clay Science*, 146, 343-349.
- Aragaw, T. A. (2020) Utilizations of electro-coagulated sludge from wastewater treatment plant data as an adsorbent for direct red 28 dye removal. *Data in Brief*, v. 28, p. 104848.
- Bediako, J. K., Lin, S., Sarkar, A. K., Zhao, Y., Choi, J. W., Song, M. H., Cho, C. W., & Yun, Y. S. (2020) Evaluation of orange peel-derived activated carbons for treatment of dye-contaminated wastewater tailings. *Environmental Science and Pollution Research*, v. 27, p. 1053–1068.
- Can-Güven, E., Korkmaz, M. Y., Yazici Guvenc, S., & Varank, G. (2024) Multivariate optimization of organic matter and color removal from textile dyeing industry wastewater by ultraviolet-activated oxidants. *Journal of Photochemistry and Photobiology A: Chemistry*, v. 452, p. 115572.
- Castro, M. C., Alves, E. S., Saquei, B. H. F., & Montanher, S. F. (2021) Use of passion fruit waste as an alternative adsorbent for dye adsorption. *Research, Society and Development*, v. 10, n. 14, p. e266101422059.

- De Coltre, D. S., Cionek, C. A., Meneguín, J. G., Maeda, C. H., Braga, M. U. C., De Araújo, A. C., Gauze, G. De F., De Barros, M. A. S. D., & Arroyo, P. A. (2020) Study of dye desorption mechanism of bone char utilizing different regenerating agents. *SN Applied Sciences*, 2, 2150.
- Dinarvandi, K., Samimi, A., Mohebbi-Kalhari, D., Zakeri, M., & Zakeralhosseini, R. (2024) Synthesis of mesoporous γ -alumina from a low-grade boehmite ore: Effect of thermal/chemical processing order on physico-chemical characteristics of adsorbent and regeneration of used transformer oils. *Chemical Engineering Research and Design*, v. 209, p. 72–80. DOI <https://doi.org/10.1016/j.cherd.2024.07.059>.
- Dutta, S., Adhikary, S., Bhattacharya, S., Roy, D., Chatterjee, S., Chakraborty, A., Banerjee, D., Ganguly, A., Nanda, S., & Rajak, P. (2024) Contamination of textile dyes in aquatic environment: Adverse impacts on aquatic ecosystem and human health, and its management using bioremediation. *Journal of Environmental Management*, v. 353, p. 120103.
- Elgarahy, A. M., Maged, A., Elwakeel, K. Z., El-Gohary, F., & El-Qelish, M. (2023) Tuning cationic/anionic dyes sorption from aqueous solution onto green algal biomass for biohydrogen production. *Environmental Research*, v. 216, p. 114522.
- Ezeh, K., Ogbu, I. C., Akpomie, K. G., Ojukwu, N. C., & Ibe, J. C. (2017) Utilizing the sorption capacity of local Nigerian sawdust for attenuation of heavy metals from solution: isotherm, kinetic, and thermodynamic investigations. *Pacific Journal of Science and Technology*, v. 18, p. 251–264.
- Feltrin, N., & Cechinel, M. A. Remoção de ferro de soluções aquosas utilizando casca de laranja liofilizada. *Observatório de la Economía Latinoamericana*, v. 22, p. e4211, 2024.
- Freire Boina, R., Ramos Estevam, B., Ferraz Freitas, R., Marcos Madeira Rodrigues, J., De Oliveira Boina, W. L., Henrique Sales, D., De Souza, A. E., Teixeira, S. R., & Pereira, N. C. (2024) Ceramic adsorbent material in removing reactive blue bf 5G dye from synthetic wastewater. *Separation and Purification Technology*, v. 331, p. 125555.
- Haag, A. B., & Ibsch, R. B. (2022) Produção de corantes naturais para a indústria têxtil. *Revista da UNIFEDE*, Edição Tecnologias: Engenharia, Produção e Construção, v. 1, n. 27, p. 80–98.
- Hamad, N., Galhoum, A. A., Saad, A., & Wageh, S. (2024) Efficient adsorption of cationic and anionic dyes using hydrochar nanoparticles prepared from orange peel. *Journal of Molecular Liquids*, v. 409, p. 125349.
- Kang, S., Choi, J. H., Park, J-G., & Baek, K. (2019) Pellet adsorbent derived from molasses and dewatered alum sludge for arsenic removal. *Journal of CO2 Utilization*, 33, 31–36.
- Khan, M. K. A., Abudulhameed, A. S., Alshahrani, H., & Algburi, S. (2024) Development of chitosan biopolymer by chemically modified orange peel for safranin O dye removal: A sustainable adsorbent and adsorption modeling using RSM-BBD. *International Journal of Biological Macromolecules*, v. 261, part 2, p. 129964

