

Micropollutant removal from domestic wastewater effluent by softwood-biochar and sludge-biochar for safe reuse applications

Hadeel Hosney^{IWA ID^{a,*}}, Mostafa ElShourbagy^b, Ahmed Abdelrady^c, Thomas Wagner^d, Eleonora Borén^{a,e}, Mostafa Ahmed^a and Piet N. Lens^a

^a Water Supply, Sanitation and Environmental Engineering Department, IHE Delft Institute for Water Education, Delft, The Netherlands

^b Civil Engineering Department, Technical University of Delft, Delft, The Netherlands

^c Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, The Netherlands

^d Department of Environmental Technology, Wageningen University & Research, Wageningen, The Netherlands

^e Department of Applied Physics and Electronics, Umeå University, 90187 Umeå, Sweden

*Corresponding author. E-mail: h.hosney@un-ihe.org

 HH, 0000-0002-3729-8942

ABSTRACT

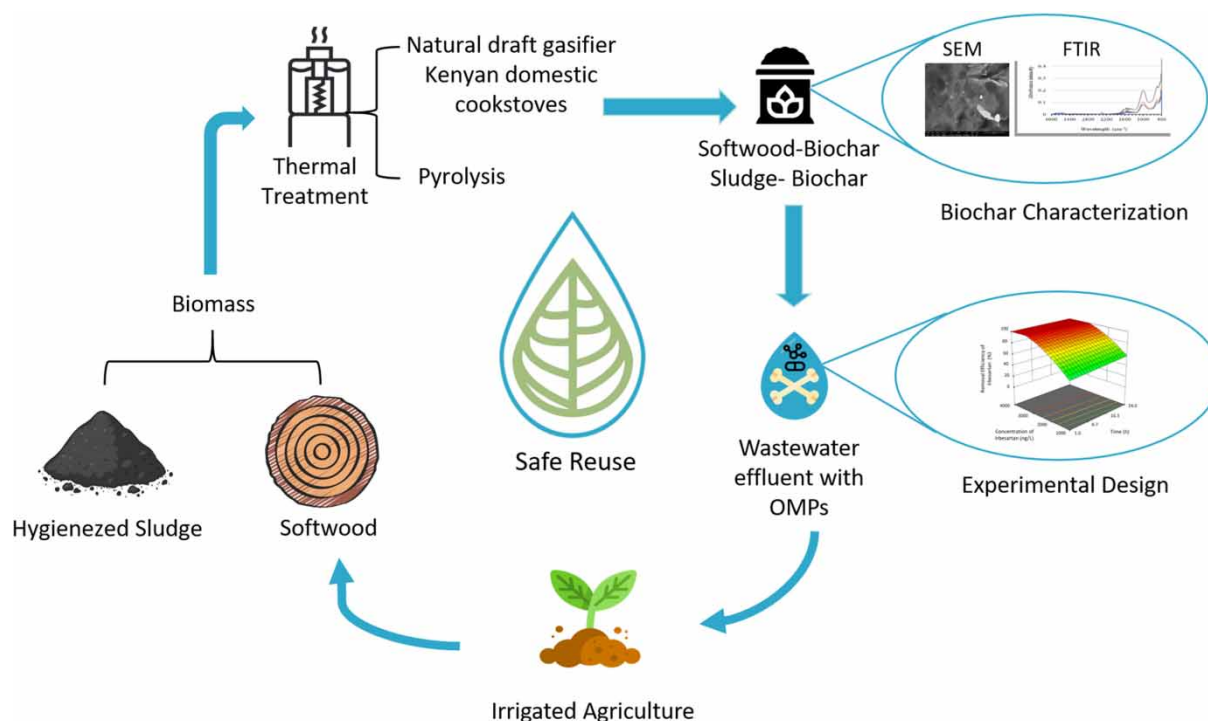
The reuse of domestic treated wastewater in agriculture poses a significant challenge as a result of the incomplete removal of micropollutants, with considerable public health, economic, and environmental consequences. Post-treatment of the treated wastewater by sorption-based technologies using biochar can mitigate these micropollutant-related concerns. Therefore, this study aims to evaluate the efficacy of various biochar types in eliminating micropollutants from treated wastewater to ensure safe reuse practices. The biochar utilised in this study was made from softwood and hygienized sewage sludge. Five indicator micropollutants were used to assess the removal efficiency of the different biochars. The experimental campaign consisted of two steps, starting with a preliminary assessment of the removal efficiency of various biochar types under constant operational conditions. This approach identified the biochar type that achieved the highest removal efficiency. Second, a response surface methodology study was then carried out to explore the interactive impacts of operational variables on the removal of selected micropollutants using the selected biochar type, softwood-biochar. This study showed that softwood-biochar can remove benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin with 98, 92, 94, 90, and 99% efficiency, respectively. These findings pave the way for the development of a low-cost sorption-based micropollutant removal technique for safe reuse.

Key words: adsorption, biochar, micropollutants, reuse, treated wastewater

HIGHLIGHTS

- Biochar characteristics are impacted by biomass sources and thermal treatment.
- The response surface approach predicts the micropollutant removal efficiency.
- Softwood-biochar can eliminate micropollutants from real domestic wastewater.
- Micropollutant type and concentration affect the sorption process efficiency.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Freshwater is a vital resource and essential to human life, agriculture, and industrial production processes. Freshwater is renewed by the hydrological cycle, but excessive consumption and progressive anthropogenic pollution lead to a shortage of supply in terms of quantity and quality. It is, therefore, no longer possible to rely on water as a renewable natural resource (Ingrao *et al.* 2023). Although wastewater reclamation is an important component of sustainable water resource management, it is still underutilised. However, a significant portion of all water sources has been used for various direct and indirect purposes, mostly through the de facto reuse of wastewater (Roccaro 2018; Christou *et al.* 2024). Such unplanned or unintended presence of wastewater in water supply sources, often in the form of inadequately treated wastewater, makes it essential to establish planned and controlled water reuse systems to ensure the safe use of reclaimed water.

Agriculture is the largest consumer of water, and to meet the food demands of growing populations around the world, more than 20 million hectares of agricultural land worldwide are currently irrigated with treated or untreated wastewater. The 20 million hectares could feed 100–200 million people with a moderate diet and average agricultural yield. In the occupied Palestinian territories, 65–70% of domestic treated wastewater is reused on farmland, including irrigated areas. Jordan reuses more than 75 million cubic metres of treated wastewater per year, either directly or indirectly, which accounts for 10% of the country's total water supply (Qteishat *et al.* 2024). The reuse of treated wastewater is also reported in developed countries such as the United States, where 67% is reused to water crops and landscapes (Tarawneh *et al.* 2024). Moreover, this practice is expected to further increase to overcome water scarcity (Al-Hazmi *et al.* 2023). However, there are also negative aspects that can pose health risks, such as the contamination of soils and plants by salt, toxic metals, and various chemical pollutants, microbial risks from pathogens that are often present in untreated or partially treated wastewater, and the accumulation of micropollutants in soils and in the food chain (Kesari *et al.* 2021). Wastewater treatment plants (WWTPs) are a major source of micropollutants release into surface waters, and even tertiary-treated wastewater might still contain these pollutants (Bai *et al.* 2018). These organic compounds include pharmaceuticals, personal care products, pesticides and their metabolites, commonly referred to as micropollutants (Bueno *et al.* 2012). In a study in Guangzhou city, China, covering several municipalities, the analysis found more than 400 micropollutants across 10 target locations with concentrations ranging from 3.99 to 1,021 ng/g in soils (Qiu *et al.* 2024). In addition,

another recent study found pharmaceuticals like atorvastatin and valsartan quickly disappeared in agricultural soils, while others, such as memantine and venlafaxine, remained (Menacherry *et al.* 2023). Prolonged exposure of agricultural soil to these micropollutants can pose a threat to human health and ecosystems, especially if combined with the use of chemical fertilizers (Srikanth 2019; Bali *et al.* 2021). To date, little attention has been paid to the presence of these pollutants in wastewater and their fate in wastewater treatment processes in the context of agricultural reuse. Because of the unknown metabolites and transformation products, inconsistent measurements for non-target compounds, sample collection complexity, analytical procedure uncertainties, and high analysis costs, there are no routine measurements for micropollutant compounds in the influents and effluents of WWTPs, which limits the understanding of their removal mechanisms (Bayabil *et al.* 2022). On this basis, the reuse of wastewater in agriculture requires the improvement of wastewater treatment processes to prevent possible environmental pollution by micropollutants and to protect human health from the associated risks (Al-Hazmi *et al.* 2023).

In low- and middle-income countries and arid or semi-arid high-income countries, wastewater is mainly used or reused in agriculture. In addition, impoverished urban farmers who depend on agriculture for their livelihoods, employment, and food security are often forced to use heavily polluted wastewater when freshwater is either unavailable or prohibitively expensive to use (Al-Hazmi *et al.* 2023). This use of polluted wastewater for irrigation is supported by claims that agricultural irrigation by wastewater allows higher crop yields, recycles organic matter and other nutrients to soils, improves the soil properties, minimises fertilizer costs, and acts as a low-cost wastewater disposal method (Jiménez 2006). Micropollutants in environmental media are constantly circulating, migrating, and transforming and have potent negative impacts, even if they exist in relatively low concentrations (Gomes *et al.* 2017). These contaminants are commonly removed through microbial, electrochemical, and adsorptive methods, as well as membrane and chemical oxidation processes. Adsorption is the popular choice among the aforementioned techniques due to the method's core advantages of being low-cost, highly efficient, and having a broad processing range (Cheng *et al.* 2021). Examples of adsorption-based technologies with high micropollutant removal efficiencies are granular and powdered activated carbon columns (Wagner *et al.* 2023) and constructed wetlands with enhanced adsorption substrate (Wagner *et al.* 2023). While different adsorbents can be used, activated carbon has the advantage of a large specific surface area, high porosity, and a large reactive surface chemistry, yet it is challenged by the relatively high production costs and reliance on non-renewable resources like coal, petroleum residues, peat, and lignite (Rodríguez-Narvaez *et al.* 2017; Tan *et al.* 2017; Kozyatnyk *et al.* 2021). Hence, there is a need for a lower-cost alternative adsorbent produced from sustainable materials with comparable efficiency to that of activated carbon that would be applicable in low- and middle-income countries where waste biomass is abundant and poorly managed.

Biochar, which is produced in a circular economy perspective by converting waste biomass such as agricultural waste and sludge, has gained recognition as an alternative adsorbent for the removal of organic and inorganic contaminants (Cheng *et al.* 2021). Recently, much emphasis has been placed on the use of these biomass resources for biochar production via various thermochemical processes that operate under oxygen-limited conditions and at relative temperatures below 700 °C. These processes include pyrolysis, hydrothermal carbonisation, and cookstove combustion (Tan *et al.* 2017). The chemical composition and morphology of the produced biochar are influenced by the initial feedstock composition, the selected thermochemical process and its operating parameters (Kozyatnyk *et al.* 2021). Biochar can remove micropollutants from wastewater streams with 85% effectiveness, depending on the precursor type, biochar production procedures, micropollutant concentrations, quantity of biochar, and mass transfer resistance rates (Tran *et al.* 2020; Cheng *et al.* 2021; Tang *et al.* 2022; Shirani *et al.* 2024). Thus, biochar is offering a solution that supports the shift towards a bio-based circular economy in low- and middle-income countries and beyond.

