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# Charge as a key physicochemical factor in adsorption of organic micropollutants from wastewater effluent by rice husk bio-silica

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## ABSTRACT

Wastewater treatment plants (WWTPs) often fail to fully remove organic micro-pollutants (OMPs), necessitating advanced treatment methods. This study examines the potential of an agricultural waste-derived adsorbent, rice husk (RH) – silica, for removing a complex mixture of 20 OMPs in MilliQ water and wastewater effluent. While RH-silica shows potential for OMP removal, its performance with multicomponent mixtures in real wastewater has yet to be investigated. Batch experiments demonstrated the efficacy of RH-silica in removing cationic, neutral, polar, and non-polar OMPs across various pH levels, with no adsorption of anionic OMPs. Column elution studies revealed that only positively charged compounds did not reach a breakthrough after 300 specific bed volumes (BVs), even when the filtration velocity was increased fivefold (3.8 m/h) and lower adsorbent-to-volume ratios (0.5 g/L) were employed. This indicates that electrostatic interactions via deprotonated silanol groups are the primary adsorption mechanism. RH-silica's ability to retain cationic pollutants regardless of their hydrophilicity degree highlights its potential as a novel adsorbent targeting positively charged persistent and mobile organic compounds (PMOCs). Moreover, the adsorption efficiency remained high in experiments with real wastewater effluent. Considering practical applications, a RH-silica column could be used to enhance removal of cationic polar compounds. This approach not only improves pollutant removal efficiency but also contributes to sustainability in WWTPs by using agricultural waste resources. Despite significant operational and end-of-life challenges for large-scale implementation, this study represents a crucial advancement in the investigation of RH-silica as an adsorbent.

## 1. Introduction

Industrialization and population growth have resulted in a notable rise in water consumption and contamination levels, increasing water scarcity and pollution issues worldwide. Among the pollutants of concern are organic micropollutants (OMPs), which include a variety of anthropogenic organic compounds (Connor & Miletto, 2023). In the environment, wastewater treatment plants (WWTPs) are a primary source of these compounds, as they only partially degrade or adsorb OMPs (Rizzo et al., 2019). In response to this issue, the European Commission proposed a revised Urban Wastewater Treatment Directive issued with the zero-pollution legislative package in October 2022,

emphasizing the need to adapt existing WWTPs to address OMPs removal through advanced treatment methods (EU Commission, 2022).

One of the most problematic OMPs are Persistent Mobile Organic Compounds (PMOCs), which are characterized by high polarity, persistence, and potential toxicity (Schulze et al., 2019). Consequently, comprehensive approaches are required for their effective removal (Tisler et al., 2022). Persistent compounds challenge conventional WWTPs, requiring ongoing research in advanced treatment technologies for their integration into WWTPs (Rizzo et al., 2019).

Ozonation is an advanced technique for removing organic micropollutants (OMPs), but its effectiveness can be hindered by factors such as nitrite concentration, bromide, and organic matter, which lead to

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early exhaustion and the formation of polar, persistent by-products (Reemtsma et al., 2016; Rizzo et al., 2019; Beita-Sandí et al., 2020; Gulde et al., 2021). While advanced oxidation processes and nanofiltration show promise for OMP removal, they carry risks of generating new contaminants and require high energy inputs (Reemtsma et al., 2016; Schollée et al., 2018). In contrast, algae-bacteria consortia represent a sustainable and low-cost alternative for wastewater treatment; however, their efficiency is influenced by factors such as pH, light availability, nutrient levels, and temperature. Effective field-scale implementation of these systems necessitates further research to improve the understanding of algal-bacterial interactions, optimize operational parameters, and integrate smart technologies while evaluating their techno-economic viability and ecological impact (Chan et al., 2021; Oruganti et al., 2022). Adsorption using activated carbon (AC) is a cost-effective solution, but it faces challenges like regeneration issues, competition with organic matter, and poor retention of hydrophilic compounds (Westerhoff et al., 2005; Gulde et al., 2021; Guillosoou et al., 2020). Modifying AC's surface charge to enhance electrostatic interactions with hydrophilic compounds can help address these challenges (Zhou et al., 2021), while naturally hydrophilic materials such as mesoporous silica may effectively remove compounds that are not adequately adsorbed by AC (Grefa et al., 2023).

Rice husk (RH)-derived silica emerges as a promising hydrophilic adsorbent, characterized by a high surface area ranging from 200 to 1500 m<sup>2</sup>/g, tunable pore and particle sizes, stability, and a net negative surface charge at neutral pH (Flores et al., 2023). In contrast to industrial silica sourced from sodium silicate, quartz sand, or SiCl<sub>4</sub>, RH-derived silica presents a more economical and environmentally friendly alternative. Moreover, addressing agricultural waste management, particularly for rice husks, is crucial due to their contribution to greenhouse gas emissions (Toan et al., 2021). Untransformed rice husks have demonstrated efficacy in adsorbing metals, dyes (Karić et al., 2021), and phenol from water (Daffalla et al., 2020), underscoring their potential as low-cost adsorbents. However, thermally treated rice husks exhibit significantly higher surface areas, resulting in enhanced adsorption efficiencies (Daffalla et al., 2020). Notably, rice husks contain 15–28 wt% silica in their dry form, increasing up to 99 wt% in the ashes (Rodríguez-Otero et al., 2023).

Previous studies have shown the potential of RH-silica-based materials for absorbing water contaminants, especially cationic organic dyes (Tsamo et al., 2020; Hou et al., 2023; Grefa et al., 2023; Mondal et al., 2024). RH-silica-based adsorbents have a point of zero charge (pH<sub>pzc</sub>) ranging from 2 to 5. At neutral pHs, the silica surface is predominantly negatively charged with some hydroxyl groups, promoting adsorption through electrostatic interactions and hydrogen bonding. Recent research shows its efficacy in removing OMPs like drugs and pesticides from water. High selectivity for cationic OMPs (e.g., methamphetamine, metformin, and carboplatin) was observed at neutral or basic pHs in MilliQ water (Swarnalakshmi et al., 2018; Grefa et al., 2023). RH-derived silica also removed hydrophilic anionic pharmaceuticals such as tetracycline, amoxicillin, diclofenac and phenol at neutral and acidic pHs (Chen et al., 2016; Asgharnia et al., 2019; Elnazer et al., 2024; Grefa et al., 2023). Neutral and lipophilic pharmaceuticals, including carbamazepine, triclosan, and caffeine were adsorbed through hydrogen bonding with protonated silanol groups at low pH (Swarnalakshmi et al., 2018; Tejedor et al., 2022). However, few studies have been examined the adsorption of multicomponent mixtures using RH-silica. Costa et al. (2020) tested polycyclic aromatic hydrocarbons in MilliQ water, and Saha et al. (2014) treated mixed-pesticide contaminated synthetic water (50 µg/L) with 10 g of RH-silica in a column experiment (Saha et al., 2014). In real water tests, RH-silica efficiently adsorbed methyl parathion from spiked surface and ground waters (Akhtar et al., 2007).

