

Antibiotic-targeted water treatment with cost-effective bioadsorbents

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Summary

The extensive use of antibiotics has introduced persistent compounds into environmental systems that pose a threat to living organisms. Many treatment processes exist for purifying drinking water, but cost-effective filtration of contaminated water discharged into the environment is still an unsolved problem. In this research, cost-effective adsorbents have been developed and tested for filtering antibiotics that are frequently detected in environmental systems. Results suggest that it is possible to develop an adsorbent mixture with high purification efficiency and low production costs for a wide range of antibiotics. The adsorbent mixture could be used in wastewater treatment and should be considered for the purification of agricultural water (e.g., irrigation water, groundwater).

Keywords: antibiotic, adsorption, desorption, bioadsorbent, cost-effective

Antibiotikum-célzott vízkezelés költséghatékony bioadszorbensekkel

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Összefoglalás

A víz, mint alapvető nyersanyag és erőforrás, nélkülözhetetlen feltétele életünknek. A biológiai szükségleteinken túl, szinte minden gyártási folyamatban felhasználásra kerül. A klasszikus három lépcsős tisztítási rendszerek nem alkalmasak egyes perzisztens anyagok (pl. gyógyszerhatóanyagok) teljes eltávolítására, továbbá a természetes tisztító folyamatok, negatív visszacsatolások révén egyre kisebb hatásokkal csökkentik a szennyezők koncentrációját a természetben. A gyógyszerhatóanyagok ng L^{-1} koncentrációban kimutathatók már az ivóvizekben is, ebből adódóan az elmúlt évtizedekben egyre nagyobb figyelmet kapott a vízminőséggel kapcsolatos problémák feltárása, elemzése és megoldása. A szennyező anyagok között kiemelt szerepe van az antibiotikumoknak, mivel antibakteriális hatásuk miatt célzottan befolyásolják a mikrobiális közösségek működését, növelik a rezisztens törzsek kialakulását, ezenkívül magasabb rendű élőlényekre is toxikus hatással lehetnek.

Az ivóvizek mikroszennyezőinek csökkentésére számos nagy hatásokkal rendelkező tisztító töltetet fejlesztettek ki (pl.: granulált aktív szén, ioncserélő gyanták, szén nanocsövek stb.), viszont előállításuk és üzemeltetésük költséges. Ezek a szűrőrendszerek a tisztított szennyvizek gyógyszerhatóanyag tartalmának csökkentésére nem alkalmasak, mivel a magas tisztítási hatások miatt gyorsan kimerülnek. A környezeti rendszerek gyógyszerhatóanyag terhelésének csökkentése a mai napig megoldatlan probléma. Kutatásunk során egy olyan többkomponensű szűrőtöltet keveréket fejlesztünk, ami alkalmas lehet tisztított szennyvizek kezelésére, emellett az előállítása, üzemeltetése nem költséges. A tisztítási hatások növelése érdekében minimális felületkezelési eljárásokat alkalmaztunk az adszorbens anyagokon, majd három antibiotikum csoport (kilenc vegyület) esetében teszteltük őket. A vizsgált antibiotikumok különböző fizikokémiai paraméterekkel rendelkeztek, annak érdekében, hogy a tisztítási hatások széles spektrumát lefedje.

Az eddigi eredmények alapján lehetséges olyan szűrőtöltetet előállítani, mely az antibiotikumok széles spektrumát képes hatékonyan kiszűrni és hosszú távon fixálni. Ez az adszorbens olcsón előállítható, nem szükséges hozzá drága kezelés és a magas porozitása miatt átfolyó rendszerekben is hatékonyan alkalmazható. Az adszorbens alapanyagok közül a vizsgált faszén felületkezelési eljárása megfelelő, a fűrézpor és szalma esetében a vegyületek visszatartását növelni kell, ezért a felületkezelést a faszénnél alkalmazott eljárással bővítjük. Ennek előnye, hogy a felületkezelés egyszerre elvégezhető mindhárom adszorbensen. Az így fejlesztett töltetkeveréket szennyvízkezelés esetében a megelőző lépcsők után lenne érdemes alkalmazni egy újabb szűrési lépésként, és megfontolandó a közvetlen élelmiszertermelési felhasználású (felszíni vagy talaj-) vizek (pl. gyökérzöltségek öntözésére) egy lépésben történő szűrése is.

Kulcsszavak: antibiotikum, adszorpció, deszorpció, bioadszorbens, költséghatékonyság

Forewords

The investigation carried out by KDP fellowship holder Anna Vancsik is of definite interest in terms of food security. Due to the consequences of climate change, extreme weather conditions, including long-term droughts, are increasing in the Carpathian Basin, highlighting the necessity of pure water for safe agricultural production. Wastewater as well as most of the surface and groundwater, are more or less polluted with pharmaceutically active compounds. The related concern has permanently emerged because of the increased use of these drugs, the high persistence of these molecules in the environment, and the incomplete wastewater treatment technology. Antibiotics are fundamental in the soil–water–plant system, potentially entering the food chain and the human body. Even though the clearance of these molecules from drinking water is technically solved, the treatment is expensive and hardly applicable, for example, for irrigation water. Thus, the present study aimed to evaluate effective and cheap bioadsorbents that can remove and hold antibiotics from water on larger scales. Preliminary results suggest that charcoal, even without expensive activation, would be helpful in removing the broad spectrum of antibiotics from water, providing the basic material of a water filter.

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Medicine and pharmacological industry have improved considerably in recent decades, contributing to the general increase of lifespan, the improvement of life quality, and fast growth of the human population. Several pharmaceutical compounds are resistant to biodegradation in the human body, hence many substances are still present in bioactive form when entering the sewage treatment network. Although wastewater treatment technologies are constantly and effectively being developed, certain groups of pharmacologically active compounds (e.g., antibiotics) still occur at a few ng L⁻¹ to a few µg L⁻¹ concentration range in both treated wastewater and natural surface waters. Due to the contamination of both treated wastewaters and surface waters, antibiotics can also reach drinking water sources and thus enter the drinking water network. However, due to the low concentrations, the

potential risks to humans are low or negligible based on theoretical human health risk assessments. At the same time, reference must be made that some drug residues are mutagenic and carcinogenic, and the total amount of active compounds in the treated wastewater, surface waters, or even in drinking water can represent an immediate risk and have an impact on aquatic organisms or in extreme cases for human population. Today, it is a scientific fact that nearly 90% of cancers affecting the population are caused by synthetic mutagens found in our environment as a result of inefficient wastewater treatment procedures. The possible interactions of active drug residues (i.e., mixture effect), including also antibiotics, can not only affect aquatic organisms, thus endanger ecosystems and biodiversity, but also can pose potential threats to human health. Keeping this in mind, the monitoring of pharmacologically active compounds and the study of their potential effects have received considerable attention and support in recent years globally. Therefore, I believe that research and innovation development such as the one presented in this manuscript by Anna Vancsik are significant and important to maintaining our long-term health ecosystem and life quality.