In addition to agricultural waste and sludge, other residual streams are available in low- and middle-income countries, of which biochar production and subsequent micropollutant removal have not yet been assessed. Therefore, this study aims to circulate the reuse of treated domestic wastewater in irrigated agriculture by improving the removal of micropollutants from wastewater effluent using newly produced biochar materials. Pyrolysis and cookstove combustion produce biochar from a variety of abundant waste biomasses in low- and middle-income countries, including softwood and sewage sludge. The effectiveness of different types of biochar in removing micropollutants was assessed through laboratory-scale experimental trials. In addition, a statistical analysis was performed to establish the optimal settings for the removal of such pollutants using a design expert central composite design (CCD) model.

2. MATERIAL AND METHODS

2.1. Materials

2.1.1. Sources of biomass and biochar preparations

Pellets of softwood (mix of spruce and pine) (Sweden) were chopped into approximately 1 cm pieces. Combustion tests were carried out using two natural draft gasifier Kenyan domestic cookstoves, both applying the natural draft concept using the pressure difference between hot (flame-side) and cold (surrounding) air (Mukarunyana *et al.* 2023; Hailu 2022). The distance in the combustion zone differed between the two types of natural draft gasifiers, with the first having a reduced natural airflow via the cookstove (named NDG). The second has a longer combustion zone between the fuel bed and the stove's outlets (named INDG), indicating an improved natural draft. At the beginning of the run, ethanol was added to obtain a rapid, stable combustion performance. Upon finishing combustion, the remaining solid was quenched and chilled at 0 °C.

Sewage sludge was collected from a municipal WWTP in northern Sweden. The sewage sludge had been left to hygienization for a year. The collected sludge was dried at 105 °C, and then 400 g of dried sludge was pyrolyzed in a cylindrical in-house-built pyrolysis reactor and placed in an external oven. The pyrolysis unit was connected to N₂ (1,000 mL/min flow unit) throughout the operation, which was flushed into the reactor at two connection points, leaving the reactor at a slight overpressure to prevent leaks. Volatiles were extracted and vented off through a top connection point of the cylinder. Pyrolysis was conducted at three distinct temperatures: 450, 550, and 650 °C (locally manufactured reactor, Sweden), with each temperature maintained for 45 min following the set-point temperature. As postprocessing for both the softwood and the sewage sludge materials, the produced biochar was ground to a nominal particle size of 75–212 µm.

2.1.2. Source of wastewater and preparation of OMP solutions

Treated effluent wastewater was sourced from the municipal WWTP in The Netherlands. The treatment technology in this plant is a conventional activated sludge. This study investigated only five organic pharmaceutical residues, all of which are listed in the revised urban wastewater treatment discharge directive of the European Parliament (Directorate General of Environment 2022). This directive mandates the monitoring of certain OMPs during the quaternary treatment of WWTP discharges in Europe. The five selected micropollutants were diclofenac, carbamazepine, benzotriazole, irbesartan, and metformin, which were also addressed for their limited removal within traditional activated sludge treatment technologies (Hagemann *et al.* 2020).

Initially, a stock solution of the targeted micropollutants (Sigma Aldrich, South Holland, The Netherlands) was prepared (total concentration: 1 g/L) and diluted to different concentrations to prepare the required concentration. Subsequently, the experimental feedwater was prepared by injecting the effluent wastewater with the desired organic micropollutants (OMPs) to reach the required concentration of the experimental campaign, in the range of 100–6,000 ng/L each.

2.2. Methods

2.2.1. Experimental setup

The first experimental campaign was an exploratory study in serum bottles to examine the effectiveness of five different types of biochar produced under various conditions to remove the targeted micropollutants from real WWTP effluent. The five biochar types were three pyrochars of sewage sludge and two cookstoves of softwood. The experiments were conducted in triplicates, with 0.1 L glass bottles filled with biochar, fed with 100 mL of the prepared feedwater, and placed on a horizontal reciprocal shaker (Brunswick Scientific Innova 2100 Platform Shaker, Boston, USA) at room temperature. The preliminary investigation was conducted under constant operating conditions, which were a contact time of 3 h, a biochar load of 0.1 g, multiple OMP concentrations, and a shaking speed of 150 rpm. This exploratory study was to select the most effective type for further investigation.

Influent and effluent samples were collected and examined to determine OMP concentrations and assess the effectiveness of OMP removal using Equation (1). Control samples were also prepared by filling the glass bottles with the same influent and micropollutant concentrations but without biochar materials. Aliquots were taken and filtered through 0.45 µm syringe filters (mixed cellulose ester, Chromafil A-45/25, and rinsed with 30 mL MilliQ water) prior to usage, following the procedure outlined by Hagemann *et al.* (2020). It should be noted that this process was conducted for 15–20 min from the start to the end of

the samples.

$$\text{Removal Efficiency of OMPs} = \frac{C_{\text{initial}} - C_{\text{time}}}{C_{\text{initial}}} \times 100\% \quad (1)$$

where C_{initial} is the concentration of OMPs in the wastewater influent before the adsorption starts (ng/L). C_{time} is the concentration of OMPs in wastewater effluent, after the biochar adsorption terminates (ng/L).

2.2.2. Experimental design

The biochar that demonstrated the highest removal effectiveness of OMPs from domestic wastewater effluent was studied further through an optimization study. The response surface method (RSM) was used to investigate the interactive influences of independent operational variables on removal efficiency and reaction progress in order to optimize the reaction conditions for OMPs removal.

After the exploratory study, a CCD was performed to efficiently calculate the order terms of the removal reactions. The CCD in this study consisted of eight factorial points augmented with four-star points and six centre points to calculate the standard deviation and pure error of the removal models. In this investigation, the following three independent operational variables were chosen: **A**: contact reaction time between biochar and aqueous OMPs feedwater (h); **B**: sorbent (biochar) amount used in the reaction (g); and **C**: OMPs concentration. The response (**Y**) is the removal effectiveness of OMPs from effluents after the biochar reaction was completed, as shown in Equation (1). Table 1 shows the codes of independent operating variables investigated.

2.2.3. Statistical analysis

Following the completion of the optimization campaigns' experimental runs, a regression equation was developed based on the generated responses. The regression equation was intended to establish a link between the obtained responses and the selected independent variables mentioned in Table 1. Certain statistical parameters, including *p*-value, *F*-ratio, coefficient of determination, and standard deviation, were used to evaluate the validity, reliability, and efficiency of the predictive models. It is worth mentioning that a model with a regression equation was established for each of the five OMPs and the pre-optimized biochar type. Thus, five models and equations were generated, and based on the aforementioned criteria, predictive models were generated for these models. The established regression equation allows us to calculate the optimal conditions for eliminating each OMP per biochar type.

2.2.4. Analytical techniques

2.2.4.1. UHPLC-MS for micropollutant concentration analysis. The concentrations of benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin were measured by ultra-high performance liquid chromatography-mass spectrometry (UHPLC-MS) analysis based on the method described by van Gijn *et al.* (2022) and Lei *et al.* (2023). Prior to UHPLC-MS/MS analysis, 2 mL liquid samples were centrifuged in Eppendorf tubes at 15,000 rpm for 10 min, and 950 µL of the supernatant was collected in amber-coloured glass (1 mL) LC-MS vials for analysis. A total of 25 µL of an internal standard solution containing carbamazepine-D10, diclofenac-D4, benzotriazole-D4, and irbesartan-D7 to reach a final concentration of 500 ng/L was added to compensate for the variation in the response of the UHPLC-MS/MS over time. Furthermore, 25 µL of acetonitrile was added to the sample to match the eluent composition at the start of each run. UHPLC-MS was performed with an ExionLC AD-30 UHPLC (Sciex, South Holland, The Netherlands) containing a Kinetex 1.7 µm Phenyl-Hexyl 100A column (2.1 × 150 mm) (Phenomenex, USA) coupled to a Triple Quad 5500+ QTRAP tandem MS (Sciex, South Holland, The Netherlands). The sample injection volume was 25 µL. Ultrapure water with 0.1%

Table 1 | Independent coded variables and the values that correspond to each code level

Independent variables	+ 1	0	- 1	+ α	- α
Time (h)	24.00	15.25	6.50	29.96	0.53
Sorbent (g)	1.61	1.03	0.45	2.00	0.05
Concentration of OMP (ng/L)	4,784	3,000	1,217	6,000	100

formic acid and acetonitrile with 0.1% formic acid was used as the mobile phase. The column temperature was 35° C, and the eluent flow was 0.4 mL/min. The ultrapure water/acetonitrile ratio of the mobile phase changed from 95%/5% (0–0.5 min) to 20%/80% (0.5–3.5 min), kept stable until min 7.5, then changed to 95%/5% (min 7.5–8.5) and kept stable until the end at 12.4 min. Qualification of the target micropollutant was done by scheduled multiple reaction monitoring according to the parameters provided in Table SM 1. An external calibration curve consisting of 100–250–500–750–1,000–2,000–3,000–4,000–5,000 ng/L, of which the r^2 was >0.99, was used for quantification using Sciex OS-MQ software.

2.2.4.2. Biochar characterization. The characteristics of different types of biochar were identified using different analytical techniques. Fourier transform infrared spectroscopy (FTIR) was used to identify functional groups such as organic, polymeric, and, in certain cases, inorganic parts in biochar surface areas using the PerkinElmer Spectrum 400 (FT-IR/FT-Near-Infrared (NIR) spectrometer, Waltham, Massachusetts). For elemental analysis, CHNS analysis was performed on the biochar particles to identify the percentages of carbon, hydrogen, nitrogen, and oxygen in the biochar particles. The elemental analysis was carried out using the Perkin Elmer 2400 elemental analyser (Waltham, USA). In addition, specific surface area (Specific Surface Area measured using the Brunauer-Emmett-Teller (SBET)) analysis was conducted with the analyzer manufactured by Quanta chrome model of NOVA touch 2LX (QCM, Q-senses, Biolin Scientific, Linthicum Heights, MD, USA). It was used to explore the pore volume, distribution, total surface area, and specific surface area of the biochar particles.

The zeta potential analysis was conducted by a zeta sizer analyzer (Malvern Panalytical Ltd, Malvern, UK) at neutral pH to describe dispersion stability, whereas the NS500-Model of the NanoSight was used for this application. An X-beam diffractometer (XRD) functioning at a current of 40 MA, a voltage of 40 kV, and a step filter of 0.01 (D8-Find, Bruker, with CuK radiation (1.5418), Madison, WI, USA) was used to determine the physical properties. The morphology of biochar particles was studied using scanning electron microscopy (SEM). SEM pictures were captured with a Zeiss LEO Supra 55VP Field Emission SEM and a Zeiss 1530 SEM (Jena, Germany), whereas a small portion of biochar was placed on a polished aluminium sample holder for sample preparation, and afterwards, gold-coated with an EMITECH K450X sputter coater. Another method to investigate the surface characteristics of the biochar particles, in terms of shape and texture, was a high-resolution transmission electron microscope (TEM) with a magnification of 20× and an accelerating voltage of 250 kV (JEOL TEM-2100, Tokyo, Japan). Prior to TEM measurements, samples were sonicated infusion by sonication prop under plus every 1 s for 30 min at 85% amplitude power. Finally, 50 µg biochar is added to TEM grade and air-dried for 5 h.

