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Reuse of drinking water treatment sludge for the removal of antibiotics: The case study of sulfamethoxazole and trimethoprim based on advanced statistical physics models

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ABSTRACT

This study reports the valorization of drinking water treatment sludge (DWTS) to remove antibiotics from water. Sulfamethoxazole and trimethoprim were used as model antibiotic molecules to analyze the removal capacity of DWTS. A detailed physicochemical characterization of this DWTS was performed including a leaching assay to determine its chemical stability. Kinetic and equilibrium studies were performed at pH 6.5 and 20–40 °C in single and binary aqueous solutions containing the tested antibiotics. Different models including statistical physics theory were applied to correlate and analyze the antibiotic adsorption on DWTS. The application of DWTS to remove the tested antibiotics from real treated wastewater was assessed. The leaching analysis proved that this sludge was chemically stable and can be used safely in (waste)water treatment. The results showed that DWTS can remove both antibiotics with uptake capacities up to 36 mg/g. This sludge displayed better adsorption properties to remove sulfamethoxazole in both single and binary systems. The binary studies indicated the presence of antagonistic removal of both antibiotics. The oxygenated functional groups of the DWTS were involved in the adsorption mechanism of the tested antibiotics via hydrogen bonding. The results in wastewater showed uptake capacities up to 18 mg/g, namely for trimethoprim, despite the presence of chemical species that interfere with their removal. Therefore, DWTS are an alternative that can be used to reduce the costs of treatment systems, namely in the removal of antibiotics, besides contributing to the sustainability and circular economy in the water sector.

1. Introduction

Antibiotics have been a significant advancement in public health. However, the effectiveness of many of these pharmaceuticals is facing challenges due to the rapid evolution of bacteria resistance mechanisms (Aslan et al., 2018; Sambaza and Naicker, 2023). The discharge of antibiotics into the environment is associated with the emergence of antimicrobial resistance (AMR), which is of significant concern not only to public health but also to food security and the economy, as underscored by the World Health Organization (Vasilachi et al., 2021). The threat posed by AMR is evidenced by approximately 700,000 annual deaths, which could reach 10 million by 2050 (Sambaza and Naicker, 2023). AMR is not the only threat posed by the environmental presence of antibiotics. For example, the exposure to sulfamethoxazole (SMX) and trimethoprim (TMP), which are two antibiotics featured in the European Union Watch List mechanism (European Commission, 2020, 2022), can

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result in toxicological effects including the bioaccumulation in aquatic organisms (Chaves et al., 2022), oxidative stress in mollusks (e.g., *Ruditapes philippinarum*) (Nicolussi et al., 2022), and impacts on the swimming activity and heartbeat rate of some species (e.g., *Danio rerio*) (Lin et al., 2014). Therefore, it is of utmost importance to reduce the presence of antibiotics in the environment.

SMX is one of the sulfonamides that is commonly used in human medicine. This antibiotic inhibits dihydropteroate synthase, a pivotal precursor in the folic acid synthesis, which plays a crucial role in bacterial growth (Prasannamedha and Kumar 2020). SMX has been used in combination with TMP to minimize the impact of AMR (Prasannamedha and Kumar 2020; Thiebault, 2020). On the other hand, TMP is a chemotherapeutic agent that inhibits dihydrofolate reductase, which catalyzes the conversion of dihydrofolate to tetrahydrofolate (Thiebault, 2020). These two antibiotics cover a wide antibacterial spectrum and can be used to treat respiratory and urinary tract infections. They are also used by patients with acquired immunodeficiency syndrome or other immunosuppressive conditions to treat opportunistic infections (Frascaroli et al., 2021; Thiebault, 2020). However, these two compounds are poorly absorbed and not completely metabolized by humans, resulting in the excretion of active compounds (around 20 % for SMX and 50 % for TMP) via urine and feces (Phoon et al., 2020; Thiebault, 2020). After excretion, these antibiotics usually end up in Wastewater Treatment Plants (WWTP). However, the conventional treatment systems of WWTP cannot effectively remove them (Cui et al., 2023). Some studies have reported that the removal efficiencies for SMX and TMP are ~50 % because of their high resistance to the biodegradation (Wang et al., 2020). The high capacity to resist conventional removal processes besides the environmental and public health impacts (toxicity and antibiotics resistance) of these compounds show that is essential to adapt and improve purification systems of WWTP to reduce the concentration of antibiotics and other compounds of emerging concern (CECs) (Guillossou et al., 2019; Rizzo et al., 2020). The concentration of these antibiotics in wastewater can range between ng/L and μg/L. For example, in Europe, the concentrations of SMX and TMP range from 0.09 to 1.55 μg/L and from 0.06 to 1.44 μg/L, respectively (Thiebault, 2020).

The adsorption process is pointed out by several authors as an effective treatment technology for CECs removal including antibiotics since it is simple to design and operate, has low investment, enables the reuse and regeneration of the separation media (i.e., solids used as adsorbents) and does not generate toxic by-products (Dias et al., 2021; Guillossou et al., 2019). In particular, different studies have concluded that the mechanism of TMP and SMX adsorption from water implies interactions with the adsorbent surface via hydrogen bonding, electrostatic interactions, complexation, π-π, and hydrophobic forces (Mpatani et al., 2021; Prasannamedha and Kumar 2020). Activated carbon (AC) is the universal adsorbent used in WWTP but its cost can limit its implementation. Therefore, circular economy-based research has focuses on low-cost materials, such as biochar and waste-based adsorbents (Li et al., 2019; Mitra et al., 2021; Nielsen and Bandosz, 2016), to reduce water purification costs and to improve process sustainability.