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Introduction

Over the last decades, the presence of Pharmaceutically Active Compounds (PhACs) in environmental systems has received global attention due to their potential impacts on human and animal health (*Deblonde et al. 2011*). PhACs are chemicals that are designed to the medical uses of animal and human health, including (but not limited to) antibiotics, hormones, psychoactive compounds, fungicides, anti-inflammatories, analgesics and many other categories (*Mondal et al. 2019; Peng et al. 2020*). These substances can enter environmental systems in a number of ways. The most obvious source of contamination for these compounds may be the discharges from the production site itself. High concentrations of pollution (mg L⁻¹) can occur, as there is no clear

limit on the maximum concentration of each compound that can be released. Despite strict EU regulation, high environmental concentrations have been documented in several countries in Europe as a result of pharmaceutical production (Cardoso *et al.* 2014; Hernández-Tenorio 2023). However, pre-treatment methods used by pharmaceutical manufacturers to reduce the concentration of PhACs released are becoming more common. These may include Fenton oxidation, coagulation/flocculation, fermentation, extraction, chemical synthesis and so on (Epa-of Water 2006; Prabakar *et al.* 2018). Hospitals may also be an important emitter of pollution, but the concentration of PhACs will be diluted as they enter the sewage system. The large quantities of growth promoters, antibiotics and other medicines used in animal husbandry are not discharged into the sewerage system, but directly into surface waters or soils where they can leach into groundwater (Cardoso *et al.* 2014). In addition, treated wastewater (TWW) from wastewater treatment plant (WWTP) outfalls is a constant source of pollution, as a significant proportion of the PhACs used excretes in their original form in urine and faeces. Although this is considered low concentration compared to others, but it is a constant source of pollution. The excretion of PhACs substances from the body can be well over 50%. Kunin *et al.* (1959) reported that the excretion of tetracycline (TC) and oxytetracycline antibiotics was 62% and 85% of the dose taken. Conde-Cid *et al.* (2019) mentioned that TCs have such a low absorption when used in animals that up to 90% can be excreted in their unchanged form. For ofloxacin the excretion can be 73% when orally administered (Wolfson and Hooper 1991), for analgesics diclofenac 20–30% (Willis *et al.* 1981), and for antibiotic sulfamethoxazole 54% (Cribb and Spielberg 1992). WWTPs, with the three-step treatment system were not originally designed to remove these pharmaceutical molecules, so the effluent with various concentrations of PhACs is discharged into water bodies or soil. Another important source of pollution from WWTPs is sewage sludge from the biological treatment and sedimentation, which is disposed in large quantities on agricultural land, composted or used for recultivation. In Hungary, more than half of the urban sewage sludge produced each year is deposited on land in some form (Figure 1). In the period 2011–2022, an average of 198 thousand tonnes of sewage sludge was produced each year, of which an average of 135 thousand tonnes was disposed on agricultural land, used as compost or landfill (“Statistics|Eurostat” *n.d.*). The last ten years have also showed an increase in production and in the amount of land applications.

The study of PhACs pollution can be divided into three main research themes: 1, the determination of pollutant sources and concentrations; 2, their impact on the environment and wildlife; 3, research on the reduction of pollutants. The study of pollutant sources and pollutant concentrations in water bodies dates back to the 1970s (Jones *et al.* 2005). Following a growing number

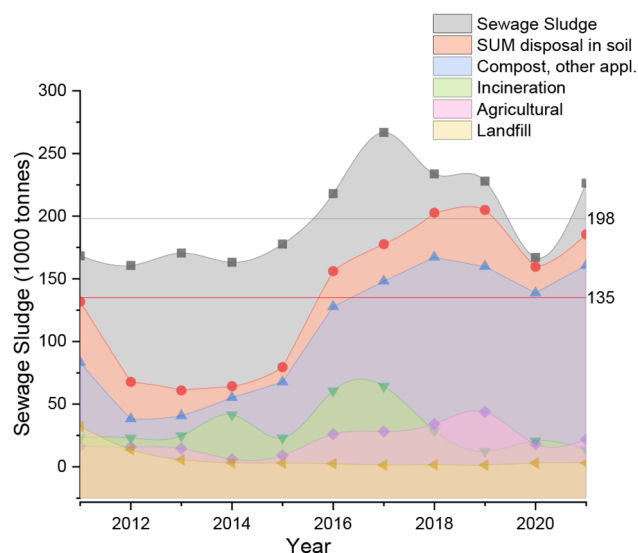


Figure 1 Annual production and disposal of sewage sludge in Hungary in the separate economic sectors. The black reference line is the ten-year average production of sludge; the red reference line is the ten-year average sludge application in soils

Source: Own elaboration based on “Statistics | Eurostat”.

of publications, the first Watch List was established in the 2000s under the Water Framework Directive by the EU. This involved a limited number of PhACs that had to be monitored EU-wide for up to 4 years, and the component list has now been updated in its 4th version (Carvalho *et al.* 2015; European Commission 2020). Since then, several studies have been published on the emissions and concentrations of Watch List substances and other potentially hazardous PhACs in surface water, groundwater and drinking water (Alygizakis *et al.* 2019; Kondor *et al.* 2020a, 2020b; Maasz *et al.* 2019; Molnar *et al.* 2021). Research shows that PhACs are continuously present in environmental systems, and sometimes in drinking water.