The use of RH-silica can address the challenges previously identified in the context of WTPs. It represents a sustainable option that does not require significant energy input, does not result in the production of new chemicals, and has a sustainable origin that aligns with the principles of

the circular economy. Additionally, the presence of silanol groups renders silica hydrophilic, thereby enhancing its capacity to attract polar persistent compounds of concern, particularly cationic compounds (Zeb et al., 2020).

While previous studies on RH-silica have demonstrated its potential as an adsorbent, they often focus on limited experimental conditions, such as using only a narrow range of organic micropollutants (OMPs) or employing simplified systems like MilliQ water. These studies rarely account for the complexities of real wastewater matrices or multicomponent adsorption, which are critical for practical applications. Additionally, most investigations have been conducted under batch conditions, which do not accurately reflect continuous flow processes in wastewater treatment plants. Our research seeks to overcome this research gap by evaluating RH-silica in more realistic, multicomponent systems and under continuous flow conditions, thereby providing a more comprehensive understanding of its performance and establishing its potential for practical wastewater treatment applications.

The study aimed to characterize RH-silica as a sorbent for a complex mixture of 20 OMPs in water. The OMPs selected for this study represent a diverse group of contaminants, exhibiting a wide range of polarities and charges commonly observed in wastewater. This selection includes key pharmaceuticals frequently detected in Danish wastewaters (Kilpinen et al., 2023), such as carbamazepine, citalopram, clarithromycin, metoprolol, and benzotriazole, which are specifically highlighted in the EU Urban Waste Water Treatment Directive (2022/0345/COD) as requiring 80 % removal by advanced treatments. Furthermore, other persistent contaminants, including the herbicide terbuthryn, per- and polyfluoroalkyl substances (PFAS), and 6-ppd-quinone, were included in the study to ensure comprehensive coverage of substances of regulatory and environmental concern. This comprehensive approach enables an evaluation of RH-silica's efficacy in actual wastewater treatment settings and its capacity to meet the requirements of evolving regulatory frameworks.

Batch tests were conducted using RH-silica in pure water spiked with the 20 OMPs across a range of pH levels. The same setup was tested in continuous flow conditions through a column packed with RH-silica, with flow-proportional samples were taken to study the breakthrough of adsorbed OMPs. Finally, the adsorption of targeted OMPs in secondary effluent wastewater was assessed to evaluate removal efficiencies in a complex matrix, providing valuable insights for upscaling.

## 2. Materials and methods

### 2.1. Standards and reagents

A list of analytical standards are included in Table S1. Standard solutions were prepared in methanol and stored at – 18 °C. Formic acid (LC-MS grade, > 99 % Purity, Fisher Chemical, PE, USA), MilliQ water (Ultrapure, > 18.2 MΩ cm<sup>-1</sup>), LC-MS grade acetonitrile (ACN) (Chemsolute, purity > 99.95 %), LC-MS ultra Chromosolv methanol (Honeywell Riedel-de Haen, Seelze, Germany, purity > 99.9 %), sodium hydroxide (NaOH) (>98 % Purity, Sigma-Aldrich, MI, US), calcium chloride (CaCl<sub>2</sub>) (>97 % purity, Sigma-Aldrich, MI, US) and hydrochloric acid (HCl) (37 % Purity, Fisher Chemical, PE, US) were used.

### 2.2. Working solutions

To prepare the working solutions containing the 20 OMPs, individual stock solutions (1 g/L) were first made in methanol from analytical standards and combined into a mixture at 10 mg/L in LC-MS grade water. For the batch experiments, four 100 mL working solutions were then prepared by diluting the mixture to a nominal concentration of 100 µg/L in MilliQ water and adjusting to pH 4, 6, 9, and 11 using 0.1 M NaOH or HCl. The pH adjustment influenced each molecule's charge (see Table S2). For the column experiments, a 2 L working solution was prepared similarly, diluted to 100 µg/L in MilliQ water, and adjusted to

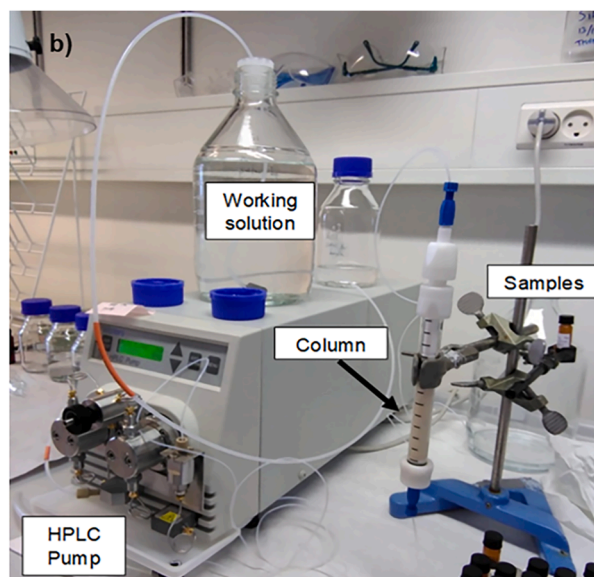
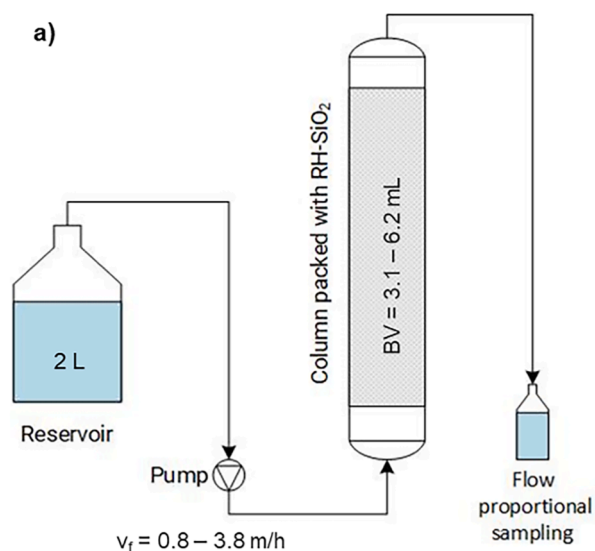


Fig. 1. Schematic representation (a) and picture (b) of the set-up for spiked water experiments on RH-silica adsorption in fixed bed column.

pH 6. The methanol concentration in all working solutions was kept below 0.2 %.

### 2.3. Secondary effluent wastewater sampling

The secondary effluent wastewater used in adsorption experiments was collected from the secondary clarifier at the Avedøre WWTP in Copenhagen, Denmark, in June 2023, just before its discharge into the environment. The effluent had an average pH of 7.2 and total organic carbon (TOC) concentration of  $13.7 \pm 1.6$  mg/L. Further details regarding the quality of the wastewater can be found in Table S3. A 20-liter grab sample was manually collected in two glass containers of 10 L each and vacuum filtered through a  $0.7 \mu\text{m}$  mesh size filter on the same day. The water was stored in 3-liter laboratory Duran glass bottles (pre-washed and heated) at  $4^\circ\text{C}$  for the 6-day duration of the adsorption experiments.