Drinking water treatment sludge (DWTS) has been identified as a potential low-cost adsorbent for CECs removal due to its physicochemical properties (Dias et al., 2023; Kulandaivelu et al., 2020). DWTS is a by-product of drinking water treatment processes and is composed mainly of organic matter and the reagents used in the purification system (Pająk, 2023). Based on the reagents that are incorporated in the treatment process, DWTS can be classified as aluminum-rich (Al-DWTS), iron-rich (Fe-DWTS) or activated carbon-rich (AC-DWTS) (Dias et al., 2023). Previous studies have proved the promising application of DWTS for the adsorption of antibiotics including TMP and SMX. For example, Jo et al. (2021) analyzed the performance of pellets prepared with pre-treated Al-DWTS for the SMX removal obtaining an adsorption capacity of 1.7 mg/g. Kulandaivelu et al. (2020) studied SMX and TMP adsorption using Fe-DWTS and Al-DWTS. The results showed that only Fe-DWTS was able to remove TMP, while SMX removal was not achieved by any of the two types of DWTS. However, the literature review indicates that the use of AC-DWTS to adsorb SMX and TMP has not yet been properly studied. In fact, there is a knowledge gap concerning the uptake capacity of this sludge, which is crucial for assessing its true potential. Additionally, it is important to understand the mechanisms that determine the removal of these antibiotics.

Based on this context, this study aims to evaluate the removal of TMP and SMX using AC-DWTS in single and multicomponent aqueous solutions. Kinetic and equilibrium studies were performed, including statistical physics modelling, to elucidate the removal mechanism of both compounds. As proof of concept, the antibiotic removal was studied using real treated wastewater.

2. Materials and methods

2.1. Drinking water treatment sludge characterization

The DWTS sample was obtained from the drinking water treatment plant after the final dewatering stage. This material contained the chemicals used in the drinking water treatment process, specifically polyaluminum chloride, lime milk, AC, and polyelectrolyte. The collected sludge was subjected to drying at 105 °C to eliminate any remaining moisture. The dried substance was then ground and sifted to achieve a particle size of 45/60 mesh (250–354 μm), which falls between the particle sizes of standard powdered and granular activated carbon (Sousa et al., 2024).

Elemental organic composition (C, H, N, and S), mineral content (Zn, Pb, P, Na, Mg, K, Fe, Cu, Cr, Ca, Al), ash content, pH at point of zero charge (pH_{PZC}), and textural parameters (pore size distribution, mesopore volume, micropore volume, total pore volume, and surface area) of DWTS were determined. Thermogravimetric (TGA) and Transform Infrared Spectroscopy (FTIR) studies were also performed to characterize DWTS. The DWTS surface characteristics and elemental composition were analyzed using Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). To conclude, a leaching test of DWTS was performed in accordance with the European standard aqueous leaching procedure for waste materials and sludges (EN 12457-2.2003, 2003). Details of all procedures and characterization techniques are reported in Supplementary Material.

2.2. Adsorption assays

All the single adsorption studies were performed via batch adsorbers using 25 mL of antibiotic solution, under a continuous agitation of 300 rpm in a multistirrer (VELP Scientifica Srl, Usmate, Italy). The solutions of adsorbates were prepared daily using distilled water or wastewater, considering the studied matrix: 5 % methanol (MeOH) (HPLC/MS purity grade >99.9 %, Honeywell Riedel-de Haën, Germany) and selected antibiotics (TMP and SMX). The purities of TMP (Fargos, Barcelona, Spain) and SMX (Sigma Aldrich, Missouri, USA) were 99.6 and 98 %, respectively. The adsorbate concentrations used in this study, which are detailed in the following sections, are higher than those typically found in the environment. This approach aims to achieve DWTS saturation in order to determine the maximum adsorption capacity of the material.

After the adsorption process, the suspensions were filtered through 1.2 μm glass microfiber filters (MFV3, Barcelona, Spain) and the filtrate was analyzed to quantify the antibiotic concentration using a UV–VIS spectrophotometer (GBC UV/VIS, model 916) with quartz cuvette with 100 mm pathlength (UNICO, Dayton, NJ, USA). The calibration curve, quantification limit (LOQ) and determination limit (LOD) for the concentration measuring of each antibiotic are shown in Table S1 of the Supplementary Material. The binary adsorption tests were performed in the same conditions as the single. For these studies, the concentration of tested adsorbates was determined using a method adapted from Bai and Acharya (2016) where HPLC was applied using the conditions reported

in Supplementary Material. The calibration curve, LOQ and LOD for HPLC-based quantification of each antibiotic are reported in Table S2 of the Supplementary Material. All the adsorption experiments were performed by duplicate.

2.2.1. Identification of the best solid/liquid ratio for antibiotic adsorption

A preliminary single adsorption study with the DWTS was performed to define the best solid/liquid ratio (S/L) for the antibiotic removal experiments. Four S/L ratios of DWTS (0.1, 0.5, 1 and 2 g/L) were tested during 24 h at pH = 6.5. The concentrations of SMX and TMP used in this study were 50 mg/L. The removal efficiency (RE, %) was calculated by Eq. (1),

$$RE\ (\%) = \frac{(C_0 - C_f)}{C_0} \times\ 100 \tag{1}$$

where C_0 and C_f are the initial and final concentrations (mg/L) of the studied antibiotics. S/L value that achieved the highest RE was selected for the kinetic and isotherm studies of antibiotic adsorption.

2.2.2. Kinetic study

The single and binary kinetic studies were performed using $m/V = 2$ g/L of DWTS with initial concentrations of 50 mg/L of the adsorbates. The contact time ranged from 0 to 96 h. The uptake capacity (q, mg/g) of DWTS at a given operating time t was determined using Eq. (2), while the results were adjusted via the following kinetic models: Pseudo-First Order (PFO), Eq. (3), Pseudo-Second Order (PSO), Eq. (4), and Elovich, Eq. (5):

$$q\ =\ \frac{(C_0 - C_f)\ \times\ V}{m} \tag{2}$$

$$q_t = q_e \times\ \left(1 - e^{-k_1 \times t}\right) \tag{3}$$

$$q_t = \frac{q_e^2 \times k_2 \times t}{1 + q_e \times k_2 \times t} \tag{4}$$

$$q_t = \frac{1}{b_E} \times ln(1 + a_E \times b_E \times t) \tag{5}$$

where q_t (mg/g) is the amount of antibiotic adsorbed on DWTS at time t; q_e is the uptake capacity at equilibrium (mg/g); k_1 is the pseudo-first-order rate constant (min^{-1}); k_2 is the pseudo-second-order rate constant (g $mg^{-1}min^{-1}$); a_E is the initial adsorption rate constant of Elovich model (mg $g^{-1}min^{-1}$); and b_E is the rate of change of the activation energy with surface coverage (g/mg) (Wang et al., 2024).