The focus of many studies is not on the concentrations of PhACs, but on their individual or synergistic effects on organisms. Staszny *et al.* (2021) found that PhACs (citalopram, propranolol, codeine and trimetazidine) can affect the phenotypic appearance of certain fish species in natural waters. Some polluting compounds may also have endocrine-disrupting (ED) effects. These compounds can disrupt reproductive processes (Sinkó *et al.* 2022) and cause feminisation phenomena in many classes of vertebrates (Kloas *et al.* 2009). Ethinylestradiol (EE2), which is an ED even at very low concentrations (1–10 ng L⁻¹), can induce feminisation effect in fish and amphibian species (Orton-Tyler 2015; Purdom *et al.* 1994; Scholz-Klüver 2009). Due to their mechanism of action, antibiotics are mainly studied on microbial communities. The study by Kovalakova *et al.* (2020) summarised the toxic effects of antibiotics (e.g. ciprofloxacin, ofloxacin, tetracycline, sulfamethoxazole) in wastewater on different classes of organisms. Based on

the collected data, high exposure has been identified mainly for cyanobacteria, algae, and aquatic plants. Among the PhACs, antibiotic contamination is particularly important because long-term, low-concentration exposure increases the emergence of antibiotic-resistant strains (Kümmerer 2009). Many researches focus not only on the effect of antibiotics on aquatic, but also on soil microbial communities. Since microbial activity is one of the main drivers of soil organic matter cycling, it strongly influences the composition and amount of soil organic matter, which is the largest terrestrial carbon store (~2400 Gt carbon) (Batjes 1996; Corbeels et al. 2019; Lucas et al. 2021). In addition, soil organic matter also has a major impact on the yield of agricultural soils (Madarász et al. 2016; Nugroho et al. 2023) so antibiotic contamination, which can change the organic matter composition of the soil, may eventually affect crop production. Lucas et al. (2021) found that antibiotics in soil reduced the bacterial diversity, abundance, and efficiency of microbial carbon utilization, but increased bioavailable carbon. Molaei et al. (2017) and Toth et al. (2011) pointed out that different antibiotics can affect the microbiological composition of soil in different ways. Sulfamethoxazole clearly reduced soil microbial biomass carbon and cumulative respiration (as an indicator of the active microbial biomass), but oxytetracycline only reduced respiration, whereas both compounds had a clear toxic effect on the soil microbiome by the Iron (III) reduction tests.

Since PhAC contaminants are permanent and widespread in environmental systems, and the effects of pollution can be monitored with increasing certainty, research on the natural or induced removal of these substances is becoming increasingly popular. Studies of the natural attenuation of pollutants such as bank filtration, or photo- and biodegradation, and adsorption has formed the basis for the development of controlled purification systems. Since research into PhACs contamination dates back 50–60 years, there are a number of existing treatment systems known to purify water for various uses. Protecting human health is a priority, which is why drinking water purification is perhaps one of the most advanced applied research areas. However, the efficiency of current drinking water treatments for removal of some PhACs is still low. In general, drinking water treatment plants use coagulation, flocculation and filtration followed by some form of disinfection like chlorination and ozonation (Couto et al. 2019). Chlorination can be effective for many compounds depending on pH and the physicochemical parameters of the compound, but some potentially hazardous compounds can still be released into drinking water at concentrations of ng L⁻¹ (Huerta-Fontela et al. 2011; Kondor et al. 2020a). The most effective forms of drinking water treatment are ozonation, granular activated carbon (GAC) filtration and reverse osmosis (RO) filtration (Couto et al. 2019; Simazaki et al. 2015). However, there are also some negative conse-

quences of these techniques e.g.: in the case of GAC and RO, the high production costs and rapid depletion can be problematic; for ozonation, the potential generation of toxic by-products.

A more responsible way to manage PhAC contamination is to prevent them from entering the environment in the first place. The difficulty with this is that the treatment processes commonly used in drinking water treatment are inefficient in WWTP. The operating and material costs of chemical treatments are too high to operate in a WWTP (Moreira et al. 2016; Renita et al. 2017). RO membranes and nanofiltration can have the same problems and their efficiency is very dependent on the quality of the effluent (Abdel-Fatah 2018; Bartels et al. 2005). Biological treatment options, such as aerobic and anaerobic methods, are less costly to operate, but have a lower cleaning efficiency. The most appropriate treatment method for the WWTPs in terms of applicability is the adsorption process (Renita et al. 2017). There is a lot of research on adsorbents with different properties and selectivities, e.g., different forms of activated carbon, cyclodextrin bead polymer, carbon nanotubes, chitosan, minerals, rocks, plant residues, industrial waste, agricultural waste, etc. (Dai et al. 2018; Fenyvesi et al. 2020; Maheshwari et al. 2013; Nguyen et al. 2023; Ramesh et al. 2014; Renita et al. 2017; Simazaki et al. 2015). For special adsorbent materials such as activated carbon or carbon nanotubes, the production costs can be high. It also raises the question of how to regenerate or dispose the depleted adsorbents. For industrial waste, there is no cost as long as the material is treated as waste or as a by-product, but if it is needed to supply several WWTPs, it can be turned into a product and its purchase value can increase, or there may not be enough to supply the treatment plants. The use of various plant residues as bioadsorbents could be a solution to these problems. They have low material costs, are easily accessible anywhere, and as plant residues are combustible, there is no need for regeneration and disposal, and by incineration the adsorbed pollutants are destroyed. Their disadvantage is that their adsorption capacity is often lower than that of the more expensive GAC or carbon nanotubes, but by mixing more of these materials, the adsorption capacity can be increased and they will be less sensitive to changes in the chemical parameters of the effluent (Mangla et al. 2022).

In the frame of the KDP research, a multi-component adsorbent mixture is currently being developed that is targeted to remove antibiotics. The results reported in this article are preliminary results of an ongoing adsorbent development. Bioadsorbents undergo various pretreatment processes that reduce their organic matter content and increase their specific surface area, but it does not considerably increase the purchasing/supply costs. As we are designing a multi-component mixture, it covers a wider range of antibiotics depending on their physicochemical parameters and will also be less sensitive

to changes in the composition of the effluent. The antibiotics tested were 3–3 components from the fluoroquinolone (FQs), tetracycline (TCs) and sulphonamide (SAs) groups, as these are, in order, zwitterionic, positively and neutrally/negatively charged compounds respectively. This gives full coverage based on the dissociation state of the compounds, which is the most important parameter influencing adsorption besides pH. The developed adsorbent mixture will be used in a flow-through cleaning prototype developed at the HUN-REN Research Centre for Astronomy and Earth Sciences to extend the range of components that can be removed. In the current phase of development, the purification efficiency of the modified surface adsorbents is being tested for the 9 antibiotics and further surface modifications are being carried out to improve the efficiency. The present study provides the adsorption efficiency results for the three adsorbents and 9 antibiotics.