3. RESULTS AND DISCUSSIONS

3.1. Sorbents performance

The five biochar types investigated had variable performance with the removal of the selected micropollutants (Figure 1). The softwood-biochars, thermally treated by NDGs, showed better performance than the sludge-biochars. Softwood-biochars showed an average removal of 62, 72, 67, 81, and 90% for metformin, irbesartan, diclofenac, carbamazepine, and benzotriazole, respectively, while softwood-biochar (NDG) had a superior removal capacity. Consistently, a recent study investigating the use of biochar removal for pharmaceutical and personal care products showed 19–55% removal of diclofenac by softwood (NDG) and 77% by forced draft gasification (FDG), while it showed 51–53% removal of carbamazepine by softwood (NDG) and 61% by FDG (Mukarunyana *et al.* 2023). Furthermore, several studies investigated the removal of micropollutants by different plant-based biochars, where 60–90% removal for benzotriazole and its derivatives (BTAs) was observed by wild-plum and apricot-based biochar (Pap *et al.* 2023) and by oakwood residue biochar (Hasanzadeh *et al.* 2022), while more than 80% removal of diclofenac was achieved by pitch pine sawdust-biochar (Tam *et al.* 2020). This variability found in the literature can be attributed to the different origins of biochar and the treatment process conditions during its synthesis.

In contrast to the high micropollutant removal with softwood-biochars, sludge-biochars showed an average removal efficiency of 9, 38, 34, 29, and 39% for metformin, irbesartan, diclofenac, carbamazepine, and benzotriazole, respectively (Figure 1). This lower removal efficiency of the sewage sludge-based biochar is in alignment with the work presented by Calisto *et al.* (2015), whereas the adsorption capacity of paper mill sludge-biochar was around 10 times lower than that of commercial activated carbon, relative to the removal of carbamazepine and other pharmaceuticals. The micropollutant removal efficiency of the sludge-biochars depended on the combustion temperature with higher pyrolysis temperature

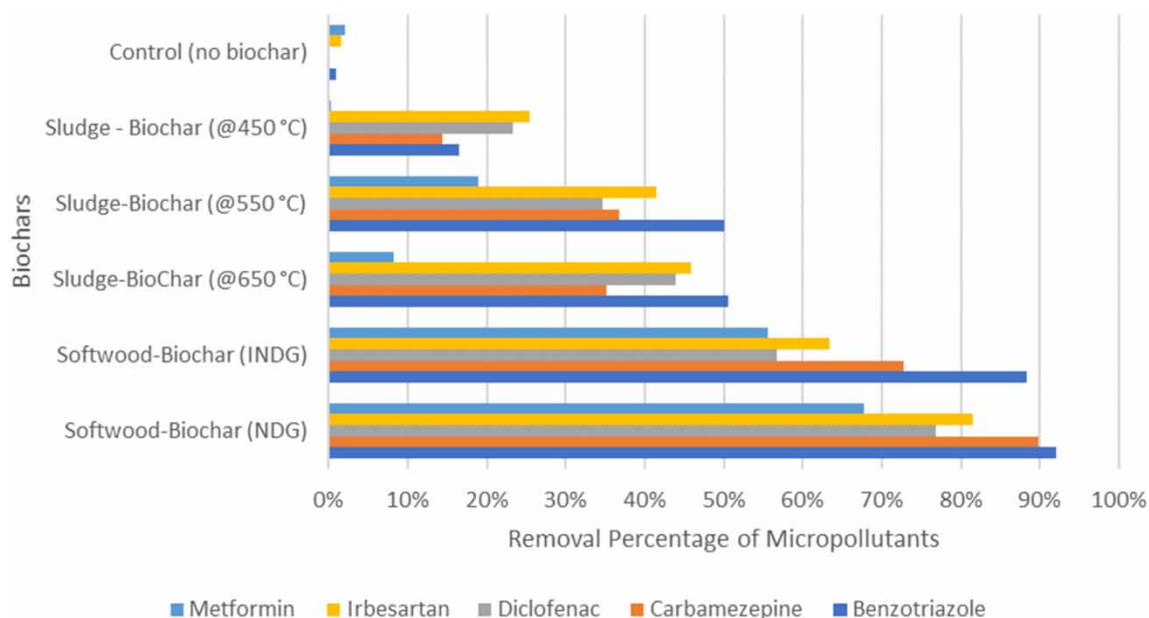


Figure 1 | Efficiency of OMP removal by different biochar.

resulting in higher removal efficiencies for irbesartan, diclofenac, and benzotriazole (Figure 1). A similar carbamazepine removal efficiency was observed for sludge-biochar at 550 and 650 °C (Figure 1). This observation is consistent with other reported findings, where it was shown that the adsorption characteristics were enhanced with increased pyrolytic temperature for sludge-biochar relative to diclofenac removal (Czech *et al.* 2021) and for pine sawdust-biochar relative to carbamazepine removal (Chu *et al.* 2019). In contrast, metformin showed a distinct performance, while the sludge-biochar showed the lowest removal efficiency for metformin at 450 °C, reaching a maximum of around 550 °C, and then declined again at around 650 °C.

3.2. Biochar characterization

3.2.1. Fourier transform infrared spectroscopy

Peaks in the fingerprint zone of the sludge-biochar FTIR spectrum, at $\sim 537\text{ cm}^{-1}$, indicated the presence of halogenic stretching bonds with either iodide (C-I) or bromide (C-Br) (Figure 2(a)). Moreover, sludge-biochar at 650 °C showed more than 50% reduction in absorbance intensity compared to that at 450 °C at the band-peak of $\sim 980\text{ cm}^{-1}$, corresponding to a C=C bending of alkenes (Figure 2(a)). Smaller peaks were also detected in the sludge-biochar within the band range of $1,360\text{--}1,660\text{ cm}^{-1}$, corresponding to a group of functions active in that region such as N-O stretching with nitro compounds, N-H bending of amines, and C=C stretching with alkene, and unsaturated ketones. The sludge-biochar showed a decreasing absorbance intensity for its band peaks with an increasing combustion temperature (Figure 2(a)), underlining the role of temperature in the decomposition and conversion of different compounds. This is in line with the findings of Xu *et al.* (2018), who highlighted the decomposition of compounds containing alkyls and nitrogen groups when increasing temperature over 500 °C, reflected by a reduction of their peaks in the FTIR analysis.

In the spectrum of sludge-biochar, the absorbance within the band range of $670\text{--}850\text{ cm}^{-1}$ was lower for char produced at 550 and 650 °C, compared to 450 °C. This might be an indication of an elevation in the aromaticity of the biochar, while the degradation of such compounds would have started around 700 °C (Xu *et al.* 2018). Aromaticity of the sludge-biochar would have triggered more $\pi\text{--}\pi$ interaction sites with aromatics, which is in accordance with the better removal of carbamazepine, irbesartan, diclofenac, and benzotriazole (aromatics) at those temperatures compared to 450 °C, while metformin (non-aromatic) was showing a different behaviour.

Softwood-biochar exhibited different functional groups, whereas the spectrum showed three consecutive peaks at 739, 792, and 865 cm^{-1} , related to C-H bending of mono- and disubstituted hydrocarbons (Figure 2(b)). The band shown at $\sim 1,145\text{ cm}^{-1}$ can be attributed to C-O stretching of tertiary alcohols and aliphatic ethers. Peaks observed at $\sim 1,560\text{ cm}^{-1}$

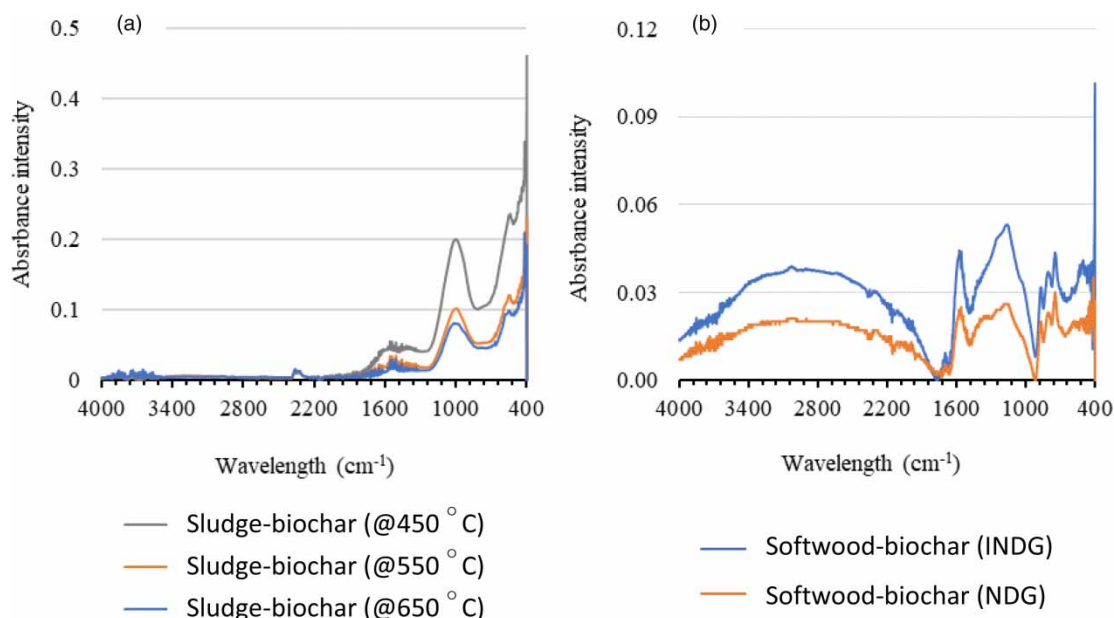


Figure 2 | Effect of thermal treatment approach on the functional groups of (a) sludge-biochar and (b) softwood-biochar (explanation by FTIR spectra).

could be again related to nitro-compounds with N–O stretching and C = C related to cyclic alkenes. The spectrum then showed a broad parabolic shape with small peaks within the band range of 1,800–3,800 cm^{-1} . Several functional groups could be detected in that region, such as O–H stretching related to carboxylic compounds, N–H stretching attributed to primary or secondary amines, C–H bending of aromatic compounds, and C = O stretching related to anhydrides. Although the peaks might be attributed to low concentrations of functional groups, the diversity of the surface and its richness might highlight the better removal of contaminants by different mechanisms. With a variety of functional groups, more adsorption mechanisms could develop between the adsorbent and the contaminants. Oxygen-related as well as carbonyl groups could trigger the formation of hydrogen bonds and n – π interactions, and other carbon functions could induce better interaction with the aromatic contaminants through π – π interactions (Pap *et al.* 2023).

3.2.2. Detailed investigations of softwood-biochar

Since softwood-biochar demonstrated the highest micropollutants removal efficiency, it was further analysed to identify the characteristics and the corresponding mechanism underlying such high performance. Distinctively, the CHNO analysis for softwood-biochar (NDG) showed a molar H/C ratio of 0.32, in the range with similar biochar documented in the literature, whereas values of 0.46 for pine-softwood biochar (Jiang *et al.* 2017) and 0.37 for cornstovers-biochar (Lee *et al.* 2010) were reported. Jiang *et al.* (2017) highlighted that even plants from similar botanical genera could have different H/C ratios, under different origins and thermal treatment conditions. Furthermore, in this research, the synthesis of softwood-biochar using a draft gasifier cookstove might have an effect on the H/C ratio. Moreover, the H/C ratio of the softwood-biochar (NDG) could point out a relatively moderate level of carbonization and aromaticity ($\text{H/C} > 0.2$) (Kuhlbusch 1995) and a potentially good biochar stability (Spokas 2010).