2.2.3. Equilibrium studies

The adsorption isotherms were determined at three temperatures (20, 30 and 40 °C) using m/V = 2 g/L of DWTS. The contact time for these studies was selected according to the results of the kinetic study (i.e., 24 h). The initial concentration of each antibiotic ranged from 20 to 250 mg/L. The binary equilibrium study was performed under the same conditions as those used in the single solutions. The initial concentration of each antibiotic ranged from 20 to 300 at a ratio of 1:1 (e.g., 20 mg/L of SMX / 20 mg/L of TMP). The experimental data of both the single and binary equilibrium studies were correlated using the following isotherm models.

i. Langmuir model:

$$q_e = \frac{K_L \times q_m \times C_e}{1 + K_L \times C_e} \tag{6}$$

where C_e (mg/L) and q_e (mg/g) are the concentration and the adsorption capacity at equilibrium, respectively; q_m is the calculated maximum adsorption capacity (mg/g); and K_L is the Langmuir equilibrium constant (L/mg) (Wang et al., 2024).

i. Freundlich model:

$$q_e = K_F \times Ce^{1/n_F} \tag{7}$$

where K_F ($L^{1/n_F}\ g^{-1}\ mg^{1-1/n_F}$) is the Freundlich constant that characterizes the strength of adsorption and n_F is the adsorption intensity (Lima et al., 2021).

i. Sips model:

$$q_e = \frac{K_S \times q_m \times C_e^{1/n_S}}{1 + K_S \times C_e^{1/n_S}} \tag{8}$$

where $K_S\left((L/mg)^{1/n_S}\right)$ is the Sips equilibrium constant and n_S is the Sips exponent (dimensionless, $1/n_S$ ranging from 0 to 1) (Lima et al., 2021).

i. BET model:

$$q_e = q_m \frac{K_S \times C_e}{(1 - K_{L\ BET} \times C_e)(1 - K_L \times C_e + K_{S\ BET} \times C_e)} \tag{9}$$

where $K_{S\ BET}$ (L/mg) and $K_{L\ BET}$ (L/mg) are the equilibrium constants for the first and second layers, respectively (Ebadi et al., 2009).

i. The multi-step isotherm model:

$$q_e = \sum_{i=1}^{S} \frac{a_i \times k_i \times [(C_e - b_i) + abs(C_e - b_i)]^{n_i}}{2^{n_i} + k_i \times [(C_e - b_i) + abs(C_e - b_i)]^{n_i}} \tag{100}$$

where S is the number of steps of the isotherm; a_i is the maximum adsorption capacity (mg/g) of the layer n_i; k_i is equilibrium constant $[(L/mg)]^{n_i}$ of the layer n_i; and b_i is the critical concentration limit (mg/L) (Czinkota et al., 2002; Tolner, 2008).

2.2.4. Statistical physics modelling

A monolayer model (MM), formulated via the theory of statistical physics (Edi-Soetaredjo et al., 2023; Sellaoui et al., 2015), was also applied to examine the adsorption mechanism of TMP and SMX on DWTS. This MM assumed that the functional group of DWTS can accept a variable number of antibiotic molecules at different adsorption temperatures, in contrast to the Langmuir model. It is expressed as follows (Edi-Soetaredjo et al., 2023; Yazidi et al., 2020):

$$q_e = \frac{n_{an} F}{1 + \left(\frac{C_{1/2}}{C_e}\right)^{n_{an}}} \tag{111}$$

where the n_{an} parameter can estimate the number of antibiotic molecules adsorbed per DWTS functional group, F represents the functional group density (mg/g), and $C_{1/2}$ is the concentration at half-saturation (mg/L).

This model was extended to explain the binary adsorption of TMP and SMX. The binary model (BM) considers that both TMP and SMX are adsorbed on the same DWTS functional group to justify the competition of these adsorbates (antagonistic removal) during the multicomponent adsorption process. It is given by Edi-Soetaredjo et al. (2023), Yazidi et al. (2020):

$$q_{e,1} = \frac{n_{1b} D_b \left(\frac{C_e}{C_{1b}}\right)^{n_{1b}}}{1 + \left(\frac{C_e}{C_{1b}}\right)^{n_{1b}} + \left(\frac{C_e}{C_{2b}}\right)^{n_{2b}}} \quad (122)$$

$$q_{e,2} = \frac{n_{2b} D_b \left(\frac{C_e}{C_{2b}}\right)^{n_{2b}}}{1 + \left(\frac{C_e}{C_{1b}}\right)^{n_1} + \left(\frac{C_e}{C_{2b}}\right)^{n_2}} \quad (13)$$

In both expressions, the n_{1b} parameter represents the number of TMP molecules adsorbed per DWTS functional group in the binary systems, the n_{2b} parameter estimates the number of SMX molecules adsorbed per DWTS functional group, D_b is the density of DWTS functional groups, and C_{ib} (i = 1,2) is the concentration (mg/L) at half-saturation, respectively.

2.2.5. Model selection

The parameters of all adsorption models were determined via a Non-Linear Least Square method. The model comparison and selection for both kinetic and equilibrium studies was based on three criteria: (i) the adjusted determination coefficient (R^2_{adj}), (ii) the residual sum squares (RSS), and (iii) the Chi-square test (χ^2).

$$R^2_{adj} = 1 - (1 - R^2) \times \left(\frac{n-1}{n-p-1}\right) \quad (14)$$

$$RSS = \sum_i^n \left(q_{exp} - q_{mod}\right)^2 \quad (15)$$

$$\chi^2 = \sum \frac{\left(q_{exp} - q_{mod}\right)^2}{q_{mod}} \quad (16)$$

where R^2 is the determination coefficient, n is the number of experimental results, p is the number of parameters in the fitting model, q_{exp} is the experimental adsorption capacities (mg/g) and q_{mod} is the adsorption capacities obtained with the models (mg/g). The model with the highest R^2_{adj} and lowest value of RSS and χ^2 was selected as the most accurate fit (Ho, 2004; Lima et al., 2021).