### 2.4. Adsorbent rice husk silica (RH-silica)

Silica was extracted from rice husk obtained from a commercial mill *Arrocería del Pirineo Brazal* located in Zaragoza, north-east Spain. Highly mesoporous silica was produced from rice husks through a thermochemical method involving acid leaching and calcination: the rice husks were first washed with deionized water and then leached with 0.1 M HCl at  $100^\circ\text{C}$  for 3 h. Subsequently, they underwent thermal treatment, and silica was obtained after calcination at  $700^\circ\text{C}$  with a heating rate of  $2^\circ\text{C}/\text{min}$  for 3 h. Porosity of RH-silica was analyzed using  $\text{N}_2$  adsorption isotherm instruments, revealing a BET surface area of  $329 \text{ m}^2/\text{g}$ , a pore volume of  $0.35 \text{ mL}/\text{g}$ , an average pore diameter of 6.4 nm. The BET surface area is crucial for assessing RH-silica's adsorption capacity, as a larger surface area provides more active sites and pores for adsorbate interaction and capture. The dry-bulk density of RH-silica was determined to be  $320 \text{ kg}/\text{m}^3$ . RH-silica exhibited a broad size distribution, consisting of particles of 100–200  $\mu\text{m}$ , particles of 50  $\mu\text{m}$  and some of 5–30  $\mu\text{m}$  confirmed by SEM (Fig. S1). The material was passed through a 120-mesh sieve to eliminate larger artefacts (Rodríguez-Otero, 2024). The  $\text{pH}_{\text{pzc}}$  of RH-silica was calculated by measuring the zeta potential (DDL Zetasizer, Malvern Analytical, UK), where  $\text{SiO}_2$  particles were equally suspended in ultra-pure water and solutions at different pHs (2–9) prepared with  $\text{HNO}_3$  (0.1 M) and  $\text{NaOH}$  (0.1 M) solutions. The results were obtained using the Smoluchowski theory approximation, and each sample was measured 3 times at  $25^\circ\text{C}$  (Gulicovski et al., 2008).

The  $\text{pH}_{\text{pzc}}$  indicates the adsorbent's surface charge at different pH levels, helping to understand how RH-silica interacts with charged contaminants, thereby elucidating the adsorption mechanisms. The  $\text{pH}_{\text{pzc}}$  was determined to be approximately 2 (Fig. S3). Above this pH, the silica surface begins to be deprotonated, while below this pH, it becomes protonated.

### 2.5. Experimental set-up for batch tests

The RH-silica particles were placed in a beaker and dried for 12 h at  $180^\circ\text{C}$  in a furnace overnight before the adsorption experiments. To study the effect of pH on adsorption, four pH-adjusted working solutions, each with 20 OMPs at a nominal concentration of  $100 \mu\text{g}/\text{L}$ , were used for the experiments (Table S2). Although this concentration was higher than levels typically found in real wastewater, it was selected to align with comparable ranges used in studies involving synthetic water in the literature. RH-silica concentration in all batch tests was  $1 \text{ mg}/\text{mL}$ , the total volume used in each batch test was of 10 mL. Controls were made with 10 mL of each working solution without adsorbent, and blanks with 10 mL of Milli-Q water adjusted to each working pH. Batch tests were carried out in triplicates in 15 mL glass vials, shaken horizontally at 300 rpm for 48 h. After the contact time, the samples were centrifuged in glass tubes for 5 min at 2100 rpm. Then, 750  $\mu\text{L}$  of supernatant was diluted with 50 % methanol into 1.5 mL vials and refrigerated until analysis.

### 2.6. Experimental set-up for column elution studies and sample preparation

#### 2.6.1. Adsorption of OMPs spiked in working solution

The experimental protocol involved eluting the OMP mix working solution (pH 6) through a fixed-bed column. The adsorbent material was packed in a 150 mm long, 10 mm internal diameter Omnifit EZ Benchmark column (Merck, Darmstadt, Germany), with a bed volume of either 3.1 mL or 6.2 mL. Both the inlet and outlet were fitted with 10  $\mu\text{m}$  PTFE frits, and the PTFE tubing had an external diameter of 1/16".

The 2-liter working solution was pumped upward through the column from a 2 L glass container with a 515 HPLC pump (Waters, MA, USA) at flow rates of 1 to 5 mL/min, or expressed in filtration velocities, 0.8 m/h to 3.8 m/h (Fig. 1).

Dried RH-silica particles, with a dry-bulk density of  $320 \text{ kg}/\text{m}^3$ , were packed into the column with bed volumes (BVs) of 3.1 or 6.2 mL,