Materials and Methods

Antibiotics such as fluoroquinolones (FQs): Ciprofloxacin (CPX), Norfloxacin (NFC), Ofloxacin (OFC), tetracyclines (TCs): Tetracycline (TC), Doxycycline (DC), Chlortetracycline (CTC), sulfonamides (SAs): Sulfanilamide (SA), Sulfamethoxazole (SMX), and Sulfadiazine (SD) were purchased from Sigma-Aldrich, analytical grade purity (>98.6%) from VETTRANAL™. Ultra-pure water was used with a quality of 0.055 $\mu\text{S}/\text{cm}$ (LaboStar® PRO TWF) in the laboratory experiments. Acetonitrile and methanol were HPLC grade for fluorescence detection (Fisher Chemical™). For surface modification ultra-pure water and o-Phosphoric Acid 85% (Fisher Chemical™) was used. The tested bioadsorbents were straw (SZLM) purchased from a local supplier, sawdust (FPR) made of Black locus (*Robinia pseudoacacia*) purchased from a local supplier and charcoal (FSZN) of Terra-Grill hardwood purchased from a commercial supplier.

Adsorbent properties and pre-treatments

The adsorbent materials were chopped and crushed before treatment. The size range was <0.5 mm for all adsorbents. It should be pointed out that the particle size of SZLM is not completely homogeneous, as its longitudinal structure may have resulted in larger pieces in one dimension. The initial surface treatment of the SZLM and FPR adsorbents was 24 hours of mixing in ultrapure water on a heated magnetic stirrer. A 1:20 mixing ratio, 80 °C heating and 50 rpm mixing speed were used for 24 hours. To keep the adsorbent production low cost no aggressive chemical treatment or high pressure and temperature oxidation has been applied. If the results show that it is necessary to increase the adsorption efficiency, the treatment procedure will be modified. For FSZN, the surface modification was carried out at a ratio of 1:20

in 1M H_3PO_4 solution at 40 °C heating and 50 rpm stirring speed for 24 hours. All three adsorbents were filtered after treatment, washed three times with ultrapure water and dried on a sand bed at 40 °C. Elemental composition of the adsorbents (carbon, nitrogen, hydrogen, and sulphur) were measured by Vario Macro cube elemental analyser with a TCD detector, (Elementar Ltd., Deutschland) before and after surface treatment. Scanning electron microscope images of the adsorbents were taken with a Jeol JSM-IT700HR (JEOL Ltd., United States).

Adsorption experiments

Adsorption and desorption experiments were carried out using the Batch equilibrium method according to OECD guideline 106 (OECD 2000) in dark-walled tubes at 15 °C. For each adsorbent-antibiotic group, the syringe filter material used, the solution-to-adsorbent ratio and the initial concentration were determined separately. For the FQs (CPX, NFC, OFC) and the TCs (TC, DC, CTC) 1:120 solution-to-adsorbent ratio, 0.45 μm nylon syringe filter and a concentration range of 1–6 mg L^{-1} were used. As the SAs (SA, SD, SMX) are neutral and negatively dissociating compounds and therefore have lower adsorption, thus a 1:24 solution-to-adsorbent ratio, 0.45 μm glass syringe filter and a concentration range of 0.01–2 mg L^{-1} were used. In all cases, adsorption was 24 hours, desorption was initially in 24-hour intervals from 0–72 hours, with a final 144-hour sampling. Desorption was carried out in a 0.01 M CaCl_2 solution. After adsorption and desorption the samples were centrifuged for 15 min. at 5200 RPM and 15 °C (MPW-352RH), then filtered through the syringe filters before measurements. Antibiotic concentrations in solution were measured by UHPLC (Shimadzu, Nexera X2 LC 30-AD) using a fluorescence detector (Shimadzu, RF 20A XS), and C18 core-shell column (Kinetex®, 2.6 μm XB-C18). 0.01M H_3PO_4 was used as eluent “A” and acetonitrile as eluent “B”. Table 1 shows the detailed gradient elution parameters, and detection wavelengths for each compound.

The amount of compounds (mg) adsorbed on 1 g of adsorbent material was calculated using the following equation (Eq. 1)

$$q_e = (c_0 - c_e) \frac{V}{m} \quad \text{Eq. 1.}$$

where c_0 is the initial experimental concentration (mg L^{-1}), c_e is the not adsorbed concentration i.e., equilibrium concentration (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the adsorbent (g). The Freundlich isotherm fitted to the experimental data was performed using the ORIGIN pro 2020 software (Eq. 2).

$$q_e = K_F c_e^n \quad \text{Eq. 2.}$$

Table 1 | The UHPLC method of the test compounds

Compound	Proportion of eluent „B” (%)			Temperature (°C)	Flow rate (ml/min)	PDA (nm)	Fluorescent Excitation/Emmission (nm)	
CPX	0–2.0 min	2.0–3.0 min	6.5–7.0 min	28	1.0	–	280	450
	10%	14.5%	10%					
NFC	0–2.0 min	2.0–3.0 min	7.0–8.0 min	28	1.0	–	280	450
	10%	18%	10%					
OFC	0–2.0 min	2.0–3.0 min	6.5–7.0 min	28	1.0	–	298	490
	6%	15%	6%					
TC	0–3.0 min	3.0–4.0 min	4.0–5.0 min	30	1.8	270	–	–
	8–40%	40–8%	8%					
CTC	0–3.0 min	3.0–3.5 min	3.5–5.0 min	25	1.1	265	–	–
	8–40%	40–8%	8%					
DC	0–5.0 min	5.0–5.5 min	5.5–7.0 min	25	2.2	270	–	–
	8–40%	40–8%	8%					
SA	0–3.0 min	3.0–3.5 min	3.5–5.0 min	28	1.2	–	265	340
	5%	5–40%	4%					
SMX	0–0.2 min	0.2–2.0 min	2.0–3.5 min	28	1	–	258	340
	8%	8–35%	35%					
SD	0–2.0 min	2.0–3.0 min	3.0–3.2 min	28	1.2	267	–	–
	5–14%	14%	14–40%					

Source: Own elaboration

K_F is the relative adsorption capacity ($(mg\ g^{-1}) (L\ mg^{-1})^{1/n}$), and n is a dimensionless number which refers to the nonlinearity between the equilibrium concentration and the amount of antibiotic adsorbed (non-linearity factor). The distribution coefficient (K_d) values were calculated using Eq. 3:

$$K_d = q_e / c_e \quad \text{Eq. 3.}$$

where q_e is the adsorbed antibiotic on 1 g adsorbent ($mg\ g^{-1}$), c_e is the not adsorbed concentration i.e., equilibrium concentration ($mg\ L^{-1}$). The distribution coefficients were calculated for each experimental concentration, and then averaged. The hysteresis index was calculated by Eq. 4:

$$HI = q_{des} / q_{ads} \quad \text{Eq. 4.}$$

where q_{des} is the amount of antibiotic desorbed, q_{ads} is the amount of antibiotic adsorbed. In all cases, the hysteresis index was calculated as the total amount desorbed after 144 h.