2.3. Adsorption assays using wastewater

2.3.1. Wastewater – origin and characterization

A sample of treated wastewater was collected in an urban WWTP with an average flow of 19 300 m^3/day. The WWTP system included preliminary, primary, and secondary treatment stages (oxidation ditches followed by clarifiers). The sample was collected after a secondary clarifier. The characterization of the wastewater included the determination of the following parameters: 5-day biological oxygen demand (BOD_5), chemical oxygen demand (COD), permanganate index (PI), total solids (TS), total fixed solids (TFS), total volatile solids (TSV), total suspended solids (TSS) Kjeldahl nitrogen, phosphate, chloride, sulphate, nitrate, pH and turbidity. Details of these analyzes are given in Supplementary Material.

2.3.2. Adsorption assay in treated wastewater

The adsorption studies with treated wastewater were performed using $m/V = 2$ g/L of DWTS, with initial concentrations of 50 mg/L for both SMX and TMP under continuous agitation, and a contact time of 24 h using both single and binary solutions. *RE (%)* and q_e were calculated according to Eqs. (1) and (2), respectively.

3. Results and discussion

3.1. Drinking water treatment sludge characterization

The ash content, elemental composition, and pH_{PZC} of DWTS are listed in Table S3. The ash content obtained was comparable to what is found in the literature for AC-DTWS (Dias et al., 2021; Lee et al., 2020), but it was lower than the values reported for Al-DWTS (80 %) (Hou et al., 2018). Based on the findings of Dahhou et al. (2023), the usual carbon content in DWTS falls between 14 and 18 %. On the other hand, Siswoyo et al. (2014) reported that the carbon content can be below 9 %. The carbon content of AC-DWTS reported in this study was higher than 18 %, which may be due to the incorporation of AC and the presence of other organic matter (Lee et al., 2020; Dias et al., 2021). This sludge sample also exhibited acidic properties ($pH_{PZC} = 5.5$), indicating a high concentration of acidic surface groups (Bernardo et al., 2020). This outcome could be linked to the inclusion of activated carbon and organic acids in the sludge composition, resulting from the presence of organic material in the raw water.

N_2 adsorption-desorption isotherm of DTWS sample (Fig. S1, Supplementary Material) can be classed as a mixture of types I and IV, with both microporosity and mesoporosity. The relatively large hysteresis of type H3 indicates the presence of nonrigid aggregates of plate-like particles with large mesopores (Thommes et al., 2015). According to textural analysis, the pore volume was essentially associated with the mesopores, see results reported in Table 1. The surface area (S_{BET}) was similar to those values reported in several studies (Dias et al., 2021; Lee et al., 2020; Shen et al., 2019). The micropore volume was low (Table 1), and the PSD results (Fig. S2 of the Supplementary Material) showed that DTWS had mainly micropores with widths below 1.5 nm. It is convenient to recall that microporosity is an important parameter because the adsorption of antibiotics such as TMP is usually related to the micropore-filling mechanism (Liu et al., 2015).

The results of the mineral analysis (Table S4 of the Supplementary Material) showed that the elements of DTWS present in highest concentrations were aluminum (Al) and magnesium (Mg), which agreed with previous studies (Bal Krishna et al., 2016; Dias et al., 2021; Hou et al., 2018). The Al content was linked to the specific coagulant used in the treatment of drinking water, which is polyaluminum chloride. The presence of Mg might indicate the properties of the source water and the methods implemented to modify water hardness.

The mass loss of DTWS observed in TGA results (Fig. S3 of the Supplementary Material) up to 105 °C was associated with the sample moisture. However, the most significant mass loss occurred between 200 and 480 °C, which could be related to the degradation of the organic matter (Pellenz et al., 2023). The total mass reduction was 28.6 %, indicating that a considerable amount of mass could be lost during the regeneration and/or activation process of DTWS.

The FTIR spectrum (see Fig. S4 in the Supplementary Material) of DTWS exhibits absorption bands linked to the presence of aluminum hydroxides (3200–3600 and 400–800 cm^{-1}), which may be associated with the coagulant utilized in the drinking water treatment process (Lee et al., 2020). The absorption bands that could be related to Si compounds (1010–1090 cm^{-1}) were also identified (Coates, 2000; Lee et al., 2020), although they can overlap with the bands arising from the

Table 1
Textural properties of DTWS obtained from N_2 adsorption-desorption isotherms.

Parameter	Value
S_{BET} (m^2/g)	165
V_{total} (cm^3/g)	0.154
$V_{mesopores}$ (cm^3/g)	0.114
$V_{micropores}$ (cm^3/g)	0.040

stretching vibration of the Al-O bond (Wang et al., 2014). The absorption bands of silicon could be associated with the composition of raw water, specifically the presence of clays and riverbeds (Martins et al., 2022), or aluminosilicate complexes. An additional absorption band was identified at 1400 cm^{-1} that was probably associated with carbonates and/or carboxylate ions (Coates, 2000). The absorption band located at ~1700 cm^{-1} was associated with the presence of carboxylic acids, which was confirmed by the acidic nature of DWTS (see pH_{PZC} in Table S3).

SEM-EDS results (see Fig. S5 of the Supplementary Material) showed the heterogeneity of the DTWS material where carbon was the element more representative, suggesting the presence of AC particles. Siswoyo et al. (2014) also identified AC particles in the SEM images of DWTS. SEM results also confirmed the presence of particles (zone C reported in Fig. S5) in DWTS sample with a high content of oxygen, silicon, and aluminum. This type of particle has also been identified in previous studies (Martins et al., 2022).

The findings from the leaching assay (see Table S5 in the Supplementary Material) showed a variation in pH that was associated with the pH_{PZC} of DWTS, as the acidic characteristics led to a decrease in solution pH due to the release of H^+ ions (Muisa et al., 2020). In the leaching samples, a conductivity increase of 677.9 μS/cm was observed at 20 °C. The observed results may be linked to the amount of chloride ions (Cl^-) released during the leaching process. This released Cl^- could be associated with the coagulants used in DWTP, particularly polyaluminum chloride. Among the chemical species analyzed, calcium (Ca) and sodium (Na) exhibited the highest relative mobilities. The relative mobility of Al was lower than 1 %, indicating a leaching of 0.05 μg/g. These results elucidate the low mobility of metallic elements from DTWS to water, indicating that this material is chemical stable and can be safely used in aqueous media.