Softwood-biochar (NDG) had a surface area (Brunauer-Emmett-Teller (BET)) of 55 m^2/g ; more insights about the characteristics of softwood-biochar (NDG) are illustrated in Table 2. This value was much lower than that addressed for similar types of biochar originating from wooden sources, such as wood-waste biochar, which showed 83.6 m^2/g (Tomczyk *et al.* 2020), pine-softwood biochar that showed 219.35 m^2/g (Jiang *et al.* 2017), and softwood biochar of forestry residue showing a range of values between 139 and 289 m^2/g (Mukarunyana *et al.* 2023). El-Gamal *et al.* (2017) argued that one of the main parameters affecting the available biochar surface area was the cellulose and lignin content and their corresponding degradation temperature, highlighting the potential effect of the biochar origin on its characteristics.

The softwood-biochar consisted mainly of meso-sized pores, which, in addition to the previously mentioned surface characteristics, were in accordance with the results of the SEM and TEM analysis (Figure 3). SEM images (Figure 3(a) and 3(b))

Table 2 | Physico-chemical properties of several wooden and sewage sludge biochar types were investigated in this study and those reported in the literature

Biochar type	Physico-chemical properties			
	BET surface area (S_{BET}) (m^2/g)	Total pore volume (VT) (CC/g)	Average pore size (nm)	Zeta potential (mV)
Softwood-biochar (NDG) (<i>this study</i>)	55	0.1	3.9	−17.8
Sludge biochar (Nicholas <i>et al.</i> 2022)	3.52	0.011	–	−20
Pine-softwood biochar (Jiang <i>et al.</i> 2017)	219.35	0.125	–	−5
Softwood biochar of forestry residue (Mukarunyana <i>et al.</i> 2023)	139	–	2.6	–

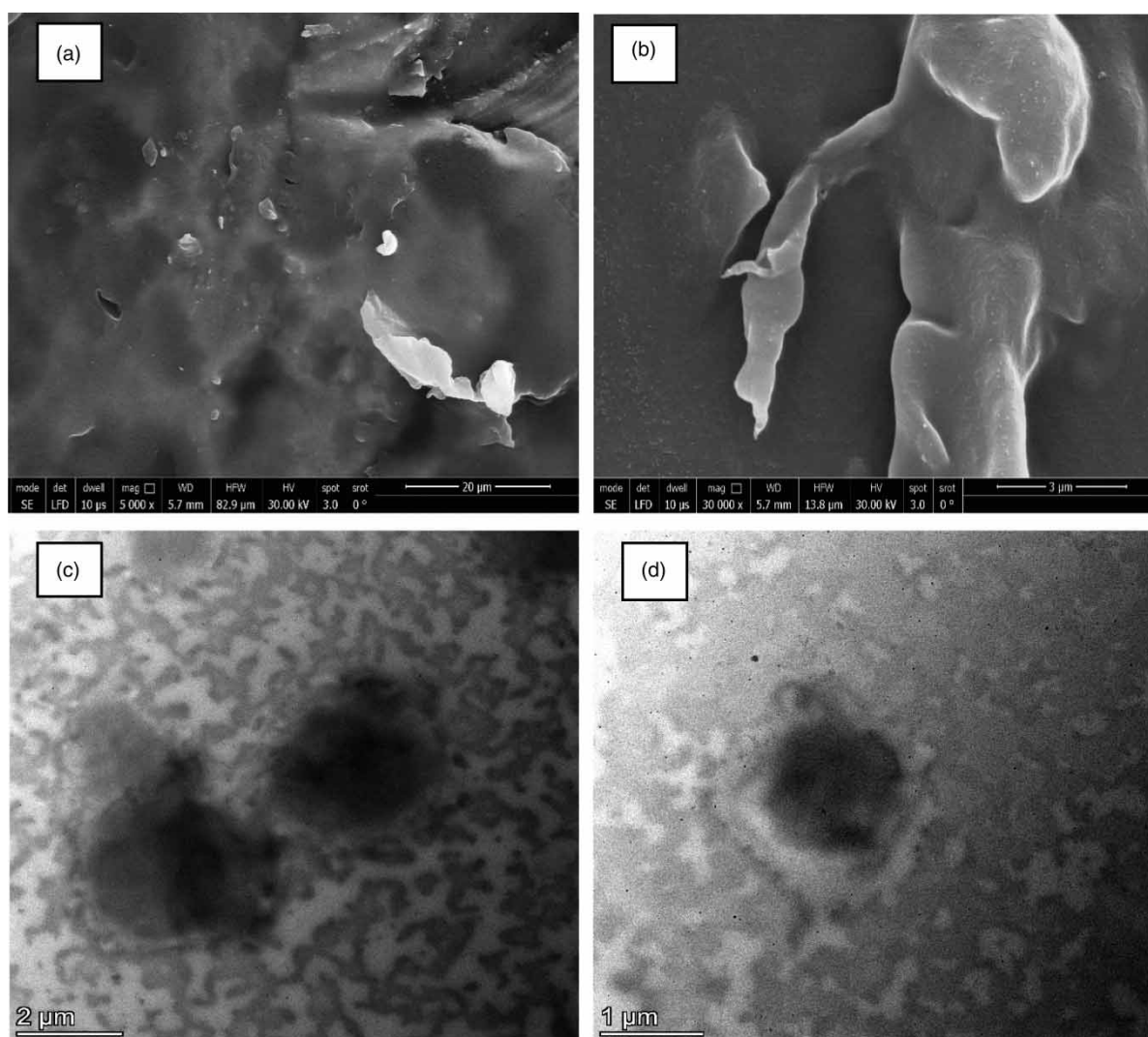


Figure 3 | SEM analysis of the softwood-biochar (NDG) with magnification scale $\times 5,000$ (a), $\times 30,000$ (b), and TEM analysis with a $2\ \mu\text{m}$ (c), and $1\ \mu\text{m}$ (d).

revealed a relatively smooth biochar surface, lacking the abundant cavities and well-developed micropores that would typically increase surface area (BET). This observation aligned with the TEM analysis in Figure 3(c) and 3(d), which showcased the scale of pores relative to the surface. While the literature highlighted that the presence of mesopores was essential for

accessing the smaller scale pores, micropores were addressed for playing a crucial part in the adsorption capacity of biochar and the detected BET surface area (Downie *et al.* 2009; Jiang *et al.* 2017). Adding to the small surface area (BET), this further confirms the poor removal of contaminants through pore filling. The zeta potential of the softwood-biochar amounted to -17.8 mV, which highlights the potential utilization of such biochar for cationic adsorption (Jiang *et al.* 2017), such as heavy metal neutralization (e.g., cadmium in soil (Hong *et al.* 2019)). Xu *et al.* (2020) reported that one of the main parameters that affects the produced zeta potential was the conditions of the thermal treatment process, as well as the corresponding potential interactions and decomposition of the surface functional groups. In addition, Yang *et al.* (2020) illustrated that the relatively low value of the zeta potential of biochar could be advantageous in soil applications for the adsorption of aromatic-based compounds (e.g., sulfamethazine), by which the low potential would produce less mobile biochar and correspondingly less co-transport of contaminants in soil media.

The XRD analysis had a specific angular range (20° – 70°), where the 20° angular range showed distinctive peaks at 25.5° and 43.2° for the softwood-biochar (NDG). The broad peaks showed that the sample had a more amorphous structure, highlighting again the impact of the thermal treatment process on the conversion of crystallized forms to amorphous ones (Fernandes *et al.* 2020). The amorphous structure of biochar is advantageous related to micropollutant removal, by which it would have fewer constraints on the diffusion of the micropollutant's molecules into the structure (Pap *et al.* 2023). Peaks around 22° – 28° can be related to the cellulosic content of wooden-biochar samples (El-Gamal *et al.* 2017; Fernandes *et al.* 2020). More specifically, the peak at 25.5° can be related to aromatics with tumultuous structural arrangements (Keiluweit *et al.* 2010), while the peak at 43.2° can be attributed to more structured graphite-like carbon (Turk Sekulic *et al.* 2019).

3.3. Optimization design

3.3.1. Analysis of variance

An RSM was used to investigate the interactive influences of independent operational variables on removal efficiency and reaction progress to optimize the reaction conditions for OMP removal. The high coefficients of determination, R^2 values of 0.9968, 0.9997, 0.9958, 0.9980, and 0.9868 for the generated models of the removal of benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin, respectively, indicate a confident statistical correspondence between the selected variables and the response (Table 3). Furthermore, the adjusted R^2 , which describes the fit of each model to the training data, is in reasonable agreement with the predicted R^2 , which evaluates the model's performance for unseen data, with a difference of less than 0.1 in most of the total predicted models, which was acceptable. Furthermore, the Adeq precision ratio for all produced models was greater than 4, implying that these models can be applied to navigate the design space.

Table SM2 summarizes the sum of squares, df, mean square, F -value, and p -value for independent variables, variable interactions, residuals, and generated models of the removal of the targeted micropollutants using softwood-biochar. F -values of 343.95, 3,446.49, 260.39, 567.78, and 82.86 for the removal models of benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin, respectively, revealed substantial variations in the means of the groups that were compared. As a result, the effectiveness with which micropollutants are removed varies significantly.

3.3.2. Regression analysis

The regression analysis of datasets was used to develop model equations with the purpose of predicting, modelling, and optimizing, as well as identifying significant variables. A p -value lower than 0.05 indicates that the model and related terms are significant. In this study, the p -values for all proposed models were lower than 0.0001, indicating that these five models were significant. The p -values of variable A (reaction contact time) in the suggested five models were less than 0.0001 for carbamazepine and diclofenac removal, 0.027 for irbesartan removal, and higher than 0.05 for benzotriazole and metformin removal. This suggested that the time of reaction was significant only for three models, i.e., carbamazepine, diclofenac, and irbesartan removal. While the p -values of variable B (sorbent amount) in the proposed five models were less than 0.0001 for carbamazepine, diclofenac, and irbesartan removal, 0.0365 for benzotriazole removal, and larger than 0.05 for metformin removal. This suggested that the amount of sorbent had significance only for four models: carbamazepine, diclofenac, irbesartan, and benzotriazole removal. In this work, the p -values for the initial micropollutant concentration (variable C) were less than 0.0001 in all optimization models, indicating the significance of the initial concentration in the removal process.