Results and discussion

SZLM and FPR are lignocellulosic adsorbent materials, consisting mainly of lignin, cellulose and hemicellulose

(Dai et al. 2018; Salleh et al. 2011). Cellulose contains primarily hydroxyl and carbonyl functional groups, lignin additionally contains methyl and carboxylic functional groups (El Mansouri-Salvador 2007; Md Salim et al. 2021). The surface treatment process can increase the specific surface area of the adsorbents, thus increasing the available functional groups that can participate in the adsorption. Figure 2 shows SEM images of adsorbent materials after surface treatments. In the FPR and SZLM adsorbent, the matrix was loosened, fragmented, and separated, increasing the specific surface area. Since no chemicals were used, an increase in available functional group could only be achieved by increasing the specific surface area and the porosity (Figure 2a and 2b). In contrast, the FSZN adsorbent material was treated with phosphoric acid, which did not increase the specific surface area, but made the material more hydrophilic and increased the number of surface functional groups like hydroxyl, carboxylic and phosphorus-containing surface groups. (Demiral et al. 2021; Puziy et al. 2002). Taha et al. (2014) pointed out that phosphoric acid treatment also changed the physical parameters of charcoals, like porosity and the textural characteristics. The SEM image shows the pitted elements of the original wooden structure, and the debris from the milling process (Figure 2c).

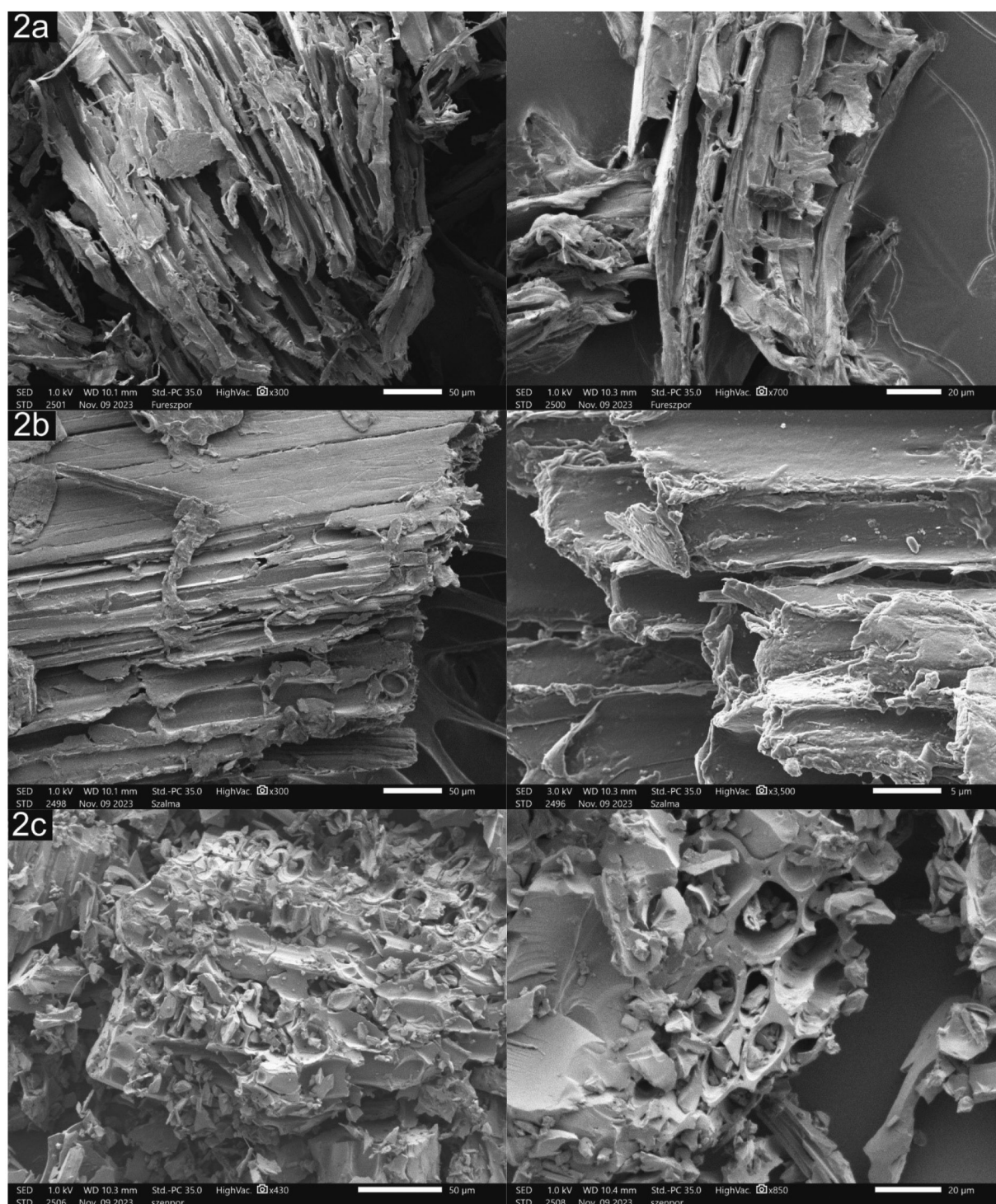


Figure 2 Scanning electron microscopy images of surface treated adsorbents at different magnifications. a, FPR adsorbent at 300x and 700x; b, SZLM adsorbent at 300x and 3,500x; c, FSZN adsorbent at 430x and 850x