3.2. Antibiotic adsorption assays

3.2.1. Preliminary study

The preliminary study results (Fig. 1) showed that DWTS without any type of activation/functionalization treatment can be used for the removal of SMX and TMP. In contrast to the expected outcome, no significant difference in the affinity between antibiotics and DWTS was observed. Note that adsorption studies were conducted at pH 6.5 to simulate the typical pH of wastewater samples (Michael et al., 2013). At this pH value, the DWTS surface is negatively charged because of its pH_{PZC} = 5.5 (Table S3). The molecule of SMX is deprotonated at tested pH (pK_{a2} = 5.7) (Esteki et al., 2020) and, consequently, electrostatic repulsion between SMX and DWTS surface is expected. Since TMP is protonated (pK_{a2} = 7.45) (Esteki et al., 2020) at the pH of the preliminary study, it would be expected a higher removal of TMP than that for SMX, but no significant differences were observed. This result suggests that electrostatic interactions are not the primary mechanism for SMX adsorption on DWTS. This conclusion also agreed with the study reported by Mitra et al. (2021), which also found a low influence of electrostatic interactions on SMX adsorption onto acid-leached carbon black waste. The highest removal efficiencies were achieved with the highest S/L ratio for both antibiotics, corresponding to adsorption capacities of 17.6 mg/g.

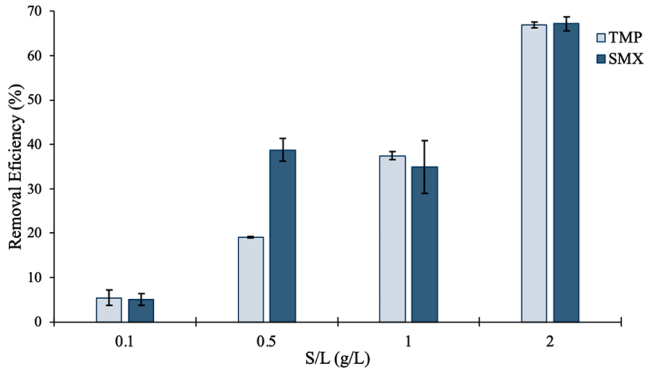

Fig. 1. Effect of S/L ratio on the removal (%) of Trimethoprim (TMP) and Sulfamethoxazole (SMX) using DWTS. Experimental conditions: Initial adsorbate concentration = 50 mg/L; solution volume = 25 mL; initial pH = 6.5; contact time = 24 h.

The type of DWTS used in this study showed better results for the antibiotics removal than those reported for other sludge samples with different compositions. For example, Kulandaivelu et al. (2020) analyzed the removal of these two antibiotics using Fe-DWTS and Al-DWTS. The results showed that only Fe-DWTS was able to remove TMP, while SMX was not removed by any of the two types of DWTS. However, Fig. 1 indicates that it was feasible to remove both antibiotics using AC-DWTS, achieving removal values > 60 % for S/L = 2 g/L. This performance may be related to the incorporation of AC into DWTS. Jo et al. (2021) also studied the removal of SMX using pellets produced with Al-DWTS where the sludge sample was subjected to a thermal pre-treatment at 400 °C. The final adsorbent displayed a SMX removal between 40 and 80 % for an initial SMX concentration of 50 mg/L using 15 g/L of DWTS pellets. S/L ratio of 2 g/L for DWTS was used in the subsequent kinetic and equilibrium adsorption experiments reported in this manuscript.

3.2.2. Kinetic study

The kinetic results reported in Fig. 2 indicated that the equilibrium conditions were achieved for both compounds in the single solutions between 18 and 24 h. Therefore, an equilibrium time of 24 h was chosen for the adsorption isotherm quantification. After the equilibrium time, the q_t values remained constant at approximately 18 and 17 mg/g for SMX and TMP, respectively. Regarding the binary aqueous solutions, the equilibrium conditions were also achieved between 18 and 24 h for both compounds (see Fig. 2c and 2d). However, the binary adsorption capacities decreased, indicating the competition between antibiotics for the active sites on DWTS surface (Dos Santos et al., 2023).

The single experimental data for both antibiotics were best fitted by the PSO model, with R^2 = 0.989 for SMX and R^2 = 0.963 for TMP (Table S6 of the Supplementary Material). PSO model had the highest R^2_{adj} value and the lowest values of χ^2 and RSS values for SMX in comparison to other tested kinetic equations. For TMP, it was possible to observe the same results, except for χ^2. In the binary solution, the PSO model also achieved the best fit. The results obtained for PSO model performance agreed with other adsorption studies on SMX and TMP in aqueous solutions (Ahmed, 2017; Jo et al., 2021; Li et al., 2019; Nielsen and Bandosz, 2016). In both single and binary solutions, it was possible to observe that the TMP adsorption rate was slightly higher than that to remove SMX (Table S6). This may be related to the hydrophobic properties of these molecules. TMP has an octanol-water partition coefficient (Log K_{ow}) between 2.2 and 2.6, while Log K_{ow} of SMX ranges between 0.8 and 1.8 (Prasannamedha and Kumar 2020). Therefore, the tendency of TMP to be adsorbed was higher than that of SMX, resulting in faster TMP adsorption, as reported by Xue et al. (2023).