- Ma, Z., Chang, H., Liang, Y., Meng, Y., Ren, L., & Liang, H. (2024) Research progress and trends on state-of-the-art membrane technologies in textile wastewater treatment. *Separation and Purification Technology*, v. 333, p. 125853.
- Maeda, C. H., Araki, C. A., Moretti, A. L., De Barros, M. A. S. D., & Arroyo, P. A. (2019) Adsorption and desorption cycles of reactive blue BF-5G dye in a bone char fixed-bed column. *Environmental Science and Pollution Research*, 26, 28500–28509
- Maheshwari, U., Thakur, R. V., Deshpande, D., & Ghodke, S. (2023) Efficiency evaluation of orange and banana peels for dye removal from synthetic industrial effluent. *Materials Today: Proceedings*, v. 76, p. 170–176.
- Martins, D. S., Estevam, R. B., Perez, I. D., Américo-Pinheiro, J. H. P., Isique, W. D., & Boina, R. F. (2022) Sludge from a water treatment plant as an adsorbent of endocrine disruptors. *Journal of Environmental Chemical Engineering*, v. 10, n. 4. DOI <https://doi.org/10.1016/j.jece.2022.108090>.
- Minho, G. U. (2023) *Estudo da modelagem da adsorção em batelada do fármaco nimesulida em solução aquosa utilizando carvão ativado como adsorvente*. 2023. p. 13-41. Monografia (Graduação em Engenharia Química) – Universidade Federal do Pampa.
- Mouratib, R., Achiou, B., Krati, M. El, Younssi, S. A., & Tahiri, S. (2020) Low-cost ceramic membrane made from alumina- and silica-rich water treatment sludge and its application to wastewater filtration. *Journal of the European Ceramic Society*, v. 40, n. 15, p. 5942–5950.
- Muisa, N., Nhapi, I., Ruziwa, W., & Manyuchi, M. M. (2020) Utilization of alum sludge as adsorbent for phosphorus removal in municipal wastewater: A review. *Journal of Water Process Engineering*, 35, 101187.
- Nayeri, D., & Mousavi, S. A. (2022) A comprehensive review on the coagulant recovery and reuse from drinking water treatment sludge. *Journal of Environmental Management*, v. 319, p. 115649.
- Ramos, B. De P., Perez, I. D., & Freire-Boina, R. (2022) Cu²⁺, Cr³⁺, and Ni²⁺ in mono- and multicomponent aqueous solution adsorbed in passion fruit peels in natura and physicochemically modified: a comparative approach. *Environmental Science and Pollution Research*, v. 29, p. 79841–79854.
- Ramutshatsha-Makhwedzha, D., Mavhungu, A., Moropeng, M. L., & Mbaya, R. (2022) Activated carbon derived from waste orange and lemon peels for the adsorption of methyl orange and methylene blue dyes from wastewater. *Heliyon*, v. 8, n. 8, p. e09930.
- Rendón-Castrillón, L., Ramírez-Carmona, M., Ocampo-López, C., González-López, F., Cuartas-Urbe, B., & Mendoza-Roca, J. A. (2023) Treatment of water from the textile industry contaminated with indigo dye: A hybrid approach combining bioremediation and nanofiltration for sustainable reuse. *Case Studies in Chemical and Environmental Engineering*, v. 8, p. 100498.