Source: Own elaboration

Adsorption and desorption results of adsorbent SZLM

The Freundlich isotherms of the SZLM adsorbent fitted to the experimental results of the different compounds are shown in *Figure 3a*. Only one of each group of anti-

biotics has been plotted on the diagram, as similar results were obtained between compounds of the same group. The desorption values were always located below the adsorption isotherms. Accordingly, in the desorption medium the adsorption affinity of the compounds is low and therefore they could be washed off. FQs and TCs

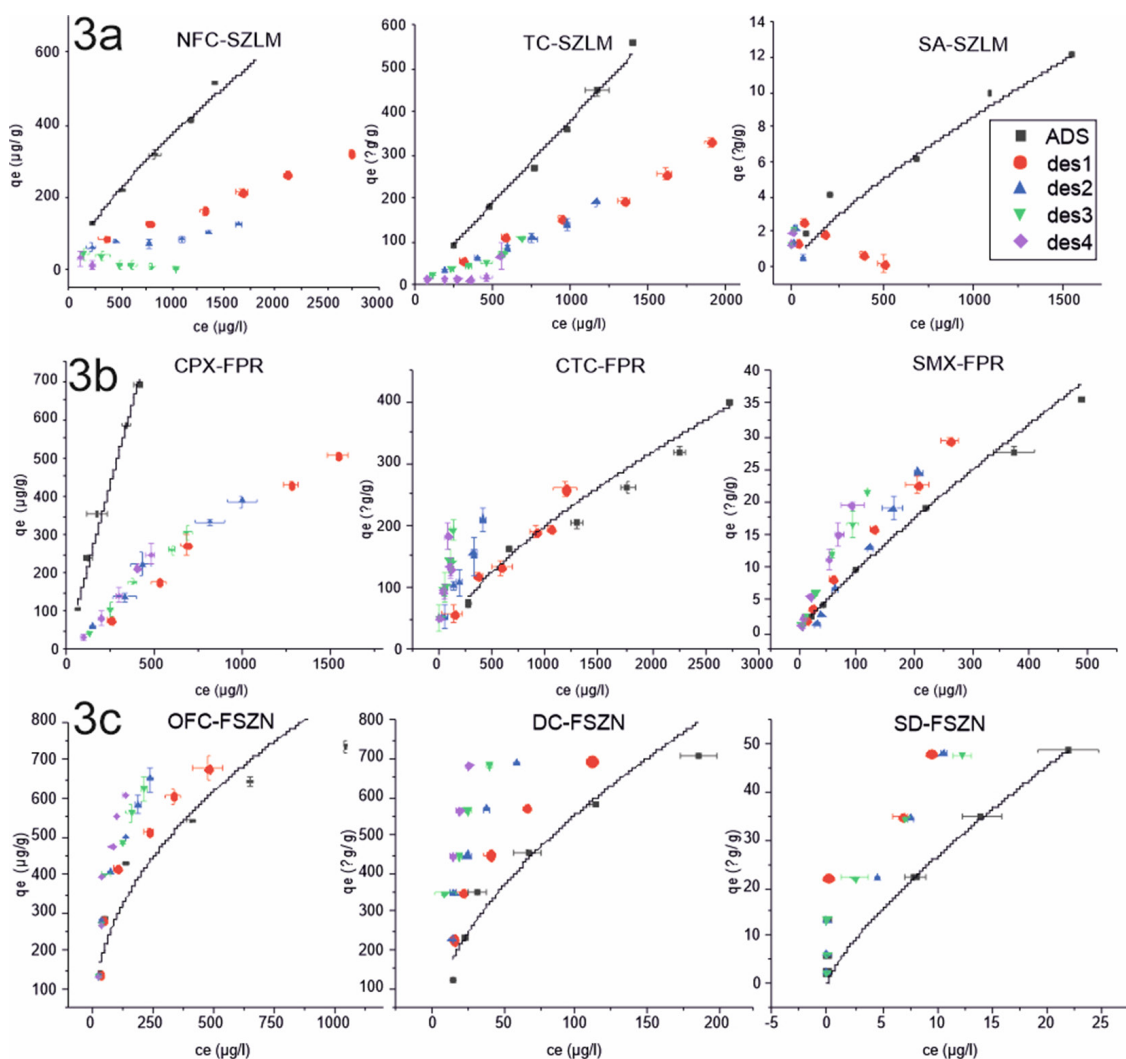


Figure 3

The Freundlich isotherms fitted to the adsorption data of the 3a: SZLM; 3b: FPR; 3c: FSZN adsorbent. Black markers are the adsorption points of the compounds, the black curve represents the fitted Freundlich isotherm, markers are the desorption points after des1: 24 h (red), des2: 48 h (blue), des3: 72 h (green), and des4: 144 h (purple). NFC-norfloxacin, TC-tetracycline, SA-sulfanilamide, CPX-ciprofloxacin, CTC-chlortetracycline, SMX-sulfamethoxazol, OFC-ofloxacin, DC-doxycycline, SD-sulfadiazin

Source: Own elaboration

were completely desorbed from the adsorbent at all concentrations. In contrast, for SAs, complete desorption was only observed at high concentrations, at low experimental concentrations (100–250 µg L⁻¹) the desorption points were above the adsorption isotherm, so part of the adsorption was irreversible. Low experimental concentrations are more relevant for environmental contamination (Alygizakis *et al.* 2019; García-Galán *et al.* 2011).

The distribution coefficient (K_d) values showed that the FQ and TC compounds had high adsorption affinity in the SZLM adsorbent (Table 2). Decreasing K_d values at desorption indicate that a part (or all) of the compounds are reversibly adsorbed and therefore re-enter the liquid phase in the desorption medium. Most of the compounds were fully desorbed after 144 h, although NFC, CTC, and SA compounds were irreversibly bound at low concentrations (100–1000 µg L⁻¹) on the adsorbent, as

indicated by the non-zero K_d desorption values. For NFC the K_F value was also high. According to Conde-Cid *et al.* (2020), SD adsorption values were similar in soils and bioadsorbent-treated soils, but desorption was not 100% for any of the compounds, however, the desorption experiment was only 24 h, so they did not have information on total desorption. The adsorption of SD and SMX on phosphoric chelating cellulose was also found to be similar as in the present study, but desorption experiments were not performed (Yang *et al.* 2019). The results show that the SZLM adsorbent had a high adsorption efficiency for NFC and CTC and that the adsorption was mostly irreversible, therefore it cannot be removed from the adsorbent after 144h. SA also showed irreversible binding, but its adsorption capacity was <60% even at low concentrations. SZLM was not a suitable adsorbent for the other compounds tested, so a different surface treatment process is needed to increase the efficiency.