3.2.3. Equilibrium study

The experimental isotherms of both antibiotics can be classified as type L, indicating that the adsorption capacity increased with increasing adsorbate concentration until the adsorption sites reached saturation, see Fig. 3. This type of isotherm suggests that the adsorption process is caused by physical forces such as van der Waals and hydrogen bonding (Piccin et al., 2017). However, the curvature of SMX adsorption isotherm is less pronounced than that for TMP. The curvature of SMX adsorption isotherm can be classified as subclass 1, which is associated with the fact that adsorption sites are not fully occupied. The curvature of TMP adsorption isotherm can be classified as subclass 2, which is characterized by the formation of a long plateau that represents the saturation of the monolayer. In this subclass, the molecules have a

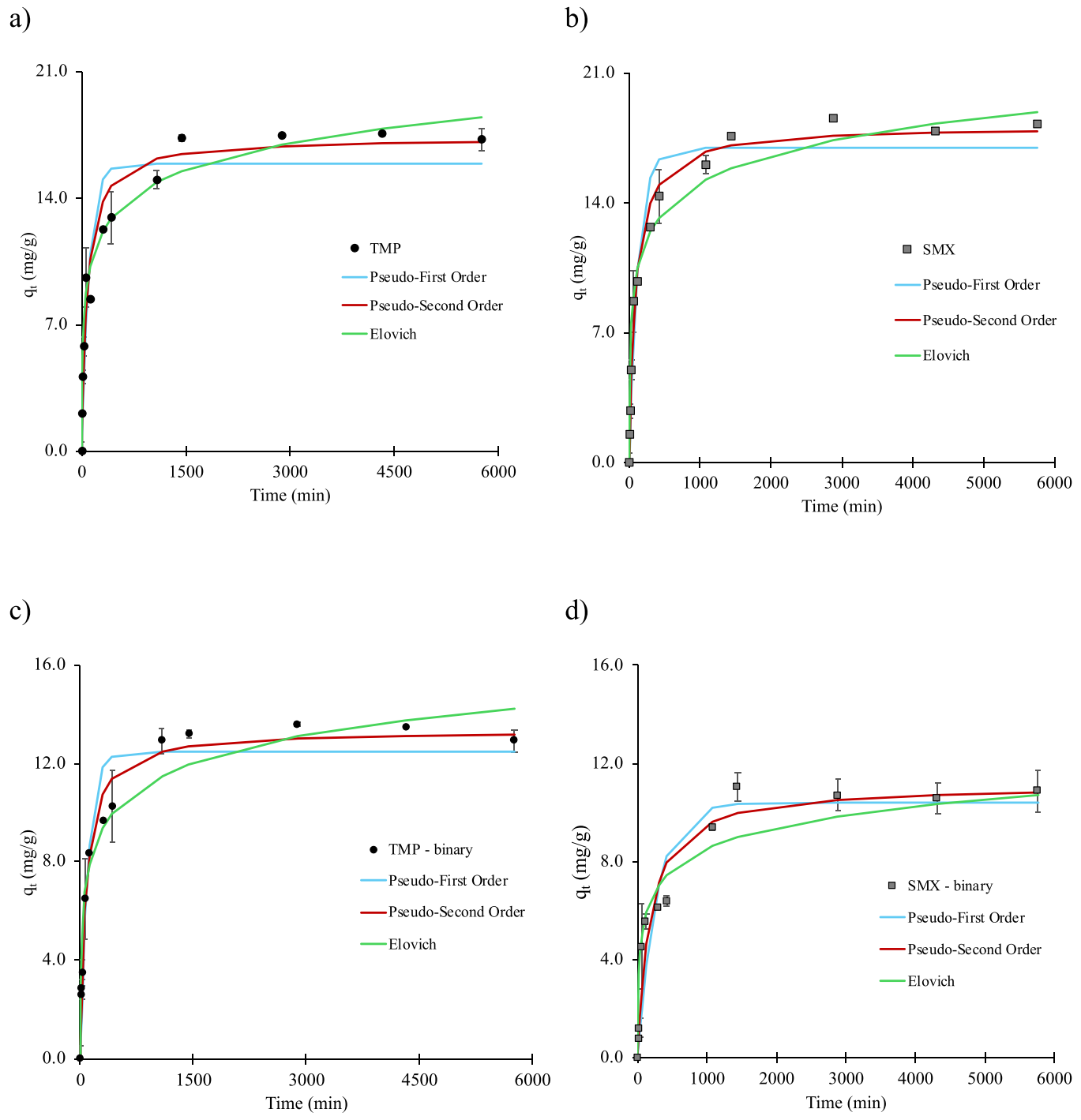

Fig. 2. Kinetic study for the adsorption of trimethoprim (TMP) and sulfamethoxazole (SMX) using DWTS in (a,b) single and (c,d) binary solutions. Experimental conditions: Initial adsorbate concentration = 50 mg/L; S/L ratio = 2 g/L; initial pH = 6.5.

higher affinity for the adsorbent, but a lower affinity for the molecules already adsorbed (Piccin et al., 2017).

The experimental single adsorption data were fitted to the different isotherm models and the results are reported in Table S7 of the Supplementary Material. Based on the mean values of R^2_{adj}, χ^2 and RSS obtained from tested temperatures, it was concluded that the Freundlich model was the best to fit the SMX experimental data (Fig. 3a). This model assumes that (i) the adsorption capacity increases exponentially with the adsorbate concentration and (ii) the energy of each activation site is not homogeneous (Lima et al., 2021). The calculated $1/n_F$ value ranged from 0.32 to 0.33 (Table S7), which indicated that the adsorption was favorable (Piccin et al., 2017). On the other hand, the best fit for TMP experimental data was obtained with the Langmuir model (Fig. 3b). This model assumed that (i) TMP was adsorbed at a fixed number of active sites, and (ii) saturation was achieved at the monolayer (Lima et al., 2021).

The maximum adsorption capacities (q_m) of DWTS for the TMP removal from the single solution at 20, 30 and 40 °C were 20.4, 23.6 and 26.8 mg/g, respectively. For the case of SMX in the single solution, the calculated monolayer adsorption capacity using the Langmuir model were 30.5, 30.8 and 36.7 mg/g. This result was unexpected because the pH conditions were unfavorable for SMX adsorption on DWTS (pH >