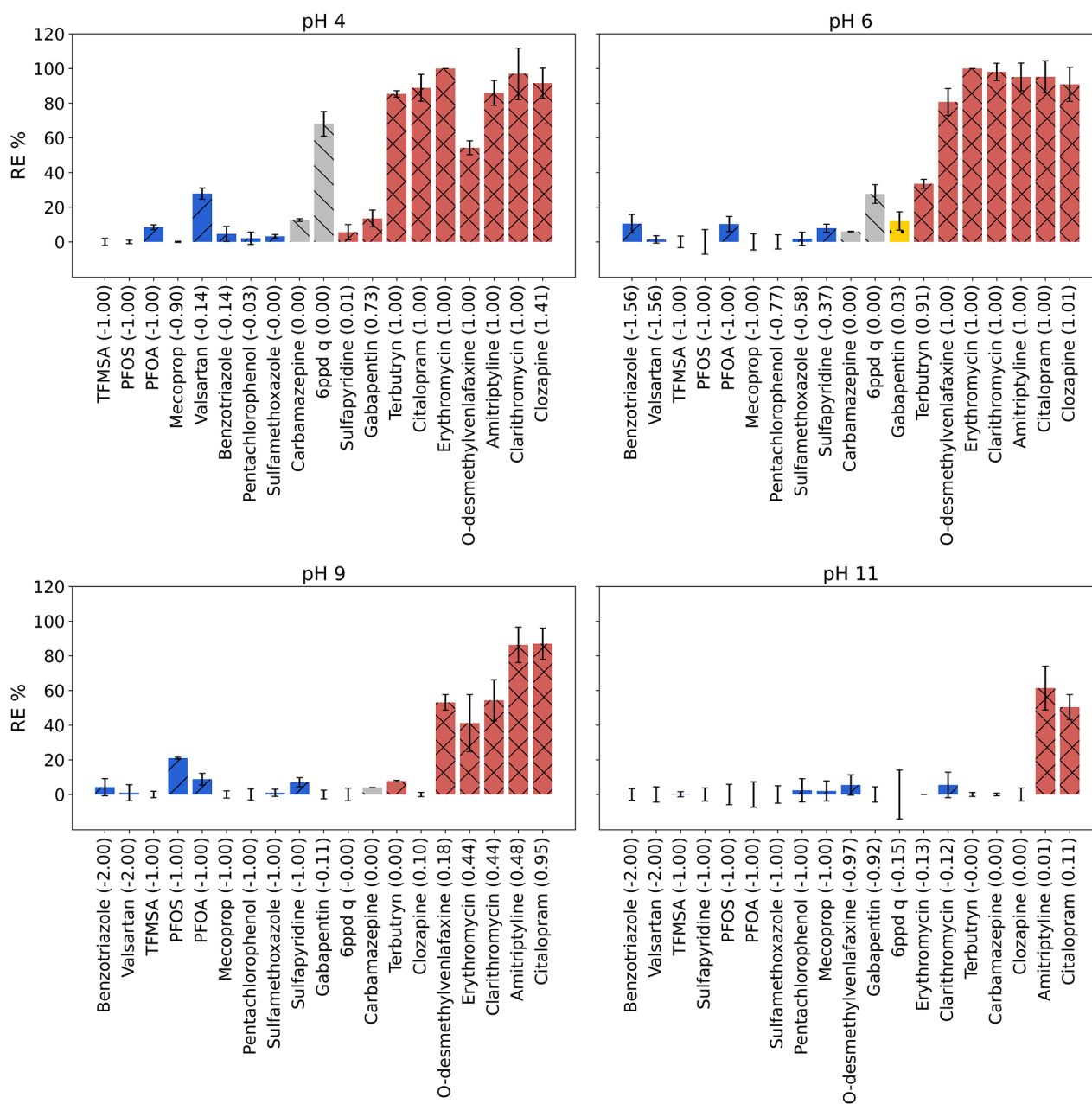


Fig. 2. Effect of pH on the adsorption of OMPs on RH-silica, the normalized charges of OMPs are included in parentheses. In all batch tests, RH-silica concentration was 1 mg/mL, the total volume was 10 mL, with a contact time of 48 h at 25 °C. Only OMPs shown with < 30 % RSD between triplicates.

corresponding to an adsorbent-to-mass ratio of 0.5 g/L and 1 g/L respectively, between two PFTE filters with 10  $\mu$ m pores. Initially, 100 mL of ultrapure water was pumped from the system at 1 mL/min to equilibrate and wet the bed. Then, the working solution passed through RH-silica at filtration velocities of 0.8 to 3.8 m/h to assess the impact of flow on the breakthrough curve of each OMP. Control experiments were carried out with the column without adsorbent, using MilliQ water as method blanks. The use of controls and blanks helps validate the experimental results by confirming that any observed adsorption is due to RH-silica and not to other factors. The column without the adsorbent serves as a reference to identify any potential interference or contamination, while the MilliQ water blanks ensure that the system remains free from impurities. All experiments were done in duplicate. Time-flow proportional samples, each 2.5 mL, were collected from the column outlet into 4 mL brown glass vials and refrigerated. The first sample was taken after 8 specific bed volumes (BVs), meaning the volume of water

that passed through the column was equivalent to 8 times the bed volume of the filter. For analysis, 750  $\mu$ L of each sample were diluted 1:1 with methanol and analyzed using LC-MS. The breakthrough point was defined when the OMP effluent area ( $A_v$ ) reached 10 % of the initial area ( $A_0$ ) ( $A_v/A_0 = 0.1$ ).

#### 2.6.2. Adsorption of target OMPs in secondary effluent wastewater

Only column experiments were performed with real wastewater, as our primary goal was to evaluate RH-silica behavior in a scenario that closely resembles real-world application, which would be in an adsorption column. Additionally, time constraints limited the feasibility of conducting both batch and column tests with real wastewater. Using the previously described setup, 1 L of secondary effluent wastewater was pumped at 2.5 mL/min or filtration velocity of 1.9 m/h, through a packed column with a fixed BV of 3.1 mL. The 100 mL samples were collected from the column outlet. The first sample (T1) was taken from 8

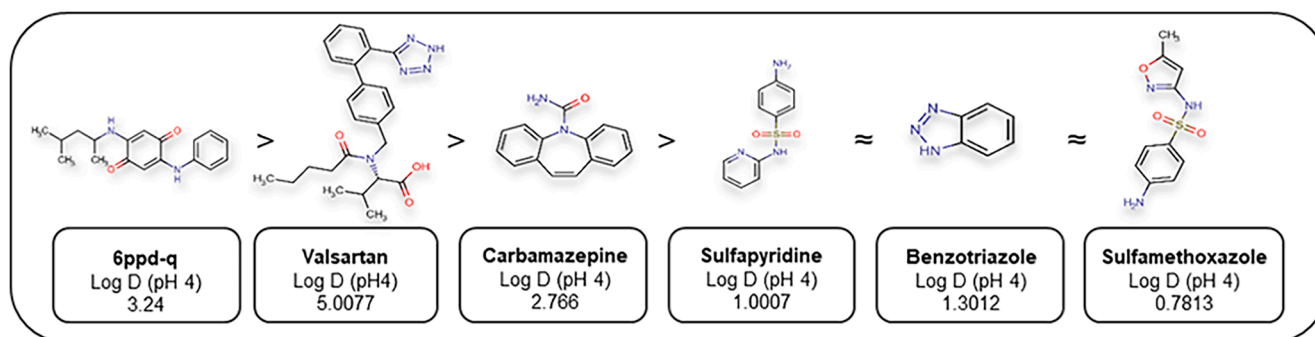


Fig. 3. Neutral and anionic OMPs at pH 4, listed in order of removal efficiency from highest to lowest, along with their Log D values retrieved from Chemicalize.

to 40 specific BVs, which represents the point at which the column efficiency is at its highest, and the second sample (T2) was taken from 290 to 323 specific BVs, where the column approaches saturation. Method blanks were prepared with MilliQ water containing 300 mg/L CaCl<sub>2</sub>. All experiments were performed in triplicate. The 100 mL samples were subjected to evaporation using a vacuum-assisted system (SyncorePlus Evaporator System, BUCHI Labortechnik AG, Switzerland). The vacuum-assisted evaporation method entailed the transfer of each 100 mL sample to a VEC round cylinder flask. The temperature of the evaporation platform was set to 55 °C, and the samples were evaporated to dryness at 20 mbar for a period of four hours, with 200–300 orbital movements per minute. Concentrates left after evaporation, were recovered with 1.5 mL of methanol from the flasks by manual rinsing of the glass vial wall, then transferred to 1.5 mL amber HPLC vials (Thermo Scientific, USA). Subsequently, the salts were removed by centrifugation for 10 min at room temperature of the HPLC vials, and the supernatants (sample without salt) were transferred with glass pipettes to new 1.5 mL amber HPLC vials. The final volume was adjusted to 1.5 mL and stored in the freezer at 4 °C until analysis by liquid chromatography with high-resolution mass spectrometry (LC–HRMS) detection. The enrichment factor was 67.

## 2.7. Chemical and data analysis of micro-pollutants in the samples

### 2.7.1. Measurement by LC-MS of 20 OMPs in the working solution

The samples were analyzed with LC connected to MS. LC-MS analysis was performed on an Acquity UPLC system with an Acquity C18 BEH column (1.7 μm; 2.1 × 50 mm) interfaced to a triple quadrupole mass spectrometer with electrospray ionization (ESI) (Waters, MA, USA). The detailed method descriptions can be found in SI.