Table 2 | Adsorption–desorption parameters for each compound. K_d : the mean distribution coefficient of all concentrations after adsorption and 144 hours of desorption, ADS% and DES%: the percentage of adsorbed and the total desorbed antibiotic at the lowest experimental concentrations. K_F : relative adsorption capacity, n : nonlinearity factor, R^2 : coefficient of determination, s.d.: standard deviation

Compound K_F		Ads						Des			ADS%	DES%
		n	R^2	K_d		s.d.	K_d		s.d.	Lowest conc.	Lowest conc.	
SZLM	CPX	0.28	1.04	0.99	0.35	±	0.02	0	±	0	69%	100%
	NFC	1.14	0.84	0.99	0.41	±	0.08	0.17	±	0.07	80%	76%
	OFC	0.23	0.98	0.95	0.17	±	0.02	0	±	0	57%	100%
	TC	0.24	1.07	0.99	0.37	±	0.02	0.09	±	0.04	76%	100%
	DC	0.05	1.29	0.98	0.35	±	0.04	0	±	0	74%	100%
	CTC	0.25	1.60	0.93	3.7	±	0.6	1.3	±	0.2	97%	30%
	SA	0.13	0.62	0.97	0.02	±	0.01	0.5	±	0.1	54%	33%
	SD	0.28	0.73	0.70	0.06	±	0	0	±	0.01	43%	100%
	SMX	0.02	0.78	1.00	0.007	±	0.00	0	±	0	34%	100%
FPR	CPX	6.78	0.77	0.95	1.78	±	0.1	0.42	±	0.1	92%	70%
	NFC	3.86	0.72	0.97	0.28	±	0.1	0.17	±	0.03	76%	64%
	OFC	2.58	0.88	0.97	1.02	±	0.08	0.09	±	0.01	88%	81%
	TC	2.82	0.57	0.96	0.11	±	0.04	1.14	±	0.31	60%	48%
	DC	2.48	0.64	0.98	0.22	±	0.1	0.81	±	0.2	77%	50%
	CTC	1.25	0.72	0.97	0.18	±	0.06	1.6	±	0.4	69%	34%
	SA	0.18	0.64	0.98	0.03	±	0.02	0.8	±	0.09	68%	22%
	SD	0.05	0.88	0.96	0.03	±	0.01	0.02	±	0.01	51%	100%
	SMX	0.22	0.82	0.99	0.09	±	0.01	0.21	±	0.03	81%	58%
FSZN	CPX	87.52	0.31	0.90	3.58	±	1.9	6.84	±	1.6	97%	10%
	NFC	79.96	0.40	0.87	5.6	±	2.5	9.5	±	2.6	97%	8%
	OFC	69.84	0.34	0.94	2.7	±	1.1	6	±	1.8	97%	10%
	TC	95.62	0.41	0.96	16.7	±	7.3	84.7	±	17.2	99%	0%
	DC	50.51	0.51	0.95	8.4	±	2.5	28.8	±	2	99%	0%
	CTC	189.99	0.48	0.81	86	±	12	320	±	-	100%	0%
	SA	12.19	0.50	0.90	5.5	±	1.2	32.4	±	8.6	100%	0%
	SD	4.98	0.78	0.85	2.6	±	0.2	4.3	±	1.6	100%	0%
	SMX	6.49	0.80	0.95	4.3	±	1.4	18	±	2.8	99%	0%

Source: Own elaboration

Adsorption and desorption results of adsorbent FPR

The Freundlich isotherm fitted to the FPR and antibiotic experiment data was different from the SZLM results (Figure 3b). The steepness of the isotherm and the K_F values showed that the adsorption was much higher for the FQs ($K_F > 2.6$) than for the TCs (K_F : 1.3–2.8) and SAs ($K_F < 0.2$) (Table 2). For FQs, the desorption points on the graph are always above the adsorption points, so the fixation was almost completely reversible even at low concentrations. In contrast, for TCs and SAs, the desorption points were located above the adsorption isotherm, indicating that a higher proportion of irreversible fixation occurred. Alidadi *et al.* (2018) observed similar removal efficiencies for TC adsorption on sawdust with modified surface area. After regeneration of the adsorbent (elimination of adsorbed contaminants

from the adsorbent surface), the removal efficiency decreased, which may indicate that the irreversibly bound TCs reduced the binding sites of the regenerated adsorbent.

Although FPR adsorbent K_F values are the highest for FQ compounds, adsorption is not fully irreversible. The total desorbed amounts were between 64–81% for FQs. The TC compounds had lower adsorption capacity, but desorption did not exceed 50%. For SA and SMX the K_F values were below 0.22, but the percentage adsorption values at low concentrations were high (SA-68% and SMX-81%) and the desorption were low. SD antibiotic differed, as its adsorption was only 51%, moreover, all the adsorbed compounds could be removed. The K_d values supported the previous findings, as only compounds for which desorption was not complete were found to have higher desorption K_d values. Even though low relative adsorption capacity values were found for

TCs and SAs, the FPR adsorbent was most effective for fixing these compounds, as a large proportion of the adsorption was irreversible. This was assumed because the lowest concentration of $1000 \mu\text{g L}^{-1}$ studied here is also several times higher than naturally occurring concentrations. At lower concentrations, the binding efficiency may increase. Since the desorbed amounts were low, the FPR adsorbent may be suitable for environmental concentrations in its investigated condition. To test this hypothesis further research is needed.

When compared to the SZLM adsorbent, the FPR had an overall lower removal efficiency, but it adsorbed a larger fraction of the components irreversibly. Presumably, the initial surface treatment procedure on the SZLM adsorbent increased the specific surface area but the amount of active binding sites less. Overall, all antibiotics except the CTC compound were more effectively removed by the FPR adsorbent, because of irreversible adsorption. Based on the research of *Ahsan et al. (2018)*, the adsorption capacity of sawdust for SMX and TC could be increased by an order of magnitude, but the surface treatment process was carried out with a heated concentrated sulphuric acid solution, which would mean a significant cost increase in the preparation of a cost-effective filter.