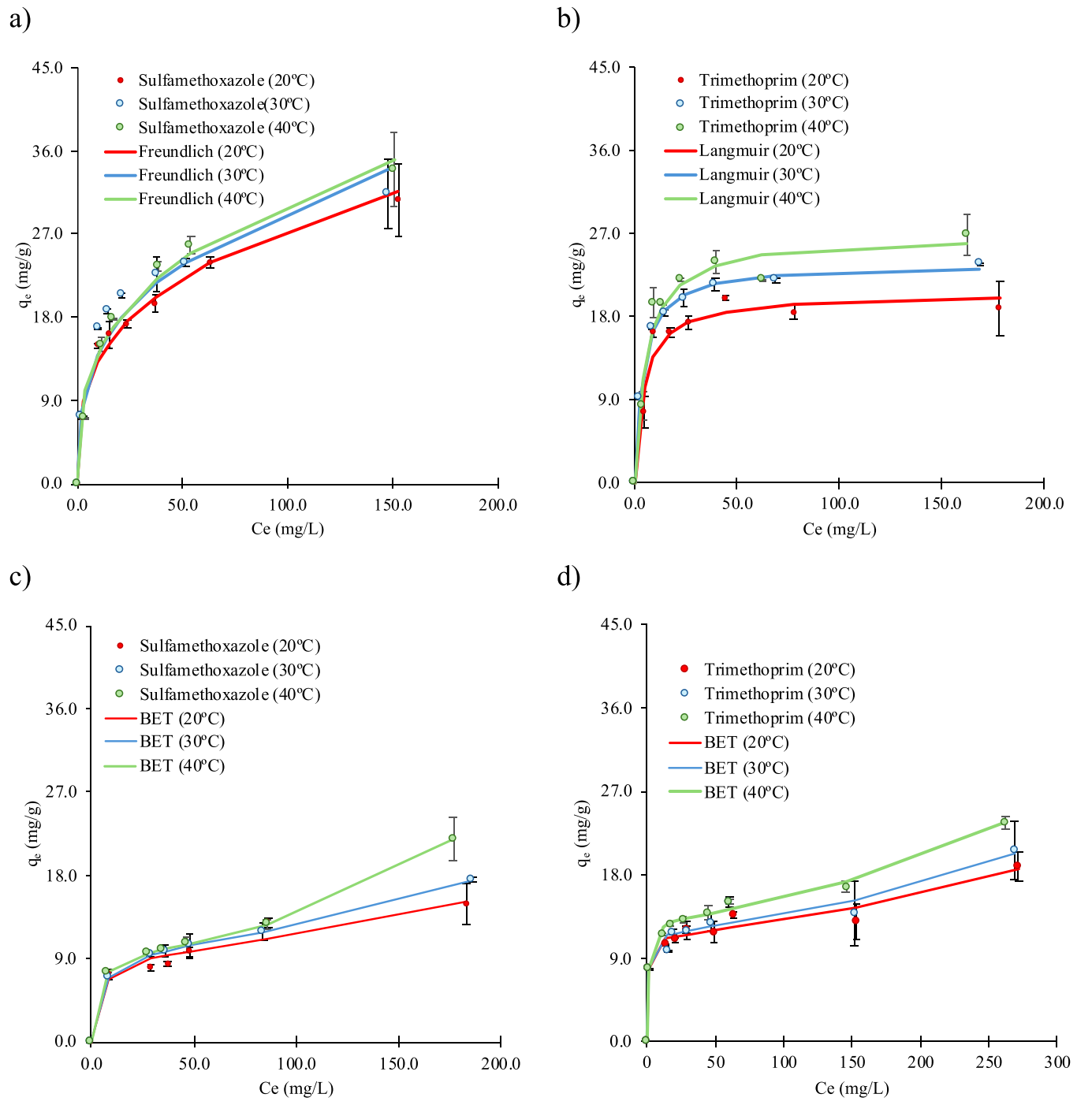

Fig. 3. Isotherms for the adsorption of sulfamethoxazole (SMX) and trimethoprim (TMP) using DWTS from (a,b) single and (c,d) binary solutions. Experimental conditions: Contact time = 24 h, S/L ratio = 2 g/L, and initial pH = 6.5.

pKa). As discussed, DWTS had a higher adsorption capacity for SMX, which may be due to the formation of more favorable adsorbent – adsorbate interactions.

To provide a comprehensive evaluation of the DWTS's efficiency, a comparative analysis with other adsorbent materials commonly accepted as benchmark adsorbents, is essential. The AC is the widely used adsorbent, the reported adsorption capacities for the SMX and TMP can range between 130 and 808 mg/g (Liu et al., 2015; Prasannamedha and Kumar 2020;Shi et al., 2019). This removal performance was associated with the AC textural properties, namely the significantly larger surface area (higher than 500 m^2/g) (Prasannamedha and Kumar 2020).

The use of AC in the context of wastewater treatment is typically discouraged due to its substantial additional cost. Given that DWTS is a by-product (typically viewed as a waste material), its incorporation offers the advantages such as cost reduction, promotion of a circular economy within the water sector, and a reduced carbon footprint.

The achieved maximum adsorption capacities of DWTS are higher than other low-cost adsorbents. Specifically, biochar (TMP - 2 mg/g), wood chippings (TMP - 8.33 mg/g) (Li et al., 2019), pyrolyzed sewage sludge (SMX - 2.5 mg/g; TMP - 7.5 mg/g), pyrolyzed fish waste (SMX - 4.6 mg/g; TMP - 13.6 mg/g) (Nielsen and Bandosz, 2016), and carbonaceous waste from refineries (SMX - 10 mg/g) (Mitra et al., 2021). A significant advantage of DWTS over other low-cost adsorbents is that it

requires no activation pre-treatment, a common step for many adsorbents discussed previously. This eliminates both the associated economic costs and the environmental impact inherent of the (re)activation process.

The results of the binary experiment showed a competitive (antagonistic) adsorption behavior for both antibiotics (Fig. 3c and 3d) where the maximum adsorption capacities from the single assays were higher than those obtained for the binary solutions. Note that the hydrogen bonding is a relevant interaction involved in the adsorption mechanism of these antibiotics (Xue et al., 2023). Therefore, the reduction in the antibiotic adsorption capacities may be due to competition for the oxygenated functional groups. The experimental binary adsorption results were also correlated using the tested isotherm models (Table S8 of the Supplementary Material). Based on the mean values of R^2_{adj}, χ^2 and RSS for the three temperatures, it was possible to conclude that the BET model was the best-fitted model for both antibiotics (Wang et al., 2024).