MassLynx software version 4.1 (Waters, MA, USA) was used for instrument control and data acquisition. TargetLynx (Waters, MA, USA) was used for automated targeted detection and integration of chromatographic analyte peaks. Integrated peak areas were used to determine removal efficiency based on the variation of the OMPs peak areas (A) in inlet and outlet ( $RE\% = (1 - (A_v / A_0)) \times 100$ ). The relative standard deviation (RSD%) was calculated using the formula ( $RSD\% = \left( \sqrt{\frac{RSD_{Av}^2 + RSD_{A0}^2}{2}} \right) \times 100$ ), where RSD<sub>Av</sub> and RSD<sub>A0</sub> represent the relative standard deviations of the OMPs peak areas in the inlet and outlet of the analytical triplicates. Compounds with removal efficiencies with RSD% higher than 30 % were discarded.

Instrument Detection limits (IDL) were determined using six concentration levels, including zero spiking level, prepared in triplicates from the 20 OMP stock solution of 100 μg/L in MilliQ water. The highest IDLs, ranging between 10.4 μg/L and 30.1 μg/L, were obtained for erythromycin, 1,2,3-benzotriazole, 6ppd-quinone, gabapentin, clarithromycin, PFOS, PFOA, sulfamethoxazole, and clozapine. The maximum removal efficiency (MRE) for these compounds was 70 % to 89.6 %. Other compounds had IDLs between 2.9 μg/L and 9.2 μg/L, with

MRE from 90.8 % to 97.1 %. OMPs that were not detected were designated as <IDL.

### 2.7.2. Measurement by LC-HRMS of target OMPs in secondary effluent wastewater

The wastewater samples were analyzed with LC-HRMS because of its suitability for both targeted and untargeted analysis of complex environmental samples. The latter approach was used for further studies that are not included in this paper. LC-HRMS analysis was performed on an Acquity UPLC system with an Acquity BEH C18 column (1.7 μm; 2.1 × 100 mm) interfaced to a G2-Si Synapt QTOFMS in the range 50 to 1000 m/z with ESI. The method followed Tisler et al. (2022) and the detailed methods descriptions can be seen in SI.

Detection, integration of chromatographic peak; and RE% and RSD% calculation was made in the same way as described in Section 2.7.1. MREs were calculated for the detected targeted compounds from the 20 OMP mix. A two-point calibration curve estimated the initial concentrations of the target compounds in the effluent wastewater. The estimated values consistent with previously calculated concentrations in samples from the same WWTP quantified by Kilpinen et al. (2023), as shown in Table S5. When a compound was below IDL in T1 or T2 samples, noise was integrated to calculate MRE compared to the concentration in wastewater, avoiding overestimation (Table S6).

## 3. Results and discussion

### 3.1. Batch test: influence of pH

In this section, the results from the batch adsorption experiments using spiked pure water are discussed. Fig. 2 shows the variation in removal efficiency of the 20 OMPs with pH. Overall, the removal efficiency decreases as the pH increases from 4 to 11. Additionally, positively charged compounds (located on the right side of the x-axis) are removed more efficiently than neutral or negatively charged compounds.

For negatively charged compounds across all pH levels (see Table S2 for detailed charge values), their adsorption by RH-silica was negligible. While some researchers (Chen et al., 2016; Asgharnia et al., 2019; Elnazer et al., 2024) found anionic compounds to be adsorbed onto silica at acidic pHs, this was not observed in this study.

Positively charged compounds at pH 4, such as clozapine, citalopram, clarithromycin, o-desmethylvenlafaxine, and amitriptyline, show removal efficiencies over 80 %. At this pH, silanol groups on RH-silica start to be protonated ( $pH_{pzc} \approx 2$ ), facilitating adsorption through hydrogen bonding (Swarnalakshmi et al., 2018; Grefa et al., 2023). Gabapentin, despite its total positive charge, is not well adsorbed at pH 4 due to its zwitterionic nature, which includes a deprotonated hydroxyl group (pKa 4.63). Thus, reducing adsorption capacity due to repulsion with the deprotonated silanol groups on the surface of RH-silica. Among neutral and anionic compounds at pH 4, 6ppd-quinone and valsartan are

the most adsorbed (Fig. 2). When RH-silica is neutral, compounds with higher log D values show better adsorption (Fig. 3), similar results to findings by Saha et al. (2014) with pesticides, suggesting hydrogen bonds and dipole interactions with neutral OMPs.

At pH 6, silica is more deprotonated, increasing its electrostatic attraction toward cations. The removal efficiency of OMPs with one positive charge follows this order: erythromycin  $\approx$  clarithromycin  $\approx$  citalopram  $\approx$  amitriptyline > clozapine > o-desmethylvenlafaxine > terbutryn. As shown in, the positively charged amino groups facilitates the electrostatic interactions with the deprotonated silanol groups on silica, resulting in high removal efficiencies regardless of their hydrophobic degree. Terbutryn, with the lowest pKa value, shows the lowest removal efficiency.

Adsorption decreases as the solution pH increases. At higher pH, more deprotonated silica surface are available for electrostatic interactions, but the proportion of cationic OMPs in the solution decreases. At pH 9, adsorption follows the order of pKa values: citalopram and amitriptyline (pKa > 9) remain well adsorbed, while clarithromycin and erythromycin (pKa = 9) show slightly reduced efficiency. At pH 11, silica is completely deprotonated favoring ionic interactions over proton donor interactions. However only citalopram and amitriptyline are cationic at this pH, leading to a reduced removal efficiency.

The high removal efficiencies of neutral and positively charged organic micropollutants (OMPs) across various pH levels indicate that RH-silica's adsorption mechanism involves both and electrostatic interactions, being the last one the predominant mechanism. RH-silica's negative surface charge at pH (>2) values above its point of zero charge (pH<sub>pzc</sub>) enhances interactions of the electrons on the oxygen-surface groups of silica toward cationic compounds. Negatively charged compounds, on the contrary, are repelled from RH-silica's negatively charged surface. While batch studies provide a simple method to study adsorption efficiency, column elution experiments offer a more realistic approximation of lab-scale studies to real-life applications.

### 3.2. Column study: influence in OMP selectivity and breakthrough behavior

This section presents the results from the fixed-bed column adsorption experiments using spiked pure water. Fig. 5 presents the results of column elution studies at pH 6 with a fixed filtration velocity of 3.8 m/h and a solid-to-volume ratio of 0.5 g/L, highlighting the differential affinities of RH-silica for various OMPs eluted through the column. The overall concentration of OMPs increased with the volume of treated water.

Positively charged compounds at pH 6, such as erythromycin, clozapine, citalopram, clarithromycin, or amitriptyline are not detected in any of the effluent samples, as observed in Fig. 5, indicating no breakthrough for these OMPs. In contrast, negatively charged compounds such as PFOA, benzotriazole, pentachlorophenol, sulfamethoxazole, and valsartan do not exhibit adsorption in any sample, as observed in the batch study with a pH 6 OMPs solution (Fig. 2). Column tests did not result in improved adsorption of anionic compounds with respect to batch tests, indicating that electrostatic repulsion is strong with the negatively charged adsorbent.

The compounds for which a breakthrough was observed are plotted in Fig. 6. In Fig. 6a, breakthrough curves are presented as a function of specific BVs to illustrate the effect of different filtration velocities, with the same amount of RH-silica used in both experiments. Fig. 6b, on the other hand, compares the adsorption performance using different adsorbent-to-volume ratios, with breakthrough curves plotted against the filtered volume to clearly demonstrate how doubling the amount of adsorbent impacts the overall volume of effluent treated.