- Sahu, A., & Poler, J. C. (2024) Removal and degradation of dyes from textile industry wastewater: Benchmarking recent advancements, toxicity assessment and cost analysis of treatment processes. *Journal of Environmental Chemical Engineering*, v. 12, n. 5, p. 113754.
- Shalaby, N. H., Ewais, E. M. M., Elsaadany, R. M., & Ahmed, A. (2017) Rice husk templated water treatment sludge as low cost dye and metal adsorbent. *Egyptian Journal of Petroleum*, v. 26, n. 3, p. 661–668.
- Siswoyo, E., Mihara, Y., & Tanaka, S. (2014) Determination of key components and adsorption capacity of low-cost adsorbent based on sludge of drinking water treatment plant to adsorb cadmium ion in water. *Applied Clay Science*, 97-98, 146-152.
- Sousa, G., Gabriel, E., Alves, A., Scalize, P. (2017) *Aplicação de análise termogravimétrica (TGA) e termogravimétrica derivada (DTG) em materiais orgânicos usados como adsorventes*. In: XIX SIMPÓSIO LUSO-BRASILEIRO DE ENGENHARIA SANITÁRIA E AMBIENTAL (SILUBESA), 19., remoto (online). Anais [...] Brasil/Portugal: ABES/APRH/APESB, p. 1-7.
- Souza, A., Cechinel, P. A. M., & Peterson, M. (2019) Avaliação do potencial sortivo da casca de laranja quimicamente e termicamente modificada na remoção de metais em solução aquosa. *Brazil Journal of Development*, v. 5, p. 7107–7128, 2019.
- Streit, A. F. M., Pereira, H. A., Moreno-Pérez, J., Mendoza-Castillo, D. I., Reynel-Ávila, H. E., Da Boit Martinello, K., Silva, L. F. O., Ahmad, N., Mohandoss, S., Bonilla-Petriciolet, A., & Dotto, G. L. (2024) New study of the adsorption mechanism of different dye molecules by high porous sludge activated carbon produced from a dairy-treatment effluent plant. *Journal of Environmental Chemical Engineering*, v. 12, n. 5, p. 113745.
- Trach, Y., Bujakowski, F., Koda, E., Mazur, Ł., Nejbert, K., Podlasek, A., & Vaverková, M. D. Characterization of adsorbents from Ukrainian kaolinite clay for the sorption of nickel: insight and practical application for water treatment in conditions of economic constraints. *Desalination and Water Treatment*, v. 278, p. 1–12, 2022. DOI <https://doi.org/10.5004/dwt.2022.28968>.
- Uğan, M., Onac, C., Kaya, A., Köseoğlu, D., & Akdoğan, A. (2024) Removal of Reactive Red 195 dye from textile industry wastewater with Deep Eutectic Solvent-based green extraction. *Journal of Molecular Liquids*, v. 398, p. 124249.
- Wong, S., Abd Ghafar, N., Ngadi, N., Razmi, F. A., Inuwa, I. M.; Matos, R., Amin, N. A. S. (2020) Effective removal of anionic textile dyes using adsorbent synthesized from coffee waste. *Scientific Reports*, v. 10, p. 1-10.
- Xu, S., Huang, J., Wei, X., Chen, Y., Liu, M., Wu, J., & Liu, Y. (2024) Preparation of amine functionalized micro-mesoporous silicon adsorbent from fly ash and its kinetic characteristics of CO₂ adsorption/desorption process. *Ceramics International*, v. 50, n. 14, p. 25150–25160. DOI <https://doi.org/10.1016/j.ceramint.2024.04.244>.
- Zanoni, M. V. B., & Yamanaka, H. (2016) *Corantes: caracterização química, toxicológica, métodos de detecção e tratamento*. 1. ed. São Paulo: Cultura Acadêmica.

Zonato, R. De O., Estevam, B. R., Perez, I. D., Aparecida Dos Santos Ribeiro, V., & Boina, R. F. (2022) Eggshell as an adsorbent for removing dyes and metallic ions in aqueous solutions. *Cleaner Chemical Engineering*, v. 2, p. 100023.

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