Based on the above-mentioned analysis and values, empirical equations were obtained as shown in Equations (2)–(6). As shown, the percentage of micropollutant removal could be predicted by substituting the values of independent variables

between the high and low values used in this study. These regression equations were used to generate the response surface plots for the five models.

$$\begin{aligned} \text{Benzotriazole Removal} = & 6.99334 + 0.125301 \times \text{Time} + 12.02701 \times \text{Sorbent} + 0.044489 \times \\ & \text{Concentration of Benzotriazole} - 0.034498 \times \text{Time} \times \text{Sorbent} - 6.88849\text{E} - 06 \\ & \times \text{Time} \times \text{Concentration of Benzotriazole} - 0.000938 \times \text{Sorbent} \times \text{Concentration of} \\ & \text{Benzotriazole} - 0.002035 \times \text{Time}^2 - 3.25126 \times \text{Sorbent}^2 - 5.31185\text{E} - 06 \times \text{Concentration of} \\ & \text{Benzotriazole}^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Carbamazepine Removal} = & -21.37368 + 0.165680 \times \text{Time} + 53.59948 \times \text{Sorbent} + 0.011858 \times \text{Concentration of} \\ & \text{Carbamazepine} - 0.311188 \times \text{Time} \times \text{Sorbent} + 0.000779 \times \text{Time} \times \text{Concentration of} \\ & \text{Carbamazepine} + 0.000629 \times \text{Sorbent} \times \text{Concentration of Carbamazepine} - 0.048391 \\ & \times \text{Time}^2 - 19.64400 \times \text{Sorbent}^2 - 1.41815\text{E} - 06 \times \text{Concentration of Carbamazepine}^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \text{Diclofenac Removal} = & -48.33687 + 1.87187 \times \text{Time} + 72.37181 \times \text{Sorbent} + 0.017295 \times \text{Concentration of} \\ & \text{Diclofenac} - 0.678028 \times \text{Time} \times \text{Sorbent} + 0.000598 \times \text{Time} \times \text{Concentration of} \\ & \text{Diclofenac} + 0.001670 \times \text{Sorbent} \times \text{Concentration of Diclofenac} - 0.073945 \times \text{Time}^2 - 24.98848 \\ & \times \text{Sorbent}^2 - 1.88818\text{E} - 06 \times \text{Concentration of Diclofenac}^2 \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Irbesartan Removal} = & -29.29842 + 0.525546 \times \text{Time} + 48.35474 \times \text{Sorbent} + 0.050716 \times \text{Concentration of} \\ & \text{Irbesartan} - 0.056676 \times \text{Time} \times \text{Sorbent} - 0.000118 \times \text{Time} \times \text{Concentration of} \\ & \text{Irbesartan} - 0.005210 \times \text{Sorbent} \times \text{Concentration of Irbesartan} + 0.000290 \times \\ & \text{Time}^2 - 0.87403 \times \text{Sorbent}^2 - 5.24476\text{E} - 06 \times \text{Concentration of Irbesartan}^2 \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Metformin Removal} = & +52.61463 - 0.556439 \times \text{Time} - 6.24312 \times \text{Sorbent} + 0.030031 \times \text{Concentration of} \\ & \text{Metformin} - 0.017249 \times \text{Time} \times \text{Sorbent} + 0.000039 \times \text{Time} \times \text{Concentration of} \\ & \text{Metformin} + 0.000036 \times \text{Sorbent} \times \text{Concentration of Metformin} + 0.013618 \times \text{Time}^2 + 3.10217 \times \\ & \text{Sorbent}^2 - 4.08203\text{E} - 06 \times \text{Concentration of Metformin}^2 \end{aligned} \quad (6)$$

3.3.3 Response surface plots

3.3.3.1. Interactive effect of initial micropollutant concentration and contact time on the micropollutant removal efficiency. The interactive relationship between micropollutant concentration and contact time variation on the percentage of metformin, diclofenac, and benzotriazole removal, as shown in Figure 4, was created using a sorbent amount of 1.025 g, which was the middle value in the examined range. For all targeted pollutants, high removal efficiencies were obtained at high micropollutant concentrations and varied with reaction duration. A lower removal efficiency was achieved for low micropollutant concentrations at any contact time. On the other hand, irbesartan showed a similar pattern to that of metformin and benzotriazole, while carbamazepine was similar to diclofenac (Figure SM 1). This is in line with *p*-values that indicated the initial micropollutant concentrations are of greater significance than the contact time in terms of micropollutant removal for the five targeted pollutants.

The competitive adsorption between the pollutants (e.g., pharmaceuticals) and functional groups on the softwood-biochar surface represents specific mechanisms, which include electrostatic attraction, hydrogen bonding, and hydrophobic contact (Czech *et al.* 2021). The removal efficiencies obtained in this reaction were explained by the relationship of low mass transfer coefficients for low micropollutant concentrations, which is similar to the findings of Sun *et al.* (2022). In their research, a magnetic polydopamine-adsorbent was used, where increasing the initial diclofenac concentration from 2 to 20 mg/L was found to increase the removal efficiency. Although our experiment proceeded in a smaller range of micropollutant concentrations with different amounts of adsorbent, it was consistent with these findings due to sharing similar functional groups. However, the effect of time is still an important factor for higher initial concentrations, which could be attributed to the slow occupation of the pollutant (e.g., diclofenac) on the adsorption sites and further blocking more contaminants from adhering to the adsorbent (Sun *et al.* 2022), suggesting that the process was dominated by diffusion (Paunovic *et al.* 2019).

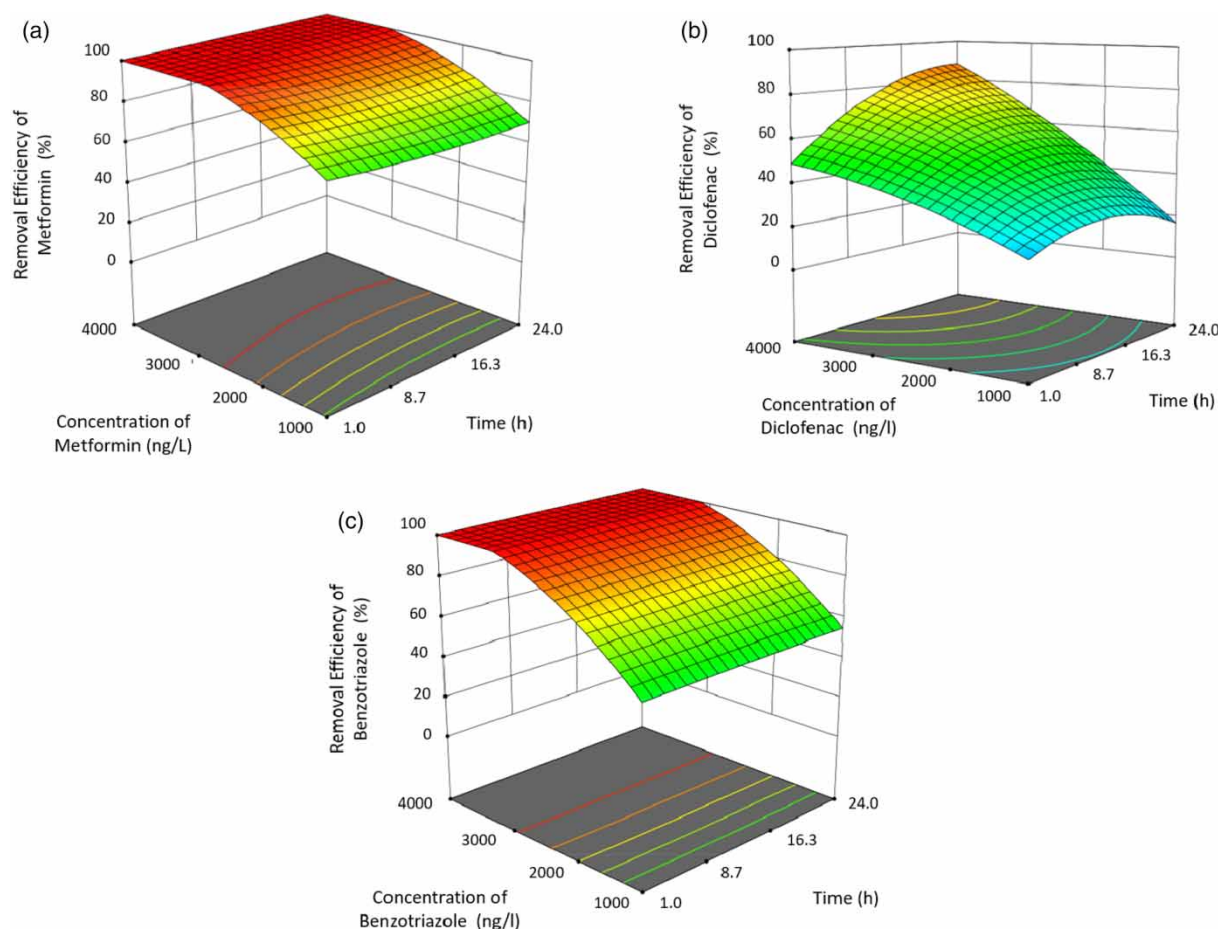


Figure 4 | Response surface of the removal efficiency of micropollutants versus both initial micropollutant concentration and contact time for (a) metformin, (b) diclofenac, and (c) benzotriazole.

Diclofenac and other OMPs exist in the environment at low concentrations (ng/L). Therefore, it is more pertinent to study the adsorption capacity of certain pollutants at lower concentrations that better mimic real ecosystems, rather than using high concentrations (mg/L) where the efficacy of biochar or any adsorbent may be changed. However, investigations with mg/L concentrations are still useful in the event of an accidental pharmaceutical spill or in the treatment of industrial or hospital effluent.

3.3.3.2. Interactive effect of sorbent amount and contact time on the micropollutant removal efficiency. The interactive effect of sorbent amount and contact time on the micropollutant removal was also analysed by RSM, by which the competitive adsorption relative to irbesartan, diclofenac, and metformin removal could be observed (Figure 5). The interactive figure was constructed with a micropollutant concentration of 3,000 ng/L, the middle value in the investigated range. For metformin, irbesartan, and benzotriazole, high removal percentages were obtained at low sorbent concentrations that reached 100% removal (Figure SM 2), with minimal changes in removal efficiency with contact time variation. Lower removal efficiencies of diclofenac and carbamazepine were attained at around 70 and 62% removal, respectively, at the largest sorbent quantity of around 1.5 g and the highest contact time of 20 h (Figure SM 2), and the lowest removal percentages were recorded at a contact time of 0.5 h and sorbent amount equal to or less than 0.1 g. Again, this confirms the *p*-values, indicating that the sorbent quantity impact was of greater significance than the contact time in this competitive adsorption process.