Only carbamazepine, gabapentin, O-desmethylvenlafaxine and terbutryn showed breakthrough curves. Negatively charged compounds were not adsorbed at any point, and positively charged compounds (besides gabapentin, O-desmethylvenlafaxine, and terbutryn) were fully

**Table 1**

Removal efficiencies of target OMPs (initial concentrations ranging from 0.033 to 1.972  $\mu\text{g/L}$ , Table S5) from secondary effluent wastewater samples by adsorption onto RH-silica (1 g/L).

OMP	Removal % at T1 <sup>a</sup>	Removal % at T2 <sup>a</sup>
Citalopram	96 $\pm$ 0.1 <sup>b</sup>	92 $\pm$ 0.1 <sup>b</sup>
Metoprolol	99 $\pm$ 0.1 <sup>b</sup>	99 $\pm$ 0.1 <sup>b</sup>
Amitriptyline	95 $\pm$ 0.1 <sup>b</sup>	92 $\pm$ 0.1 <sup>b</sup>
Erythromycin	99 $\pm$ 0.6 <sup>b</sup>	99 $\pm$ 0.2 <sup>b</sup>
Clozapine	83 $\pm$ 0.2 <sup>b</sup>	78 $\pm$ 0.1 <sup>b</sup>
Terbutryn	83 $\pm$ 0.2 <sup>b</sup>	0 $\pm$ 0.2
Carbamazepine	84 $\pm$ 0.2 <sup>b</sup>	7 $\pm$ 0.1
Gabapentin	20 $\pm$ 0.2	0 $\pm$ 0.2
Benzotriazole	32 $\pm$ 0.1	14 $\pm$ 0.1
Sulfapyridine	22 $\pm$ 0.3	9 $\pm$ 0.2
Sulfamethoxazole	0 $\pm$ 0.3	12 $\pm$ 0.2
Valsartan	49 $\pm$ 0.1	9 $\pm$ 0.1

<sup>a</sup>  $\pm$  standard deviation (n = 3)

<sup>b</sup> not detected in the outlet sample.

adsorbed in all the experiments. Fig. 6a shows the breakthrough curves of carbamazepine, gabapentin, O-desmethylvenlafaxine, and terbutryn at different filtration velocities. For neutral compounds such as carbamazepine and zwitterions such as gabapentin, the adsorption curves followed an S shape, showing initial adsorption but early breakthrough (Fig. 6a).

At lower filtration velocities (0.8 m/h), in Fig. 6a, carbamazepine's breakthrough volume was 300 mL, while at higher velocity (3.8 m/h), it reduced to 200 mL. For gabapentin's, breakthrough point was similar at both velocities, through the curve shape differed. O-desmethylvenlafaxine and terbutryn were completely adsorbed under both conditions.

However, Fig. 6b shows that at higher filtration velocities, within the explored range, and half the adsorbent-to-volume ratio (0.5 g/L), a late breakthrough is observed for both compounds. Positively charged terbutryn and o-desmethylvenlafaxine (0.9117 and 0.9993 charge, respectively), exhibited late breakthrough after 1 L of volume. This aligns with batch experiments where these two compounds were less efficiently removed than other cationic compounds.

While carbamazepine and gabapentin are initially adsorbed, breakthrough occurs earlier with a steeper curve, especially at a low adsorbent-to-volume ratio due to shorter contact time between adsorbent and adsorbate (Fig. 6b). Higher filtration velocities decrease removal efficiency, while increasing the amount of adsorbent has the opposite effect (Cuccarese et al., 2023).

Column elution experiments aligned with batch experiments: cationic compounds were selectively retained, anionic compounds were repelled, and neutral, zwitterionic, and partially cationic compounds were efficiently retained initially but eventually eluted due to weaker interactions with RH-silica.

### 3.3. Column study: adsorption of target OMPs in secondary effluent wastewater

In this section, the findings from the fixed-bed column adsorption experiments using real secondary wastewater effluent are discussed. Twelve out of the 20 target OMPs were detected and quantified in the secondary effluent wastewater at concentrations ranging from 0.033 to 1.972  $\mu\text{g/L}$ , which were significantly lower initial concentrations of OMPs in wastewater, at least 50 times less than those in the previous column experiments with artificial water. This difference means they cannot be directly compared. However, this experiment effectively demonstrates how RH-silica would perform under real conditions. The removal efficiencies for these OMPs are shown in Table 1. Similar adsorption trends were observed with real wastewater samples, despite the wastewater pH (7.2) being slightly higher than the working solution in the column adsorption studies with 20 OMPs, and having lower initial OMP concentrations. Positively charged compounds, except terbutryn,

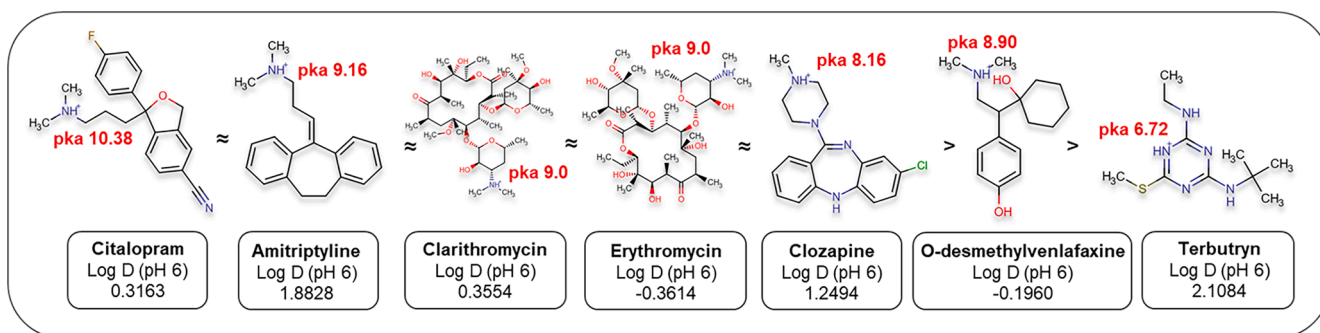


Fig. 4. Structures of OMPs with a net positive charge value close to 1 at pH 6, listed in order of removal efficiency, along with the pKa values of the basic group.