Adsorption and desorption results of adsorbent FSZN

In contrast to the two adsorbents discussed above, the desorption points were located above the adsorption isotherm for all compounds in the case of FSZN (*Figure 3c*). In the desorption medium, the equilibrium concentration decreased in each desorption time. This means that the adsorption affinity of the antibiotics for this adsorbent was high and the fixation was irreversible. At low concentrations, desorption was close to zero even on the first day. According to the Freundlich isotherm model (which showed a good fit with our experimental data) the adsorption can occur in several layers on the surface (similar to SZLM and FPR adsorbents). At higher concentrations, the desorption values increased due to saturation of the active binding sites, and the multi-layer adsorption (*Lu et al. 2020; Wang et al. 2021*).

The relative adsorption capacity values showed significant differences between the three antibiotic groups (*Table 2*). The K_F s of the zwitterionic FQs and the positively charged TCs were high ($K_F > 50$), for SAs the K_F values were low ($K_F < 12$). These values were of the same order of magnitude as the active carbon measured in the literature (*Choi et al. 2008; Rivera-Utrilla et al. 2013*), with the exception of CTC. The K_F and K_d values of the CTC compound were showing at least two times higher values compared to the other antibiotics. This was presumably due to the phosphoric acid surface modification, as other studies did not show such a large difference among TC compounds. K_d values were always

higher in the desorption medium, due to the high ratio of irreversible adsorption. The adsorbed percentages at the lowest concentrations were above 97% for all compounds. Desorption was only detected for the FQ compounds, and even for these it was only up to 10%.

Based on the comparison of the three biosorbents, the FSZN was found to be the most effective. K_F values were one to two orders of magnitude higher than that for FPR and SZLM, and adsorption was irreversible for all three antibiotic groups. Irreversible adsorption was also present on FPR and SZLM adsorbents, although in lower proportions. The value of the hysteresis index, which measures the ability of the compound to be washed off, was below 0.1 for all active substances for FSZN (*Table 3*). On average, the SZLM adsorbent had high hysteresis values (>0.6) and the hysteresis of FPR ranged widely (0.2–1).

Table 3 | Hysteresis indices indicating the adsorption–desorption rate for all antibiotic and adsorbent pairs

	SZLM	FPR	FNSZ
CPX	0.9	0.7	0.1
NFC	0.8	0.6	0.1
OFC	0.9	0.8	0.1
TC	0.6	0.5	0
DC	0.8	0.5	0
CTC	0.2	0.3	0
SA	0.4	0.2	0
SD	0.6	1.0	0
SMX	0.9	0.6	0

Source: Own elaboration

The hysteresis value itself only indicates the adsorption–desorption rate, for SZLM and FPR it only suggests that the adsorbed compounds are easily desorbed from the surface, it does not provide information about the amount of adsorbed compounds. To decide whether the adsorbent was suitable for efficient filtration, we need to look at adsorption and desorption separately. This was important because modifications to the surface treatment process should be made to either increase the adsorption (increase specific surface area) or reduce the desorption (increase functional groups, active sites). The applicability of each adsorbent to the given compounds, based on the adsorption and desorption values, has been illustrated in *Table 4* with + and – symbols. The + symbol was given for adsorption above 60% and desorption below 40%. If a compound–adsorbent pairing contains two + symbols it is suitable for cost-effective cleaning, if it contains two – symbols it is not, and some change in the surface treatment process is required either to increase the surface area or to increase the bond strength.

Table 4

The effectiveness of adsorbents for each antibiotic, based on adsorption and desorption values. + marks indicate values above 60% adsorption or below 40% desorption. – marks indicate adsorption below 60% and desorption above 40%

	SZLM		FPR		FSZN	
	ADS	DES	ADS	DES	ADS	DES
CPX	+	–	+	–	+	+
NFC	+	–	+	–	+	+
OFC	–	–	+	–	+	+
TC	–	–	+	–	+	+
DC	–	–	+	–	+	+
CTC	+	+	+	+	+	+
SA	–	+	+	+	+	+
SD	–	–	–	–	+	+
SMX	–	–	+	–	+	+

Source: Own elaboration

The FSZN adsorbent was suitable for the adsorption and long-term fixation of all components. In the SZLM adsorbent, on average, neither the adsorption amounts were high enough, nor the fixation strength, so the surface modification should be carried in the direction of increasing the surface area and active binding sites too. In the FPR adsorbent, the bound amounts were satisfactory, only the desorption amounts were too high, which made it necessary to modify the surface treatment by increasing the active binding sites. Note that all three adsorbents were suitable for CTC fixation.

FSZN adsorbent has a high adsorption capacity at environmental concentrations and a low desorption capacity, so it binds compounds irreversibly. This suggests that it could be used as only adsorbent for the filtration of antibiotics, however, it is important to consider that these results were obtained under laboratory conditions. The single use of FSZN as an adsorbent for treated wastewater would not be cost-effective, as the adsorbent would saturate rather quickly. The organic matter in the water reduces the adsorption capacity by competing with pharmaceuticals for active adsorption sites (Choi *et al.* 2008). In addition, dissolved organic matter can physically inhibit the adsorption of targeted compounds by clogging pores (Lee *et al.* 2024). SZLM and FPR adsorbents are less sensitive to organic matter in the treated effluent due to their lower surface activity (Tran *et al.* 2015). The use of SZLM in the adsorbent mixture may increase the porosity due to its larger particle size, so it can also be used in flow-through systems. It is therefore necessary to apply less sensitive biosorbents in the adsorbent mixture. Before the exact proportions of the multi-component adsorbent mixture can be determined, the surface modification method for SZLM and FPR must be revised.

Conclusion

Based on the current results, it is possible to produce a filter load that can effectively filter and strongly fix a broad spectrum of antibiotics (tested for three antibiotic groups with different physicochemical properties). This adsorbent is cost-effective to produce, does not require expensive treatment and, due to its high porosity, can be used effectively in flow-through (fix-bed) systems. Among the tested adsorbents, FSZN does not require any further surface treatment, while SZLM and FPR adsorbents require some modification to reduce the desorption amounts. The adsorbent mixture cannot be used effectively for direct filtration of wastewater due to competition. In the case of wastewater treatment, it could be applied as an additional filtration step after existing treatment processes. Another application to be considered is the one-step filtration of irrigation water for direct food production (e.g., for irrigation of root crops).

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