3.2.4. Antibiotic adsorption mechanism interpretation via statistical physics models

The analysis and interpretation of adsorption mechanism of both antibiotics in single and binary systems was based on the calculated n_{an}, n_{1b} and n_{2b} parameters for the statistical physics models, which are summarized in Table 2. As stated, the steric parameters (n_{an}, n_{1b}, and n_{2b}) represent the number of antibiotic molecules adsorbed per DWTS functional group in the single and binary systems. The calculated n_{an} values in single systems were 0.4, 0.44 and 0.61 for SMX adsorption at 20, 30 and 40 °C, respectively, while they were 3.21, 0.93 and 0.75 for TMP at the same temperature conditions. Overall, the calculated n_{an} values for SMX removal were lower than those for TMP adsorption. Note that a significant reduction of n_{an} parameter for TMP removal was observed as the solution temperature increased. It was also concluded that molecular aggregation of TMP may occur in the aqueous solution at 20 °C forming a trimer. However, the thermal agitation broke the bonds between TMP molecules in the aqueous solution (before adsorption) as the aqueous solution temperature increased. The adsorption orientation of SMX and TMP molecules on DWTS surface can be sketched via the next analysis (Ghorbali et al., 2024; Sellaoui et al., 2024):

(A) If $n_{an} < 0.5$, two DWTS functional groups can participate in the antibiotic adsorption, leading to a parallel orientation.
(B) If $n_{an} > 1$, one DWTS functional group can participate in the antibiotic adsorption, leading to a non-parallel orientation.
(C) If $n_{an} \in (0.5,1)$, the adsorption of both antibiotics can be in parallel and non-parallel orientations at the same time.

For instance, the calculated n_{an} values for SMX and TMP adsorption in single systems were lower than 0.5 and between 0.5 and 1, respectively. These results indicated that both antibiotics were adsorbed via parallel orientation, and parallel and non-parallel orientations at the same time depending on the adsorption temperature.

On the other hand, the impact of aqueous solution temperature on n_{1b} and n_{2b} for the binary systems is illustrated in Table 2. Both parameters showed two different trends as functions of aqueous solution temperature in tested binary systems. For instance, the n_{1b} value for SMX adsorption increased with temperature, while the n_{2b} value for TMP adsorption decreased. This trend can be explained by considering the exclusion and competition of both antibiotics from the same functional group of DWTS.

Table 2
Calculated values of the steric parameters (n_{an}, n_{1b} and n_{2b}) for antibiotic adsorption on DWTS at different temperatures.

	Single systems					
	SMX			**TMP**		
T (°C)	20	30	40	20	30	40
n_{an}	0.40	0.44	0.61	3.21	0.93	0.75
	Binary systems					
	SMX			**TMP**		
T (°C)	20	30	40	20	30	40
n_{ib} (i= 1, 2)	0.33	0.81	0.50	0.82	0.38	0.94

3.3. Antibiotic adsorption assays using wastewater

Table 3 shows the comparison of SMX and TMP adsorption capacities in distilled water and treated wastewater, while the wastewater characterization results are listed in Table S9. The results showed a decrease in adsorption capacity in assays with binary solutions compared to single solutions, both in distilled water and wastewater. The antibiotic most susceptible to the adsorption inhibition was SMX, which may be related to its relatively low Log K_{ow} value (Prasannamedha and Kumar 2020). On the other hand, the decrease in adsorption capacity observed for SMX could result from competition with other species present in wastewater, such as phosphate and sulphates, as the ability of DWTS to remove these compounds has been documented (Dias et al., 2023; Kulandaivelu et al., 2020). In fact, both anions are present in the used wastewater (Table S9). It was found that the TMP removal results in wastewater were similar to those in distilled water, in either single or binary solutions. Xue et al. (2023) reported that TMP achieved better removal results under competitive conditions, which agreed with the results obtained with DWTS in this study. Xue et al. (2023) posit that, in comparison with SMX, TMP establishes stronger van der Waals forces, electrostatic attraction, hydrogen bonds and hydrophobic interactions with the adsorbent material.

4. Conclusions

This study has proved that the sludge produced in the drinking water treatment process can be used as a low-cost adsorbent for the removal of sulfamethoxazole and trimethoprim from water and wastewater. This low-cost adsorbent is composed of activated carbon, organic matter and coagulant residues, particularly aluminum and magnesium. The results of leaching assay indicated that this sludge is chemical stable despite its complex composition and can be safely applied in adsorption processes for water and wastewater treatment. DWTS showed better adsorption properties to remove sulfamethoxazole than trimethoprim in aqueous solutions, and its performance is better than other low-cost materials. Antagonistic adsorption was observed for the simultaneous removal of sulfamethoxazole and trimethoprim using this sludge. The oxygenated functional groups of this material participated in the adsorption mechanism to remove both antibiotics via parallel and non-parallel orientations where hydrogen bonding is expected to be the main interaction. The results also showed that this sludge can be used to remove these antibiotics in real-life matrixes such as wastewater. Consequently, the application of this residue as an adsorbent can benefit the costs of water utilities and contribute to the sustainability in the water sector and the circular economy worldwide. However, further studies with different sludges are required to understand the properties responsible for the adsorption capacity of antibiotics, in order to promote the use of DWTS as a low-cost adsorbent for the removal of antibiotics. Conversely, subsequent studies should concentrate on the life cycle of this material, evaluating (i) the regeneration processes and (ii) the number of

Table 3
Adsorption capacity (mg/g) of sulfamethoxazole (SMX) and trimethoprim (TMP) using DWTS in distilled water and wastewater.

Matrix	SMX	TMP
Distilled water - single solution	17.59 ± 3.23	17.60 ± 2.45
Distilled water - binary solution	8.80 ± 1.23	14.70 ± 2.76
Wastewater - single solution	11.35 ± 1.25	18.10 ± 0.26
Wastewater - binary solution	4.68 ± 0.49	14.18± 0.42

regeneration cycles applicable.

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CRediT authorship contribution statement

Diogo Sousa: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Maria Bernardo:** Writing – review & editing, Supervision, Resources, Formal analysis, Conceptualization. **Lotfi Sellaoui:** Writing – original draft, Formal analysis. **Adrián Bonilla-Petriciolet:** Writing – review & editing, Visualization, Formal analysis. **Asma Mokhati:** Writing – review & editing, Visualization, Formal analysis. **Rita Maurício:** Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100737.

Data availability

Data will be made available on request.

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