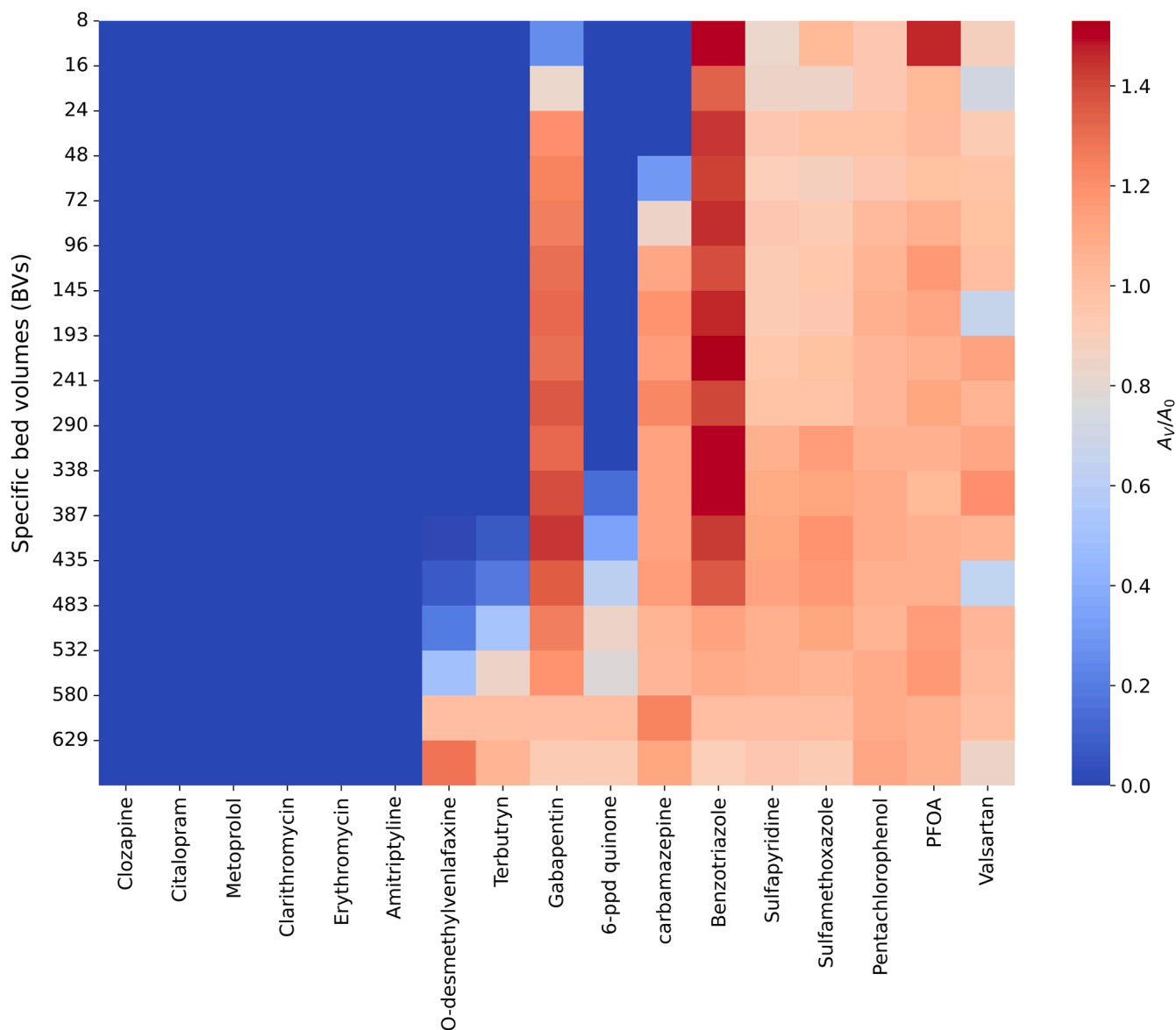


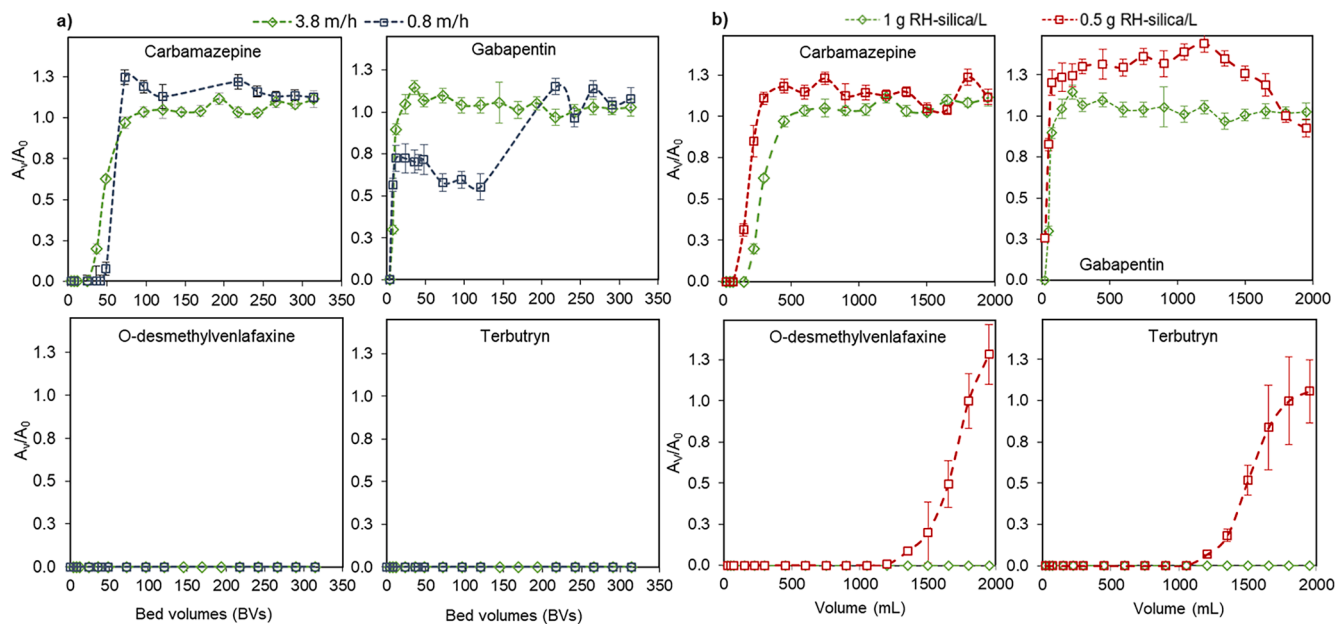
Fig. 5. Heatmap showing the  $A_v/A_0$  ratio of the OMPs (only shown those with RSD < 30 %) in each effluent sample of the column experiment at a fixed filtration velocity of 3.8 m/h and a solid-to-volume ratio 0.5 g/L. Here,  $A_v$  represents the compound area at a specific effluent volume, and  $A_0$  represents the compound area in the initial influent. OMPs are ordered on the x-axis from most positive (left) to most negative (right).

were completely retained at both sampling volumes (T1 and T2), as they were not detected in any outlet samples. Terbutryn, partially ionized at wastewater pH (Table S2), did not interact strongly enough with silica

surface, consistent with previous elution experiments with OMPs mixture in milliQ water (Section 3.2.).

Neutral compounds like carbamazepine, gabapentin, and





**Fig. 6.** Effect of filtration velocity: Breakthrough curves for carbamazepine, gabapentin, terbutryn, and O-desmethylvenlafaxine at velocities of 0.8 m/h and 3.8 m/h. The working solution contained 20 OMPs with a nominal concentration of 100  $\mu\text{g/L}$  and had a pH of 6. The mass-to-volume ratio was 1 g RH-silica/L (a). Effect of adsorbent-to-volume ratio: Breakthrough curves for carbamazepine, gabapentin, terbutryn, and O-desmethylvenlafaxine at ratios of 1 g/L or 0.5 g/L, with a filtration velocity of 3.8 m/h. The working solution contained 20 OMPs at 100  $\mu\text{g/L}$  and a pH of 6 (b).

benzotriazole showed significant breakthrough from T1 to T2. Negatively charged compounds exhibited lower adsorption, though valsartan was partially (49 %) adsorbed at T1. Cationic compounds in 1 L of secondary effluent wastewater, with a filtration velocity of 1.9 m/h, were effectively treated with 1 g of RH-silica. To the best of our knowledge, no prior tests have used RH-silica for multiple OMPs in real water samples.