Similar to our study, the relative enhancement of the pharmaceutical removal by sorbents with increasing both the sorbent amount and the contact time has been reported by several authors (Wakejo *et al.* 2022; Solmaz *et al.* 2023), whereas it was

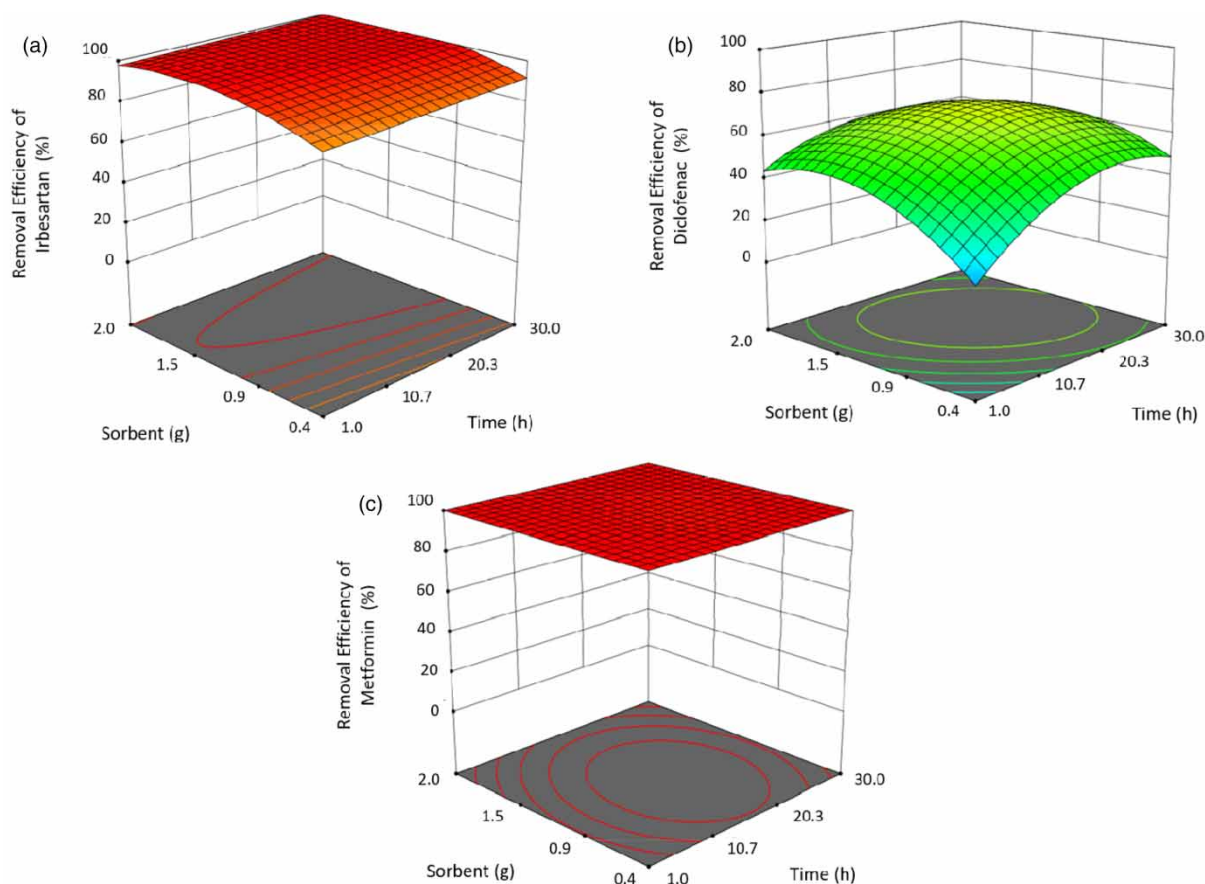


Figure 5 | Response surface of the removal efficiency of micropollutants versus both sorbent amount and contact time for (a) irbesartan, (b) diclofenac, and (c) metformin.

correlated to having excess active sites and contact time for efficient adsorption between contaminant molecules and functional groups of the sorbent physical surface (Solmaz *et al.* 2023). Interestingly, the diclofenac and carbamazepine surfaces also showed the potential impact of long contact time and high sorbent quantities, indicated by a lower removal efficiency (Figure 5). This could be related to the potential impact of competition over adsorption sites (Chang *et al.* 2015) and/or sorbent agglomeration (Naghdi *et al.* 2019; Qiu *et al.* 2021). The diclofenac and carbamazepine could have experienced a higher adsorption rate in the beginning under the impact of having better diffusivity; however, another compound with higher affinity to the surface could have replaced them after a certain contact time. This is similar to the findings of Chang *et al.* (2015) using another mixture of compounds, where they showed that after the initial phase, diclofenac and sulfamethoxazole had replaced acetaminophen on the activated carbon surface, which decreased in the adsorption capacity. On the other hand, agglomeration of biochar could lead to a decrease in the net active area and elongate the diffusion pathway, in addition to potentially replacing the loosely bounded sorbates, leading to a desorption-like process (Shukla *et al.* 2002).

3.3.3.3. Interactive effect of initial micropollutant concentration and sorbent amount on the micropollutant removal efficiency. Figure 6 depicts the interactive relationship between micropollutant concentration and sorbent amount variations on the percentage of metformin, diclofenac, and benztiazole removal. The interactive diagram was created using a contact time of 15.25 h, which is the middle value in the examined range. A similar trend of diclofenac was observed with carbamazepine, while irbesartan was more similar to metformin and benztiazole (Figure SM 3). A higher concentration of micropollutant showed a better removal efficiency at mostly all addressed sorbent amounts, which was consistent with the addressed *p*-values, revealing that the micropollutant concentration was of greater significance than the sorbent amount in the micropollutant adsorption process. The impact of additional sorbent amount on enhancing the

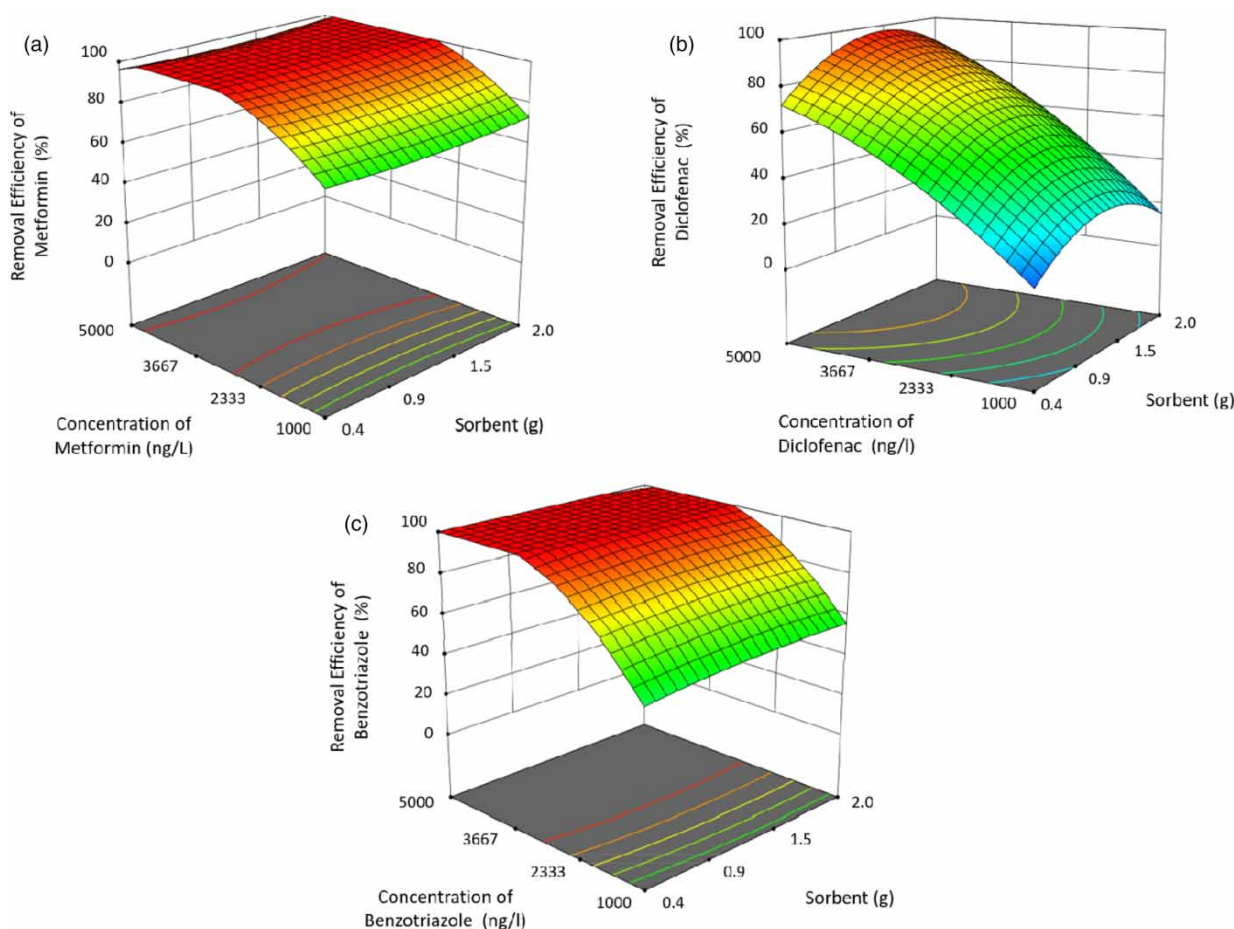


Figure 6 | Response surface of the removal efficiency of micropollutants versus both micropollutant concentration and sorbent amount for (a) metformin, (b) diclofenac, and (c) benzotriazole.

adsorption of pharmaceuticals was also reported by [Paunovic et al. \(2019\)](#) when using plum-biochar in a single solute observing a potential competition experiment with carbamazepine.

This RSM experimental investigation demonstrated that softwood-biochar effectively removed benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin. Additionally, the study revealed that the concentration of micropollutants had a significant role in the removal process. The RSM-generated models could predict the most optimal experimental conditions with a removal efficiency of over 90% under certain conditions. It is worth mentioning that an enhanced adsorption process with 90% removal efficiency might be reached with a different interaction matrix for the operational variables. This method helps in predicting the adsorption capacity and removal efficiencies of these targeted OMPs when employing softwood-biochar under various operating conditions addressed in this research.

3.4. Adsorption mechanism and potential competition

The pH and ionization of the compounds played a role in the potential removal capacity and mechanisms. At neutral pH conditions, benzotriazole and carbamazepine are mostly present in neutral forms with a pKa of (~8.3) ([Antonijevic et al. 2009](#)) and (13.9) ([BIZI 2019](#)), respectively, while diclofenac is mostly anionic (with acidic pKa ~4.2) ([Czech et al. 2021](#)) and metformin mostly cationic (pKa ~2.4 and 12.4) ([Elezović et al. 2021](#)). However, irbesartan would have both neutral and anionic forms with a pKa of (~7.4) ([Jansook et al. 2014](#)). Corresponding to the order of contaminants that showed the higher removal efficiency with softwood-biochar (NDG) ([Figure 1](#)), benzotriazole, carbamazepine, and irbesartan, with neutral/semi-neutral forms, appeared to establish diverse mechanisms related to softwood-biochar sorption. Their characteristics and active groups would have the ability to construct hydrogen bonds and hydrophobic (π)-

interactions related to the N- or O-components and the aromaticity, respectively (Nielsen & Bandosz 2016; Naghdi *et al.* 2019). In addition, softwood-biochar enhanced removal of hydrophobic compounds has been reported elsewhere (Kozyatnyk *et al.* 2021).

While diclofenac could have a similar aromatic interaction with biochar, the negative ionized form of the compound would have produced a repulsion force with the biochar surface (Czech *et al.* 2021). This electrostatic attraction could be favoured for metformin (+ve charged); however, the compound, as an aliphatic-chain structure, would still have a different behaviour due to its hydrophilic nature (Foretz *et al.* 2014). The spatial structure of the compounds can also play a role in the adsorption mechanisms. Czech *et al.* (2021) mentioned that the butterfly-like structure of diclofenac, with aromatic rings on both sides, stimulated more (π)-interaction points between the compound and adsorbent; this hypothesis could also be valid for irbesartan. Even though this was the scenario in terms of individual contaminant performance on the biochar, the sorption mechanisms during competition could be different. The analysis of micropollutant competition for adsorption could give more insights into the performance of biochar-based adsorption processes under real conditions with wastewater streams (Kozyatnyk *et al.* 2021).