In similar studies using other adsorbents, AC with an adsorbent-to-volume ratio of 10 mg/L with WWTP effluent successfully adsorbed 12 OMPs present at average concentrations ranging from 0.04 to 1.7  $\mu\text{g/L}$ . While AC was effective at adsorbing positively charged compounds, it demonstrated low removal efficiency for larger OMPs, such as erythromycin (734 g/mol), due to steric hindrance caused by dissolved organic matter (DOM) within its pores (Guilossou et al., 2020). This observation was further supported by Svahn and Borg (2023), who also suggested that the presence of basic functional groups in OMPs might reduce the adsorption efficiency of GAC in full scale with specific BVs larger than 8500. In contrast to these findings, RH-silica (as shown in Fig. 4) favored the adsorption of OMPs with basic groups, effectively removing macromolecular compounds like erythromycin and clarithromycin, even maintaining high removal rates for erythromycin in real wastewater. A previous study from Back et al. (2020) demonstrated that using gasification char and powdered AC at concentrations of 60 mg/L and 10 mg/L, respectively, achieved over 80 % removal of hydrophobic compounds (such as carbamazepine, benzotriazole, and diclofenac) from WWTP effluent. This suggests that these dosing levels could be viable for pilot-scale applications. In contrast, our experiment focused on a higher dose of 1 g/L. Therefore, it would be worthwhile to explore lower concentrations, such as 10 mg/L.

Additionally, there are other limitations to consider: RH-silica completely fails to remove negatively charged compounds, and its efficiency in removing neutral compounds diminishes rapidly in real effluents; for instance, the removal of carbamazepine dropped from 84 % to just 7 % (Table 1). In contrast, GAC effectively removes cationic compounds and also targets hydrophobic compounds, especially those with aromatic rings (Back et al., 2020; Svahn & Borg, 2023). Although GAC is negatively charged at wastewater pH, it can adsorb negatively charged compounds, suggesting a broader range of adsorption

mechanisms compared to RH-silica. Additionally, the negatively charged DOM in wastewater can adsorb onto GAC, potentially altering its overall surface charge (Svahn & Borg, 2023). While micropores constitute the majority of the GAC surface area, making it inaccessible to larger compounds, mesoporous adsorbents like RH-silica, with larger pore sizes, can accommodate bigger molecules. Overall, RH-silica exhibited high selectivity toward specific compounds. This selectivity can be advantageous for targeting compounds that GAC fails to adsorb. By combining both adsorbents in continuous columns, a more comprehensive removal of contaminants could be achieved. Furthermore, RH-silica could be functionalized to target specific compounds; for example, ordered mesoporous silica-based adsorbents grafted with amino groups have shown high adsorption capacity for PFOA (649 mg/g) in batch experiments (Dudarko et al., 2024).

#### 4. Conclusions and further remarks

This study characterized rice husk-derived silica (RH-silica) as an effective sorbent for removing OMPs from water. Batch experiments showed that RH-silica effectively removed cationic and neutral compounds across various pH levels, with its adsorption performance being highly dependent on the surface charge of the adsorbent. The results indicate that RH-silica's adsorption efficiency is strongly influenced by electrostatic interactions.

Column elution studies showed no breakthrough for positively charged compounds regardless their hydrophobicity degree, even when the filtration velocity was increased fivefold or at lower adsorbent-to-volume ratio, indicating strong electrostatic interactions. Similarly, to batch tests, negatively charged compounds were repelled, while neutral lipophilic compounds were better adsorbed.

Laboratory-scale studies with real secondary effluent wastewater demonstrated complete removal of cationic OMPs using an adsorbent-to-water ratio of 1 g/L. When comparing the retention of cationic and neutral compounds, we found that only the cationic compounds were completely retained at the higher specific BVs of 300. This suggests that the presence of organic matter and other ions in wastewater may not significantly impact the adsorption of these compounds at the tested runtimes, but it did impact negatively on the adsorption of neutral

compounds. However, the wastewater experiments monitored only a limited number of target compounds, which doesn't fully represent all the potential contaminants present in wastewater. Therefore, a more comprehensive analysis using non-target screening should be conducted to evaluate RH-silica's broader adsorption efficiency for a wider range of OMPs before and after treatment. Additionally, despite RH-silica's hydrophilicity suggests it could potentially avoid fouling by organic matter, this should be investigated further with longer run-times, higher filtration velocities and lower adsorbent-to-volume ratios.

Several challenges must be addressed before RH-silica's real-world implementation, including operational issues related to its powder form and heterogeneous size distribution. Exploring methods to homogenize particle size, such as converting the powder into pellets or silica monoliths, could enhance its manipulability. Additionally, it's crucial to consider the sustainability of RH-silica throughout its life-cycle. Investigating regeneration and reutilization methods, like proton exchange, could be beneficial, especially since cationic compounds are retained by electrostatic interactions. However, the disposal of the exhausted adsorbent and management of the recovered effluent should be considered, with one potential solution being the repurposing of exhausted RH-silica as a filler in construction materials to support circular economy principles.

In conclusion, despite the limitations of this laboratory-scale study, RH-silica has demonstrated potential as an efficient biomass-derived adsorbent for advanced wastewater treatment, providing a foundation for further research. Combining RH-silica with activated carbon post-ozonation could target compounds that activated carbon alone cannot remove, leading to a more comprehensive adsorption treatment.

## Supporting information

List of standards in the working solutions (Table S1), list of the charge of standards at selected water pHs spiked into pure water and pH of wastewater (Table S2), quality of wastewater sampled from Avedøre WWTP, SIR/SIM acquisition parameters for each compound (Table S4), estimated concentrations of targeted compounds in secondary effluent wastewater compared with literature (Table S5) and maximum removal efficiencies for targeted compounds in wastewater not detected in T1 and/or T2 samples (Table S6), SEM pictures of RH-silica (Fig. S1), STEM-HDAAF-energy-dispersive X-ray spectroscopy (EDX) image of RH-silica and EDX spectra with elemental identification (Fig. S2), zeta potential measurements for RH-silica (Fig. S3).

## CRedit authorship contribution statement

**Alba Rodríguez-Otero:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Selina Tisler:** Investigation, Data curation. **Lisa M. Reinhardt:** Investigation, Data curation. **Mathias B. Jørgensen:** Investigation, Data curation. **Brice Bouysièr:** Validation, Supervision, Project administration. **Jan H. Christensen:** Writing – original draft, Validation, Supervision, Project administration.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Alba Rodríguez-Otero reports financial support was provided by European Union. If there are other authors, they 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

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## Data availability

Data will be made available on request.

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