The competition between micropollutants present in the wastewater may reduce or amplify the overall adsorption capacity of the adsorbent compared to the individual cases, where only one micropollutant is present (Chang *et al.* 2015; Mansouri *et al.* 2015; Nielsen & Bandosz 2016). This is consistent when comparing the anticipated behaviour of each compound in a competitive nature with their individual performance. On the one hand, carbamazepine and diclofenac showed a lower removal efficiency (<50%) (Figure 5(b)) in a competitive environment with longer reaction contact time compared to their individual performance (>75%) (Figure 1). In a competitive environment that included diclofenac, acetaminophen, and sulfamethoxazole, diclofenac was the least affected compound by competition by preserving the biggest ratio of its adsorption capacity compared to the other two in a competitive environment, highlighting that diclofenac had a better affinity compared to the other two compounds for activated carbon (Chang *et al.* 2015). Kozyatnyk *et al.* (2021) also reported that the lower removal of carbamazepine and diclofenac in a multi-component system that included caffeine, chloramphenicol, bisphenol A, and triclosan, using softwood, could be justified by the relative hydrophobicity of these compounds with respect to the presence of meso-sized pores with biochar. However, complementary adsorption can still be expected. Metformin showed indications of better removal at higher concentrations in a competitive environment (~99%) (Figure 5(c)) compared to their individual performance (<70%) (Figure 1) at lower concentrations. The improvement could be associated with the creation of a multilayer of adsorbates, thereby increasing the potential for metformin to establish H-bonds with layers that were adsorbed earlier (Nielsen & Bandosz 2016).

More research is required on combining different biochar types, such as bagasse-biochar with softwood-biochar or coffee husk-biochar with softwood-biochar. This combination may have distinguishing characteristics that include the various biomass sources. Furthermore, it is vital to investigate the processes and dynamics of the sorption reaction (such as adsorption mechanisms, isotherms, and kinetics rates) for micropollutant removal. Finally, the findings of this study would shed light on the potential integration of softwood-biochar with existing wastewater treatment technologies, such as adding softwood-biochar to an aeration tank of activated sludge, combining softwood-biochar with gravel in constructed wetlands, or fabricating a membrane from softwood-biochar. It is worth noting that biochar could be further utilised as an adsorbent in agricultural areas to remediate soil and remove accumulated micropollutants that reduce field productivity.

4. CONCLUSION

Five biochar types derived from softwood and sewage-dried sludge were used to assess the removal efficiency of five micropollutants, i.e., diclofenac, carbamazepine, benzotriazole, irbesartan, and metformin, from domestic wastewater effluent. The experimental campaign started with a preliminary investigation of the different biochar types under constant operating conditions with a contact time of 3 h, a biomass loading of 0.1 g, at 150 rpm, and multiple initial micropollutant concentrations. This approach allowed us to identify the most efficient biochar type: softwood-biochar. A RSM study was then conducted to investigate the interactive effects of operational variables on the removal of micropollutants from treated wastewater using softwood-biochar. Five optimization models were generated and significantly fitted quadratic models with p -value <0.0001. Softwood-biochar removed benzotriazole, carbamazepine, diclofenac, irbesartan, and metformin with an effectiveness of 98, 92, 94, 90, and 99%, respectively, at a contact time of 24 h, 2 g of sorbent, and 5,000 ng/L of OMPs concentration. Furthermore, five other micropollutants present in the actual wastewater were measured over a 24-h contact time with a 2 g

sorbent. The pollutants included caffeine, clarithromycin, hydrochlorothiazide, and propranolol, all of which had a removal efficiency of approximately 99%.

ACKNOWLEDGEMENTS

The IHE Delft Water and Development Partnership Programme, financed by the Dutch Ministry of Foreign Affairs, provided support for this research through the 'SafeAgroMENA' project.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Al-Hazmi, H., Mohammadi, A., Hejna, A., Majtacz, J., Esmaeili, A. & Habibzadeh, S. (2023) *Wastewater reuse in agriculture: prospects and challenges*, *Environmental Research*, **236**, 116711. <https://doi.org/10.1016/j.envres.2023.116711>.
- Antonićević, M., Milic, S., Radovanovic, M., Petrovic, M. & Stamenkovic, A. (2009) *Influence of pH and chlorides on electrochemical behavior of brass in presence of benzotriazole*, *International Journal of Electrochemical Science*, **4**, 1719–1734.
- Bai, X., Lutz, A., Carroll, R., Keteles, K., Dahlin, K. & Murphy, M. (2018) *Occurrence, distribution, and seasonality of emerging contaminants in urban watersheds*, *Chemosphere*, **200**, 133–142. <https://doi.org/10.1016/j.chemosphere.2018.02.106>.
- Bali, A. S., Sidhu, G. P. & Kumar, V. (2021) Plant enzymes in metabolism of organic pollutants. In: Hasanuzzaman, M., Narasimha, M. & Prasad, V. (eds.) *Handbook of Bioremediation*: Elsevier, pp. 465–474. <https://doi.org/10.1016/B978-0-12-819382-2.00029-6>.
- Bayabil, H. K., Teshome, F. T. & Li, Y. C. (2022) *Emerging contaminants in soil and water*, *Frontiers in Environmental Science*, **10**, 1–7. <https://doi.org/10.3389/fenvs.2022.873499>.
- Bizi, M. (2019) *Activated carbon and the principal mineral constituents of a natural soil in the presence of carbamazepine*, *Water*, **11**, 2290.
- Bueno, M. J., Gomez, M. J., Herrera, S., Hernando, M. D., Agüera, A. & Fernández-Alba, A. R. (2012) *Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: two years pilot survey monitoring*, *Environmental Pollution*, **164**, 267–273. <https://doi.org/10.1016/j.envpol.2012.01.038>.
- Calisto, V., Ferreira, C., Oliveira, J., Otero, M. & Esteves, V. (2015) *Adsorptive removal of pharmaceuticals from water by commercial and waste-based carbons*, *Journal of Environmental Management*, **152**, 83–90.
- Chang, E.-E., Wan, J.-C., Kim, H., Liang, C.-H., Dai, Y.-D. & Chiang, P.-C. (2015) Adsorption of selected pharmaceutical compounds onto activated carbon in dilute aqueous solutions exemplified by acetaminophen, diclofenac, and sulfamethoxazole, *The Scientific World Journal*, **2015**, 186501.
- Cheng, N., Wang, B., Wu, P., Lee, X., Xing, Y., Chen, M. & Gao, B. (2021) *Adsorption of emerging contaminants from water and wastewater by modified biochar: a review*, *Environmental Pollution*, **273**, 116448. <https://doi.org/10.1016/j.envpol.2021.116448>.
- Christou, A., Beretsos, V. G., Iakovides, I. C., Karaolia, P., Michael, C., Benmarhnia, T., Chefetz, B., Donner, E., Gawlik, B. M., Lee, Y., Lim, T. T., Lundy, L., Maffettone, R., Rizzo, L., Topp, E. & Fatta-Kassinos, D. (2024) *Sustainable wastewater reuse for agriculture*, *Nature Reviews Earth and Environment*, **5**, 504–521. <https://doi.org/10.1038/s43017-024-00560-y>.
- Chu, G., Zhao, J., Liu, Y., Lang, D., Wu, M., Pan, B. & Steinberg, C. (2019) *The relative importance of different carbon structures in biochars to carbamazepine and bisphenol A sorption*, *Journal of Hazardous Materials*, **373**, 106–114.
- Czech, B., Konczak, M., Rakowska, M. & Oleszczuk, P. (2021) *Engineered biochars from organic wastes for the adsorption of diclofenac, naproxen and triclosan from water systems*, *Journal of Cleaner Production*, **288**, 125686.
- Directorate General of Environment. (2022) Proposal for a Directive concerning urban wastewater treatment (recast). Brussels, 26.10.2022 COM(2022) 541 final 2022/0345 (COD).
- Downie, A., Crosky, A., Munroe, P., (2009) Physical properties of biochar. In: Lehmann, J. & Joseph, S. (eds.) *Biochar for Environmental Management: Science and Technology*. London: Earthscan.
- Elezović, A., Marić, A., Bišćević, A., Hadžiabdić, J., Škrbo, S., Špirtović-Halilović, S. & Rahić, O. (2021) In vitro pH dependent passive transport of ketoprofen and metformin, *ADMET DMPK*, **9**, 57–68.
- El-Gamal, E., Saleh, M., Elsokk, I., Rashad, M. & Abd El-Latif, M. (2017) *Comparison between properties of biochar produced by traditional and controlled pyrolysis*, *Alexandria Science Exchange Journal*, **38**, 412–425. doi:10.21608/asejaigjsae.2017.3720.
- Fernandes, B., Mendes, K., Júnior, A., Caldeira, V., Teófilo, T., Silva, T., Mendonça, M., Souza, M. & Silva, D. (2020) *Impact of pyrolysis temperature on the properties of eucalyptus wood-derived biochar*, *Materials*, **13**, 5841. doi:10.3390/ma13245841.
- Foretz, M., Guigas, B., Bertrand, L., Pollak, M. & Viollet, B. (2014) *Metformin: from mechanisms of action to therapies*, *Cell Metabolism*, **20**, 953–966.

- Gomes, A. R., Justino, C., Rocha-Santos, T., Freitas, A. C., Duarte, A. C. & Pereira, R. (2017) Review of the ecotoxicological effects of emerging contaminants to soil biota, *Journal of Environmental Science and Health, Part A*, **52** (10), 992–1007. <https://doi.org/10.1080/10934529.2017.1328946>.
- Hagemann, N., Schmidt, H., Kägi, R., Böhrer, M., Sigmund, G., Maccagnan, A. & McArdell, C. (2020) Wood-based activated biochar to eliminate organic micropollutants from biologically treated wastewater, *Science of the Total Environment*, **730**, 138417. <https://doi.org/10.1016/j.scitotenv.2020.138417>.
- Hailu, A. (2022) Development and performance analysis of top lit updraft: natural draft gasifier stoves with various feed stocks, *Heliyon*, **8**, e10163. <https://doi.org/10.1016/j.heliyon.2022.e10163>.
- Hasanzadeh, M., Soltaninejad, Y., Esmaeili, S. & Babaei, A. (2022) Preparation, characterization, and application of modified magnetic biochar for the removal of benzotriazole: process optimization, isotherm and kinetic studies, and adsorbent regeneration, *Water Science and Technology*, **85**, 3036–3054.
- Hong, M., Zhang, L., Tan, Z. & Huang, Q. (2019) Effect mechanism of biochar's zeta potential on farmland soil's cadmium immobilization, *Environmental Science and Pollution Research*, **26**, 19738–19748.
- Ingrao, C., Strippoli, R., Lagioia, G. & Huisingsh, D. (2023) Water scarcity in agriculture: an overview of causes, impacts and approaches for reducing the risks, *Heliyon*, **9** (8), e18507. <https://doi.org/10.1016/j.heliyon.2023.e18507>.
- Jansook, P., Muankaew, C., Stefansson, E. & Loftsson, T. (2014) Development of eye drops containing antihypertensive drugs: formulation of aqueous irbesartan/gCD eye drops, *Pharmaceutical Development and Technology*, **20**, 1–7.
- Jiang, S., Nguyen, T., Rudolph, V., Yang, H., Zhang, D., Sik-Ok, Y. & Huang, L. (2017) Characterization of hard- and softwood biochars pyrolyzed at high temperature, *Environmental Geochemistry and Health*, **39**, 403–415.
- Jiménez, B. (2006) Irrigation in developing countries using wastewater, *International Review for Environmental Strategies*, **6** (2), 229–250.
- Keiluweit, M., Nico, P., Johnson, M. & Kleber, M. (2010) Dynamic molecular structure of plant biomass-derived black carbon (biochar), *Environmental Science and Technology*, **44**, 1247–1253.
- Kesari, K. K., Soni, R., Jamal, Q. M., Tripathi, P., Lal, J. A., Jha, N. K., Siddiqui, M. H., Kumar, P., Tripathi, V. & Ruokolainen, J. (2021) Wastewater treatment and reuse: a review of its applications and health implications, *Water, Air, & Soil Pollution*, **232** (5), 208. <https://doi.org/10.1007/s11270-021-05154-8>.
- Kozyatnyk, I., Oesterle, P., Wurzer, C., Mašek, O. & Jansson, S. (2021) Removal of contaminants of emerging concern from multicomponent systems using carbon dioxide activated biochar from lignocellulosic feedstocks, *Bioresource Technology*, **340**, 125561. <https://doi.org/10.1016/j.biortech.2021.125561>.
- Kuhlbusch, T. A. (1995) Method for determining black carbon in residues of vegetation fires, *Environmental Science and Technology*, **29**, 2695–2702.
- Lee, J. W., Kidder, M., Evans, B. R., Paik, S., Buchanan, A. C., Garten, C. T. & Brown, R. C. (2010) Characterization of biochars produced from cornstovers for soil amendment, *Environmental Science and Technology*, **44** (20), 7970–7974.
- Lei, Y., Wagner, T., Rijnaarts, H., de Wilde, V. & Langenhoff, A. (2023) The removal of micropollutants from treated effluent by batch-operated pilot-scale constructed wetlands, *Water Research*, **230**, 119494. <https://doi.org/10.1016/j.watres.2022.119494>.
- Mansouri, H., Carmona, R., Gomis-Berenguer, A., Souissi-Najar, S., Ouederni, A. & Ania, C. (2015) Competitive adsorption of ibuprofen and amoxicillin mixtures from aqueous solution on activated carbons, *Journal of Colloid and Interface Science*, **449**, 252–260.
- Menacherry, S. P. M., Kodešová, R., Fedorova, G., Sadchenko, A., Kočárek, M., Klement, A., Fér, M., Nikodem, A., Chroňáková, A. & Grabic, R. (2023) Dissipation of twelve organic micropollutants in three different soils: effect of soil characteristics and microbial composition, *Journal of Hazardous Materials*, **459**, 132143. <https://doi.org/10.1016/j.jhazmat.2023.132143>.
- Mukarunyana, B., Boman, C., Kabera, T., Lindgren, R. & Fick, J. (2023) The ability of biochars from cookstoves to remove pharmaceuticals and personal care products from hospital wastewater, *Environmental Technology & Innovation*, **32**, 103391.
- Naghdi, M., Taheran, M., Pulicharla, R., Rouissi, T., Brar, S., Verma, M. & Surampalli, R. (2019) Pine-wood derived nanobiochar for removal of carbamazepine from aqueous media: adsorption behavior and influential parameters, *Arabian Journal of Chemistry*, **12**, 5292–5301.
- Nielsen, L. & Bandosz, T. (2016) Analysis of the competitive adsorption of pharmaceuticals on waste derived materials, *Chemical Engineering Journal*, **287**, 139–147.
- Nicholas, H. L., Mabbett, I., Apsey, H. & Robertson, I. (2022) Physico-chemical properties of waste derived biochar from community scale faecal sludge treatment plants, *Gates Open Research*, **6**, 96. doi:10.12688/gatesopenres.13727.2.
- Pap, S., Paunovic, O., Prosen, H., Krasevec, I., Trebse, P., Niemi, L., Taggart, M. A. & Sekulic, M. (2023) Removal of benzotriazole derivatives by biochar: potential environmental applications, *Environmental Pollution*, **334**, 122205.
- Paunovic, O., Pap, S., Maletic, S., Taggart, M., Boskovic, N. & Sekulic, M. (2019) Ionisable emerging pharmaceutical adsorption onto microwave functionalised biochar derived from novel lignocellulosic waste biomass, *Journal of Colloid and Interface Science*, **547**, 350–360.
- Qiu, B., Tao, X., Wang, H., Li, W., Ding, X. & Chu, H. (2021) Biochar as a low-cost adsorbent for aqueous heavy metal removal: a review, *Journal of Analytical and Applied Pyrolysis*, **155**, 105081.
- Qiu, Y., Liu, L., Xu, C., Zhao, B., Lin, H., Liu, H., Xian, W., Yang, H., Wang, R. & Yang, X. (2024) Farmland's silent threat: comprehensive multimedia assessment of micropollutants through non-targeted screening and targeted analysis in agricultural systems, *Journal of Hazardous Materials*, **476**, 135064. <https://doi.org/10.1016/j.jhazmat.2024.135064>.

- Qteishat, O., Radideh, J., Alzboon, K., Abu-Hamattah, Z., Al-Azab, T. & Abu-Hammad, N. (2024) Wastewater treatment and water reuse technologies for sustainable water resources: Jordan as a case study, *Civil and Environmental Engineering Reports*, **34** (2), 177–192. <https://doi.org/10.59440/ceer/190232>.
- Roccaro, P. (2018) Treatment processes for municipal wastewater reclamation: the challenges of emerging contaminants and direct potable reuse, *Current Opinion in Environmental Science & Health*, **2**, 46–54. <https://doi.org/10.1016/j.coesh.2018.02.003>.
- Rodriguez-Narvaez, O. M., Peralta-Hernandez, J. M., Goonetilleke, A. & Bandala, E. R. (2017) Treatment technologies for emerging contaminants in water: a review, *Chemical Engineering Journal*, **323**, 361–380. <https://doi.org/10.1016/j.cej.2017.04.106>.
- Shirani, Z., Carrasco-Navarro, V., Majlesi, S., Yli-Pirilä, P., Kukkonen, J. V. K. & Akkanen, J. (2024) Efficiency and ecotoxicity of activated biochar in the treatment of artificial wastewater contaminated by pharmaceuticals, *Journal of Environmental Management*, **371**, 123224. <https://doi.org/10.1016/j.jenvman.2024.123224>.
- Shukla, A., Zhang, Y.-H., Dubey, P., Margrave, J. & Shukla, S. (2002) The role of sawdust in the removal of unwanted materials from water, *Journal of Hazardous Materials*, **95**, 137–152.
- Solmaz, A., Sari, Z., Karta, M., Turna, T., Yücel, A. & Depci, T. (2023) Production and characterization of activated carbon from pomegranate peel for pharmaceutical waste (paracetamol) removal: response surface methodology application, *Water, Air, and Soil Pollution*, **645**, 10771–10789.
- Spokas, K. A. (2010) Review of the stability of biochar in soils: predictability of O:C molar ratios, *Carbon Management*, **1** (2), 289–303.
- Srikanth, K. (2019) Emerging contaminants effect on aquatic ecosystem: human health risks, *Agricultural Research & Technology: Open Access Journal*, **19** (4), 556104. <https://doi.org/10.19080/ARTOAJ.2019.19.556104>.
- Sun, M., Sun, Q., Zhao, C., Huang, Y., Jiang, J., Ding, W. & Zheng, H. (2022) Degradation of diclofenac sodium with low concentration from aqueous milieu through polydopamine-chitosan modified magnetic adsorbent-assisted photo-Fenton process, *Separation and Purification Technology*, **289**, 120771.
- Tam, N., Liu, Y., Bashir, H., Yin, Z., He, Y. & Zhou, X. (2020) Efficient removal of diclofenac from aqueous solution by potassium ferrate-activated porous graphitic biochar: ambient condition influences and adsorption mechanism, *International Journal of Environmental Research and Public Health*, **17**, 291.
- Tan, X., Liu, S., Liu, Y., Gu, Y., Zeng, G., Hu, X., Wang, X., Liu, S. & Jiang, L. (2017) Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage, *Bioresource Technology*, **227**, 359–372. <https://doi.org/10.1016/j.biortech.2016.12.083>.
- Tang, Y., Li, Y., Zhan, L., Wu, D., Zhang, S., Pang, R. & Xie, B. (2022) Removal of emerging contaminants (bisphenol A and antibiotics) from kitchen wastewater by alkali-modified biochar, *Science of the Total Environment*, **805**, 150158. <https://doi.org/10.1016/j.scitotenv.2021.150158>.
- Tarawneh, A., Assad, S., Alkhalil, S. & Suleiman, A. (2024) Assessing acceptance of treated wastewater reuse in Jordan: a study of knowledge and preferences, *Desalination and Water Treatment*, **317**, 100030. <https://doi.org/10.1016/j.dwt.2024.100030>.
- Tomczyk, A., Sokółowska, Z. & Boguta, P. (2020) Biomass type effect on biochar surface characteristic and adsorption capacity relative to silver and copper, *Fuel*, **278**, 118168.
- Tran, H. N., Tomul, F., Thi Hoang Ha, N., Nguyen, D. T., Lima, E. C., Le, G. T., Chang, C., Masindi, V. & Woo, S. H. (2020) Innovative spherical biochar for pharmaceutical removal from water: insight into adsorption mechanism, *Journal of Hazardous Materials*, **394**, 122255. <https://doi.org/10.1016/j.jhazmat.2020.122255>.
- Turk Sekulic, M., Boskovic, N., Slavkovic, A., Garunovic, J., Kolakovic, S. & Pap, S. (2019) Surface functionalised adsorbent for emerging pharmaceutical removal: adsorption performance and mechanisms, *Process Safety and Environmental Protection*, **125**, 50–63. <https://doi.org/10.1016/j.psep.2019.03.007>.
- Van Gijn, K., Zhao, Y., Balasubramaniam, A., de Wilt, H., Carlucci, L., Langenhoff, A. & Rijnaarts, H. (2022) The effect of organic matter fractions on micropollutant ozonation in wastewater effluents, *Water Research*, **222**, 118933. <https://doi.org/10.1016/j.watres.2022.118933>.
- Wagner, T., Rempe, F., Hoek, M., Schuman, E. & Langenhoff, A. (2023) Key constructed wetland design features for maximized micropollutant removal from treated municipal wastewater: a literature study based on 16 indicator micropollutants, *Water Research*, **244**, 120534. <https://doi.org/10.1016/j.watres.2023.120534>.
- Wakejo, W., Meshasha, B., Kang, J. & Chebude, Y. (2022) Enhanced ciprofloxacin removal from aqueous solution using a chemically modified biochar derived from bamboo sawdust: adsorption process optimization with response surface methodology, *Adsorption Science & Technology*, **23**, 2699530.
- Xu, Q., Tang, S., Wang, J. & Hac Ko, J. (2018) Pyrolysis kinetics of sewage sludge and its biochar characteristics, *Process Safety and Environmental Protection*, **115**, 49–56.
- Xu, C.-Y., Li, Q.-R., Geng, Z.-C., Hu, F.-N. & Zhao, S.-W. (2020) Surface properties and suspension stability of low-temperature pyrolyzed biochar nanoparticles: effects of solution chemistry and feedstock sources, *Chemosphere*, **259**, 127510.
- Yang, W., Feng, T., Flury, M., Li, B. & Shang, J. (2020) Effect of sulfamethazine on surface characteristics of biochar colloids and its implications for transport in porous media, *Environmental Pollution*, **256**, 1.